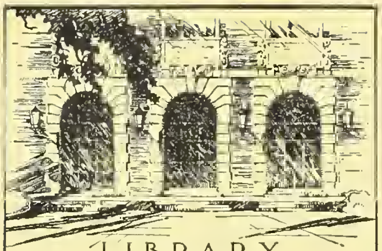

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INORGANIC SEMINARS

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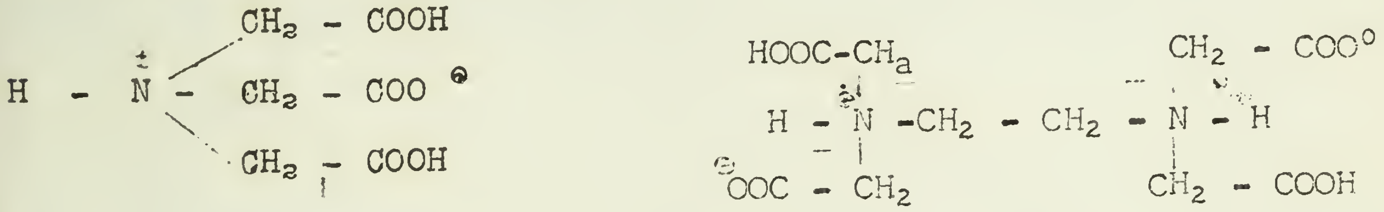
CHELATOMETRIC TITRATIONS

Malcolm L. Judd October 2, 1956

The terms chelatometric or complexometric (2), (3), (4), have been applied to titrations wherein a solution of metal ions is titrated with a standard solution of chelating agent. In order for a titration of this type to be practicle, the complex obtained between the metal cation and the chelating agent must be of sufficient stability to effectively remove all the free metal cations from the solution at the endpoint. Furthermore the mole ratio between metal ion and chelating agent in the complex should be simple, preferably 1:1. The ideal ligand then would possess both oxygen and nitrogen ligand atoms so as to be acceptable to a large variety of metals, be capable of forming five membered rings with the metal cation and be sufficiently polydentate so as to occupy all or nearly all of the coordination sites of the metal being titrated. Among known compounds nitrilotriacetic acid (NTA) (12), (14), and ethylene diaminetetraacetic acid (EDTA) (5-11) meet these criteria most effectively. EDTA is the better of the two.



Nitrilotriacetic acid NTA

Ethylenediaminetetraacetic acid EDTA

Fig. I

The reaction between a metal cation and EDTA will entail the loss of protons from the EDTA molecule. As is seen in Fig. I. the acid is a double betaine. The two carboxylic acid groups are strongly activated having pK values of about 2 and 3 while the protons attached to the nitrogens are lost at pH's of 6.2 and 10. Only above pH 10.5 does the complex correspond to the simple reaction:

$$M^{+n} + Y^{-4} \rightarrow MY^{n-4}$$

Y^{-4} = anion of EDTA

At lower pH regions a protonated complexing agent is reacting and protons will be liberated during complex formation. The hydrogen ions liberated can be titrated and indeed this was one of the first methods used to determine the endpoint of a chelatometric titration. It is more accurate however to work in buffered solutions. The stability of the complex will then depend upon the pH. range choosen, being higher at high pH.

In drawing a titration curve the quantities usually plotted are pM (pM= - log (metal ion concentration) versus the molar ration of EDTA to metal. The endpoint of a titration is shown by a rapid increase in pM. The more stable the complex formed during the titration, the smaller will be the metal ion concentration at the endpoint and consequently the PM will be higher. As the facility of endpoint detection is dependent upon the magnitude of the pM jump this is desirable. Fig. II shows the effect of pH on the pM jumps at the endpo

of the titration of
Mg^{++}, Ca^{++} and Ba^{++}

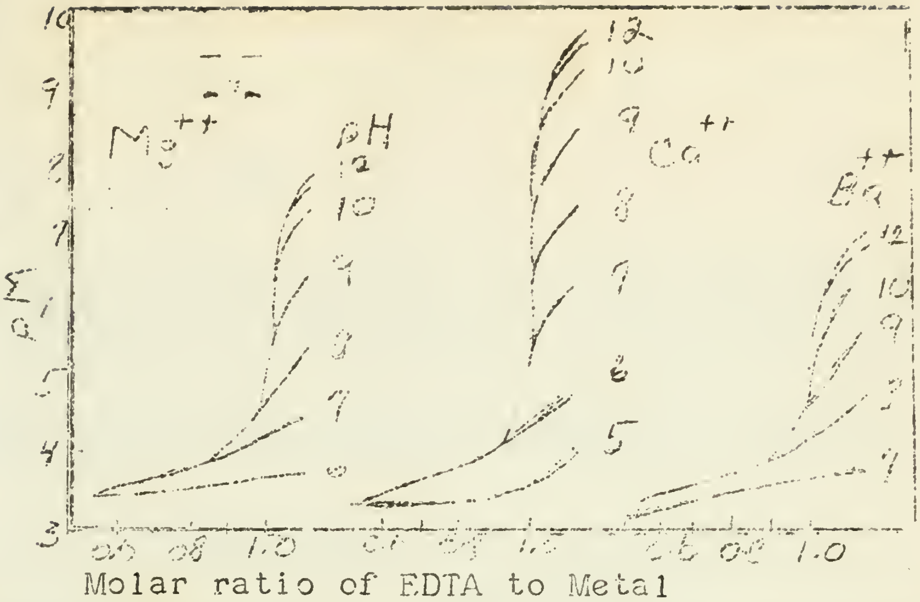


Fig. II. Titration of alkaline earth metals with EDTA at various pH values.

A similar pH dependence occurs with the heavy metal ions but here hydrolysis occurs at relatively low pH. Such precipitation must be prevented by the addition of an auxiliary complexing agent such as ammonia. In such a solution the metal is present in the form of a series of ammine complexes and the reaction would be formulated as follows:

$A = NH_3$

$$\begin{array}{l} M^{+b} \\ + \\ MA^{+b} \\ + \\ MA_2{}^{+b} \\ + \\ MA_3{}^{+b} \end{array} \quad + \, H_j\,Y^{j-4} \rightarrow MY^{b-4} + jHA + 3A$$

Because of the presence of these ammine complexes, the pM of the solution will be higher at the starting point of the titration. As this is undesirable the auxiliary complexing agent must be as weak as possible yet strong enough to prevent the precipitation of hydroxides.

Endpoints are usually detected in one of three ways.

1. An indicator electrode may be used which responds to the metal in question. However, electrodes exist for only a few metals, e.g. Cu, Zn, Cd and Pb, the amalgams of these metals being fairly good electrodes.

2. Amperometricaly

3. Most frequently dyestuff indicators are used for the detection of endpoints. These indicators are in fact coordinating agents which show different colors in the coordinated and uncoordinated states. Hence when the EDTA extracts the metal from the indicator at the endpoint a color change will occur. A suitable indicator should show a color transition in a range of 2 pM units.

Among the metals that can now be titrated directly with EDTA and a suitable indicator are: Mg, Ca, Sr, Ba, Zn, Cd, Pb, Cu, Ni, Co, Fe, Mn, Hq, Tl, In, Bi, Th and all the rare earth metals. In addition, several other metals can be determined by a back titration method or by other special procedures.

In addition to their use as titrants, EDTA and related compounds may be used as masking agents when making a separation of cations.

For example, magnesium may be precipitated in the form of $Mg\,NH_4\,PO_4$ if EDTA is first added to complex the heavy metal ions present[15]. Calcium oxalate can be precipitated in the presence of other metals mask with EDTA[16].

It is thus seen that the strong, universal coordinating ability of substances such as EDTA have substantially expanded the scope of volumetric analysis.

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LIQUID N_2O_4 SOLVENT SYSTEM

C. D. Schmulbach 9 October, 1956

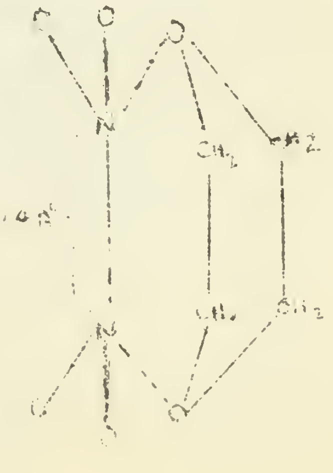
General

Liquid dinitrogen tetroxide is being employed increasingly as a non-aqueous solvent due primarily to its ready availability and its use in preparing organic oxy-nitrogen compounds. Questions concerning the structure of N_2O_4 have certainly been responsible for the increasing investigation of this solvent system.

Its low melting point, -9.3°, and boiling point, 21.3°, and the narrow range of the liquid state along with its low dielectric constant, $E=2.42^{18^\circ}$, restrict its usefulness somewhat. Its dissociation into NO_2 at temperatures above the freezing point complicates mechanism and rate studies in this solvent.

ADDUCTS OF N_2O_4 WITH ETHERS AND AMINES

As a means of emphasizing the wide scope of the investigations of C. C. Addison, a brief sketch of H. H. Sisler's experimental studies (1) will be presented first. Primarily because of his interest in Lewis acid-base reactions, Sisler conducted a series of phase studies of various ethers and amines with liquid N_2O_4. Studies were made at relatively low temperatures (in the neighborhood of -70°C); in most cases the products were thermally unstable salts of the composition $N_2O_4 \cdot 2B$. The dinitrogen tetroxide-1,4 dioxane addition compound on the other hand was stable up to +45.2°C. Spectroscopic studies with Raman and I. R. indicated that NO_2^+, NO_2^-, NO^+ and NO_3^- were not present in the adducts. Magnetic studies, which show that the compounds are diamagnetic, indicate that the formula of the compound is correctly represented as $N_2O_4 \cdot 2B$ and not $NO_2 \cdot B$. If one assumes that the compounds are truly adducts of acids and bases, then the stability of the monobasic ether-adducts should and does decrease from tetrahydrofuran to tetrahydropyran to diethyl ether. The structures of these compounds are represented as follows:



THE DENITROGEN TETROXIDE SOLVENT SYSTEM

The reactions which occur within the liquid N_2O_4 system are believed to entail the following possible ionization and dissociation reactions:

$N_2O_4 \rightarrow NO^+ + NO_3^-$ (a)

$N_2O_4 \rightarrow NO_2^+ + NO_2^-$ (b)

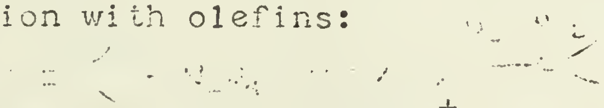
$N_2O_4 \rightarrow NO_2 + NO_2$ (c)

Several reactions were considered. (2) Of these reactions Addison selected a few for extensive investigation. The mechanism of reactions in liquid N_2O_4, the probable structure of liquid N_2O_4, the existence of specific ionic and molecular species and the equilibrium between these species were principle considerations in these studies. Considerable emphasis was placed on equation (a) above.

SUMMARY OF REACTIONS (2,3,4)

The reactions are summarized as follows:

1) Reaction with olefins:



Nucleophilic attack by NO_2^+ seems likely in this reaction mechanism.

2) Solvolysis

$[Et_2NH_2^+]Cl^- \quad [NO]NO_3 \rightarrow NOCl + [Et_2NH_2]NO_3$

$KCl + N_2O_4 \rightarrow NOCl \quad KNO_3$ (Water must be present.)

$[Et_2NH_2]NO_3 + [NO]NO_3 \rightarrow Et_2NNO + 2HNO_3$

cf. $[Et_2NH_2]OH + HOH \rightarrow Et_2NH + 2H_2O$

3) Neutralization

$2NOCl + 2M(NO_3)_2 \rightarrow 2mCl_2 + 2N_2O_4$

$[NO]NO_3 \quad 2OH^- \rightarrow NO_3^- + NO_2^- + H_2O$

cf. $[NO]ClO_4 \quad 2OH^- \rightarrow ClO_4^- + NO_2^- + H_2O$

$NO_2Cl + AgNO_2 \rightarrow AgCl + N_2O_4$

4) Esterification of N_2O_4(5)

$[NO]NO_3 + HOR + HOR \rightarrow ROH{\cdot}HNO_3 + RNO_2$ (noRNO_3)

cf. $[NO^+] + SO_4H^- + HOR + HOR \rightarrow ROH{\cdot}H_2SO_4 + RNO_2$

5) Amphoteric properties of metals in liquid N_2O_4

$ZN + 2NOCl\ (N_2O_4) \rightarrow ZnCl_2 + 2NO$

$ZN + x(Et_2NH_2)NO_3\ \ (N_2O_4) \rightarrow (Et_2NH_2)x$ [nitrozincate complex) + NO

cf. $Zn + 2NaOH + 2H_2O \rightarrow Na_2\ Zn(OH)_4 + H_2$

6) Reaction with covalent bases (oxidation-reduction)


$-NH_2 + N_2O_4 \rightarrow$ explosive

$Et_2NH\ \ N_2O_4 \rightarrow$ "

$NH_3\ \ N_2O_4 \rightarrow$ "

7) Reaction with alkali metals.

$[NO]NO_3 + Na \rightarrow NaNO_3 + NO$ (no $NaNO_2$ formed)

cf. $[NO]\ SbCl_6 + Na \rightarrow NaSbCl_6 + NO$

8) Reaction with Hg (6)

$2[NO]NO_3 + 2Hg \rightarrow (HgNO_3)_2 + 2NO$ (no nitrite present)

STUDY OF PHYSICAL PROPERTIES OF LIQUID N_2O_4

The study of certain physical properties has led to several interesting conclusions. The specific conductance of liquid N_2O_4 was found to be 1.3×10^{-12} ohm^{-1} cm^{-1}. (7,8) The conductivity may be due to the presence of ions such as NO^+, NO_3^-, NO_2^+ and NO_2^-, or perhaps due to the transfer of electrons along a Grotthuss chain of NO_2 molecules. Since N_2O_4 is diamagnetic, it is less likely to partake in an electron transfer mechanism. The application of higher voltages in determining the specific conductance by voltage decay across a condenser yielded similar results. This fact tends to minimize the possibility of the NO_2 molecules in solution being ionized to NO_2^+. Addison concludes that the reaction $N_2O_4 \rightarrow [NO]NO_3 \rightarrow NO^+ + NO_3^-$ is real though not appreciable.

The dielectric constant(9) of liquid N_2O_4 is comparable to the benzene, ($E = 2.284$). Alkyl ammonium salts in liquid N_2O_4 at concentrations as high as 30% raise the conductance to only 10^{-8} ohm^{-1}cm^{-1}

Addison concludes, therefore, that the reactions of N_2O_4 with alkyl ammonium salts result from collisions between ion pairs rather than free ions.

REACTIONS OF AMINES WITH LIQUID N_2O_4 (10)

$$(C_2H_5)_2NH + N_2O_4 \rightarrow \text{Explosive reaction}$$

$$(C_2H_5)_2NH_2Cl + [NO]NO_3 \rightarrow [(C_2H_5)_2NH_2]NO_3 + NOCl.$$

$$[(C_2H_5)_3NH]Cl + [NO]NO_3 \rightarrow [(C_2H_5)_3NH]NO_3 + NOCl^{(11)}$$

Several reactions were tried with the primary, secondary, tertiary and quaternary methyl ammonium chlorides and the corresponding nitrate salts were formed. In all of the reactions, except with triethylammonium chloride, two immiscible phases resulted. The bottom layer was red containing a large amount of NOCl. The upper layer contained the nitrates.

Et_2NNO-N_2O_4 SYSTEM (12,13)

Phase studies revealed the formation of a comparatively stable compound (m.p. -37.5°C) of the composition $N_2O_4 \cdot 2Et_2NNO$. Conductivity measurements indicated that N_2O_4 and Et_2NNO combine to form a 1:2 compound which is capable of considerable ionic dissociation according to the following equation:

$$N_2O_4 + 2Et_2NNO \rightleftharpoons N_2O_4 \cdot 2Et_2NNO \rightleftharpoons (Et_2NNO)_2NO^+ + NO_3^-$$

Solutions of Et_2NNO-N_2O_4 were electrolized at -10° in order to identify the ionic species present. The area around the cathode became green and then turned brown. At the anode no visible reaction was observed. Addison offered the following explanation.

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

At cathode:

$$NO^+ + e^- \longrightarrow NO$$

At anode:

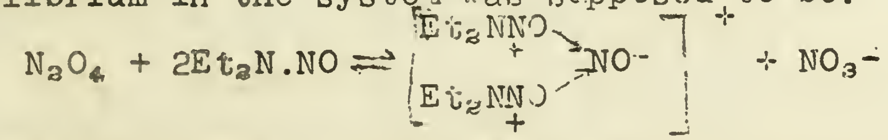
$$NO_3^- \rightarrow NO_2 + 1/2\ O_2 + e^-$$

or

$$NO_3^- \rightarrow NO_2^+ + 1/2\ O_2 + 2e^-$$

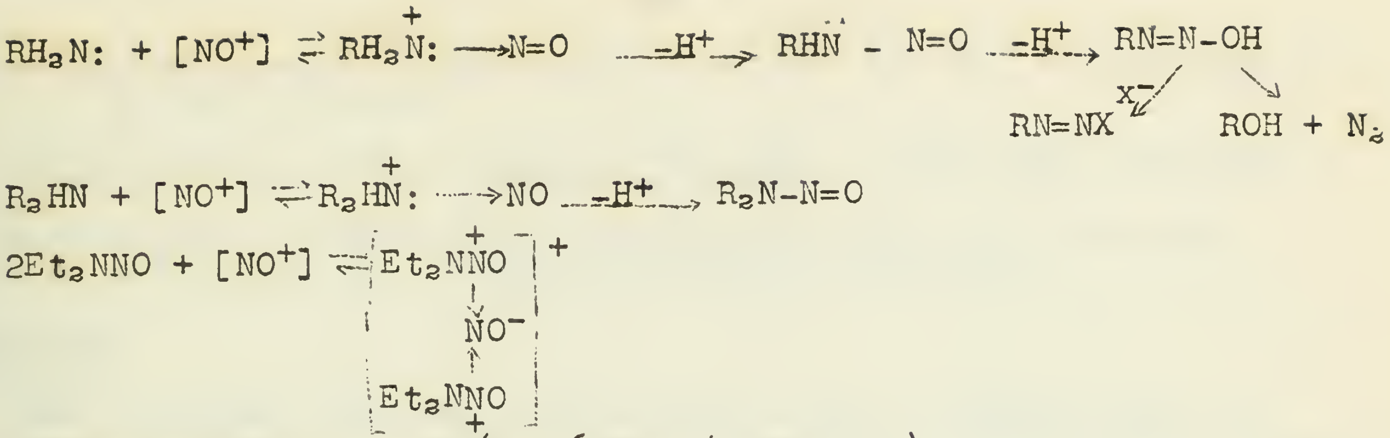
Because of the fact that 1 Faraday of electricity did not decompose one equivalent of Et_2NNO, Addison discounted the possibility of the existence of the following ionic species; $N_2O_4 \cdot 2Et_2N \cdot NO \rightleftharpoons 2N_2O_3^+ + 2Et_2N^-$. The N_2O_5 (NO_2^+ in NO_3^- medium) was considered responsible for the small amount of $Et_2N \cdot NO$ which was oxidized.

Since diethyl nitrosamine and N_2O_4 react in 2:1 ratio only, the equilibrium in the system was supposed to be:



$$N_2O_4 + 2Et_2N.NO \rightleftharpoons \left[\begin{matrix} \overset{+}{Et_2NNO} \searrow \\ \qquad NO^- \\ \underset{+}{Et_2NNO} \nearrow \end{matrix}\right]^+ + NO_3^-$$

On the basis of his study of the Et_2NNO-N_2O_4 system and the unstable amine- N_2O_4 systems Addison proposed the formation of complex ions with NO^+ as the central unit. (8,14)



$$RH_2N: + [NO^+] \rightleftharpoons R\overset{+}{H_2N}: \longrightarrow N{=}O \xrightarrow{-H^+} RHN - N{=}O \xrightarrow{-H^+} RN{=}N{-}OH$$

$$RN{=}N{-}OH \xrightarrow{X^-} RN{=}NX \qquad RN{=}N{-}OH \longrightarrow ROH + N_2$$

$$R_2HN + [NO^+] \rightleftharpoons R_2\overset{+}{HN}: \longrightarrow NO \xrightarrow{-H^+} R_2N{-}N{=}O$$

$$2Et_2NNO + [NO^+] \rightleftharpoons \left[\begin{matrix} Et_2N\overset{+}{N}O \\ \downarrow \\ NO^- \\ \uparrow \\ Et_2N\underset{+}{N}O \end{matrix}\right]^+$$

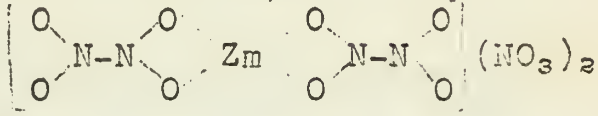
Zn-N_2O_4 AND RELATED SYSTEMS (15,16,17,18,19,20,21)

In the reaction of Zn with N_2O_4 three structures are most likely for the nitrate salt, $Zn(NO_3)_2.2N_2O_4$, which is formed.

(A) $(NO)_2\ [Zm(NO_3)_4]$

(B) $(NO_2^+)_2[Zm(NO_2)_2(NO_3)_2]$

(C)



Addison favors structure (A) because (1) the chemical properties of the compound are unlike that of $Zn(NO_3)_2$ and N_2O_4, (2) pure anhydrous Na or Ca nitrate will not form crystals of $M(NO_3)_x.2N_2O_4$ since they do not form the anionic coordination complex (3) no nitrite is present, and (4) at no particular temperature was there a pronounced change in the evolution of N_2O_4 as would be expected from a solvated salt.

Addison's investigation of the Zn-NOCl(N_2O_4) system led him to believe that his earlier assumption as to the structure of $Zn(NO_3)_2 \cdot 2N_2O_4$ was correct. This can best be illustrated in the following equations:

Since mono nitrosyl salts [e.g $NO(AlCl_4)$] are readily soluble in liquid NOCl and dinitrosyl salts [e.g. $(NO)_2SnCl_6$] are quite insoluble, Addison's assumption for the structure of $(NO)_2(Zn_2Cl_6)$ does not appear to be without foundation.

In more recent work Addison studied the Zn-$EtNH_3NO_3(N_2O_4)$ system This work illustrates the amphoteric behavior of zinc salts in liquid N_2O_4.

The tracer work of K. Clusius (22) tends to support the assumption that many reactions in the liquid dinitrogen tetroxide

system are the result of the presence of NO^+ and NO_3^- or $[NO^+][NO_3^-]$.

In the reaction

$$(CH_3)_4N^{15}NO_3 + N_2O_4 \quad \underline{\text{heat to boiling}} \quad (CH_3)_4NNO_3 + NO^{15}NO_3$$

the tetramethyl ammonium nitrate contained 2.21% ^{15}N before the reaction and only 0.35 - 0.01% ^{15}N after the reaction.

CONCLUSION

The thorough, exacting experimental work of Addison and his co-workers definitely points to the existance of a $[NO^+][NO_3^-]$ species in liquid dinitrogen tetroxide and their existence can be used to explain many reactions in this solvent system. These are not the only species present. The study of the reaction of Lewis acids (e.g. $AlCl_3$ and BF_3) with liquid dinitrogen tetroxide should prove equally interesting.

For a complete summary of the dinitrogen tetroxide system the reader is referred to the recent review by P. Gray and A. D. Yoffe (23) which contains 441 references.

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Preparation and Some Properties of Crystalline Lithium Alkyls

T. L. Brown

1. General.

The alkyl compounds of the group Ia, IIa and IIIa metals possess many unusual properties (Table I). These properties are not explained by ordinary valency concepts, but can be understood in terms of the concept of electron-deficient bonding.[1] An electron deficient bond is one in which the bond order is less than one.[2] The simplest example: H_3+. Many examples of this type of bonding exist, e.g., the metals, interstitial compounds, hydrides. Among the metal alkyls of groups Ia, IIa and IIIa, electron-deficient bonding is responsible for the polymerization which occurs. The same mechanism of bonding is doubtless the cause of the observed properties of lithium alkyls.[3]

2. Preparation.

A. $Hg\,R_2 + 2Li - C_2H_5 \overset{C_6H_6}{} 2\,\underline{L}i\text{-}R + Hg$
for all R except methyl.

$Hg(CH_3)_2 + 2\,Li\text{-}C_2H_5 \overset{C_6H_6}{} 2\,\underline{Li\text{-}CH_3} + Hg(C_2H_5)_2$

B. $R\text{-}X + 2\,Li \text{—} R\text{-}Li + Li\,X$

X= Br, Cl. Solvent is ether, hydrocarbon.

C. For Methyl-lithium,

$CH_3\text{-}I + Li\,C_2H_5 \overset{C_6H_6}{} \underline{CH_3Li} + C_2H_5I$

3. Physical properties.

A. X-ray diffraction.

B. Infrared spectra.

C. Electric moment.

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Compound	Melting, Boiling Point	Association	Complexes	Comments
AL $(CH_3)_3$[5]	M.p. 15	dimeric	etherate	bridge structure
Be $(CH_3)_2$[6]	sublimes 200	associated in solution and vapor phase	di-etherate	ΔH_s=22 Kcal. per mole
Be $(C_2H_5)_2$	b.p. 180 w. decomp.		di-etherate	
Mg $(CH_3)_2$	non-fusible		ether-distillable	stable to 200-250°
Mg $(C_2H_5)_2$	non-fusible		ether-distillable	stable to 200-250°
Li CH_3	solid, decompases at 300°C.		highly soluble in ethers	
Li C_2H_5	m.p. 95° w. decomp	6-7 fold in benzene solu.		
Li C_4H_9	Liquid			v.p. at $60^\circ = 10^{-4}$ mm. $\Delta H_v = 33$ Kcal./ mole.
Na R	non-fusible solid			insoluble in organic solvents
Zn $(CH_3)_2$	b.p. 44	monomeric		linear, zinc bonding sp.

Table I. Some Properties of Group I, II, and III Metal Alkyls[4]

THE CORRELATION OF STABILITY CONSTANTS OF COMPLEXES WITH THE IONIZATION POTENTIAL OF THE METAL ATOM

A. Seaton October 30, 1956

The stabilities of complex compounds are governed by a number of factors making difficult their interpretation on a simple basis. The nature of the ligand, the orbitals of the metal available for bonding environmental and steric considerations are of great importance. However, within a series of transition metal complexes with common ligands, the stabilities are less easily explained. Size relationships are inadequate.

Mellor and Maley (1) were among the first to note that the stabilities of bivalent transition metal complexes are not a function of the radius of the metal and that the stabilities of the first transition series rise to a maximum at Cu (II) and fall off again at Zn. The stabilities of complexes with a number of ligands for this series of metals followed this trend. The authors suggest that the series might be explained in terms of electronegativity or basicity of the metals, but did not attempt to do so. The stability constants for 8-OH quinoline, salicylaldehyde, and acetylacetone complexes of a series of bivalent metals were determined and found to correspond roughly to the standard potentials corresponding to $M \rightarrow M^{++} + 2e^-$. The stabilities are given by the following series

stabilities: $Mg > Mn > Fe > Cd\ Zn > Co\ Pb > Ni > Cu > Pd$
E_0: $Mg > Mn > Zn > Fe > Cd > Co > Ni\ Pb > Cu > Pd$

Irving and Williams (3) and Calvin and Melchior (4) independently and within the period of a month published articles in which a close correlation between the second ionization potentials and the log K_s values was observed. In the series Mn (II) to Zn (II) the ionic radii and heats of hydration are essentially constant. This correlation seems to be quite general and has been noted for a wide variety of ligands by various workers (5,6,7,8).

The first attempt to systematize the correlation between stability constants and ionization potentials was undertaken by Van Panthaleon Van Eck (9). The relationship is given by the equation:

$$\log K = p\,(I - g)$$

where

p and g = constants depending on ligand, solvent and temperature.

I = ionization potential in electron-volts for reaction $M(g) \rightarrow M^{2+}(g) + 2e^-$

$K = \dfrac{[MA^{2+}]}{[M^{2+}][A]}$ where concentrations are expressed in mol fractions.

Application of this relationship to a series of bivalent aminine complexes is presented graphically in Figure 1.

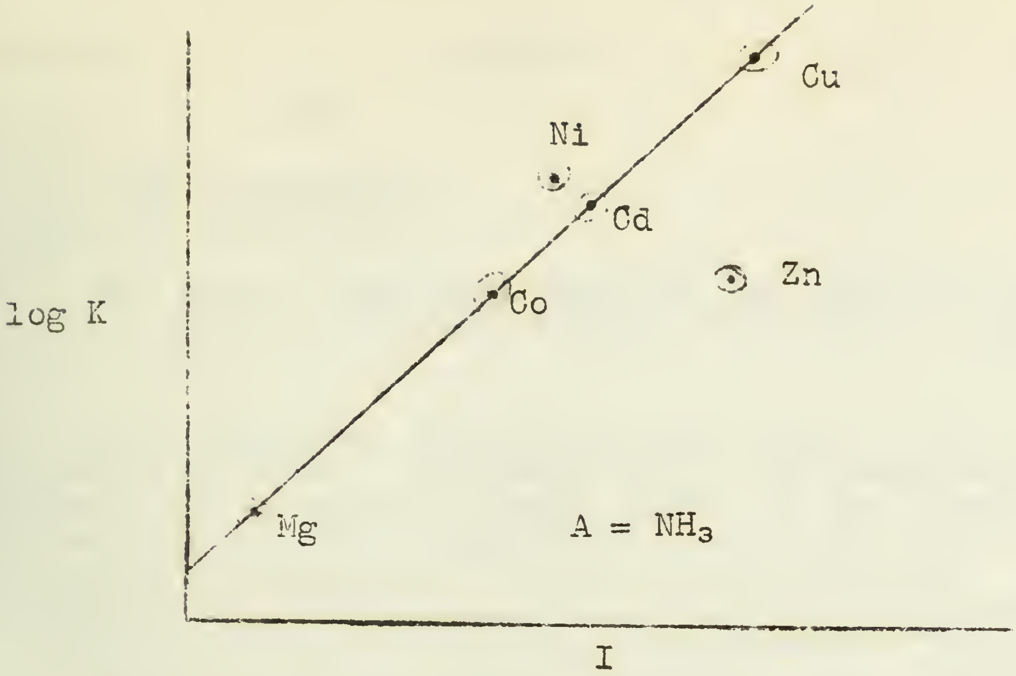
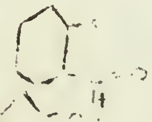
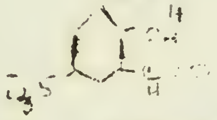
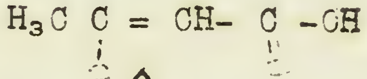


Figure 1

The slope plot is surprisingly constant from ligand to ligand provided that the ligands are similar chemically and steric factors are constant. Values for p and g, taken from Van Panthaleon Van Eck's paper, are reproduced in Table 1.

Table 1

System	Ligand		p	g
1	NH_3		0.73	19.95
2	C_5H_5N		~0.5	~19.2
3	$H_2NCH_2CH_2NH_2$		1.68	20.5
4	$N(CH_2CH_2NH_2)_3$		~2.72	~20.3
5		I II	1.51* 0.36	17.00* 4.6
6		I II	1.03** 0.30**	19.2** 5.3**
7		I	0.69	18.0
8	$H_2NCH_2COO^-$	I II	1.28 0.39	19.87 9.34
9	 $H_3C\ \underset{\underset{O}{\vert}}{C} = CH-\ \underset{\underset{O}{\Vert}}{C}\ -CH$		~1.2**	~18.8**
10			1.26**	~19.4**
11	CH_3COO^-		0.18	ca. 9

System	Ligand	p	g
12	OH^-	0.23	4.9

* 70% dioxane/H_2O
** 50% dioxane/H_2O

The type I complexes shown in the table are said to be covalent r penetration complexes, whereas the type II complexes are believed o be ionic.

A satisfactory theoretical explanation for this relationship has not been advanced. Ackermann <u>et.al</u>. (5) suggested that the similarity between the electronic energy levels in the complex to those in the corresponding metal atoms might account for the relationship. From a qualitative standpoint this might be acceptable. The free energy of formation of a complex has been related to electronegativity which in turn is a function of ionization potential. A better correlation can be obtained with ionization potentials than with electronegativities due to the fact that the ionization potentials are known to a greater degree of accuracy.

L. H. Ahrens (10) has suggested that the ionization potentials be used as a measure of the "anion affinity" of a cation, and of its polarizing power. The first ionization potential would be used for monovalent cations, the second ionization potential for divalent cations, etc. The divalent cations are divided into size groups; 0.6-0.8Å and 0.9-1.2Å. The progressive changes in coordinating properties of these metal ions are attributed to polarization by the cation which is a function of its ionization potential.

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(9) C. L. Van Panthaleon Van Eck, Rec. Trav. Chim. <u>72</u>, 50-6 (1953).
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INORGANIC COORDINATION POLYMERS

T. H. Shepherd November 6, 1956

Coordination polymers have been formed from a variety of types o ligands and most of the transition metal ions. These polymeric types are being thoroughly investigated in a search for an elastomeric material which is stable at very high temperatures.

Before entering into a discussion of coordination polymerizatio it seems advisable to review the rules of chelate formation in rela to the strength of the coordinate bond.

Rules of Chelate Formation

1. The bond between a metal ion and an atom in a negatively charged group is stronger than that between the ion and atom in a neutral group.
2. The bond between a metal ion and two atoms in the same group is stronger than that formed with two atoms in different groups (Chelate effect).
3. Coordinate bond strength varies in proportion to the basicity o the ligand.
4. The higher the charge a cation carries, the stronger the coordination bond it forms.
5. A five membered chelate ring is more stable than a four or six membered ring.

Stereochemical Considerations

A ligand containing two bidentate groups which are sufficiently separated to prevent tetra-coordination with a single metal ion, i capable of coordinating with two metal ions having a coordination o four, to fill half the coordination sphere of each, producing a linear polymer. If the metal ion has a coordination number of six, a tri-dimensional cross-linked polymer will be produced. However, instances are known where a metal ion of coordination number six fo a linear polymer, the remaining two trans positions being occupied b mono-dentate groups.

Mechanisms of Coordination

Coordination polymers may be produced by a condensation polymerization mechanism, where a small molecule or group such as water or ammonia is eliminated. The other type of mechanism, of which there are relatively few examples, involves an addition proce

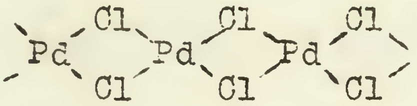
Coordination polymers seem promising as thermostable elastomer materials since they can combine the flexibility of organic molecules with the thermostable character of the chelate bond.

Polymer Types

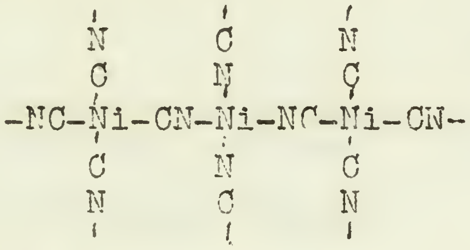
Of historical interest is the polymer formed by pent-ammine platinum II chloride[1] upon treatment with chlorine.

$$[Pt\ (NH_3)_4]\ Cl_2 \xrightarrow{Cl_2} [-Cl-Pt\ (NH_3)_4-Cl-Pt\ (NH_3)_4-]_x$$

In this material, half the platinum is in the II oxidation state, and half is in the IV state. This polymerization proceeds by an additio mechanism. Another such example is the palladium (II) chloride polymer[2] which has been shown to have the following structure.

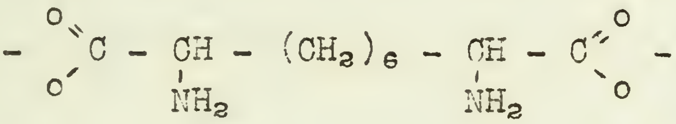


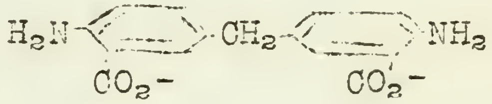
Nickel cyanide has also been shown to exist in polymeric form[3] in th solid state, probably as nickel tetracyanonickelate. Therefore, a "head to head" polymeric structure is indicated.

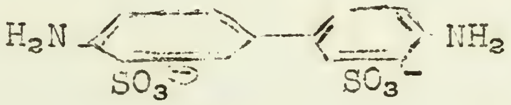


Amino Acid Type

The first reported di-α-amino acid coordination polymer was synthesized by Stephen and Weizman,[4] who prepared the copper complex of α,α'-diamino adipic acid. This work was confirmed later by Sorenson and Anderson.[5] However, Elliot,[6] who prepared the Co (III) Cr (III), Ni (II), Cu (II) and Fe (II) complexes with the following di-α-amino acids, made the first study of this type polymer.



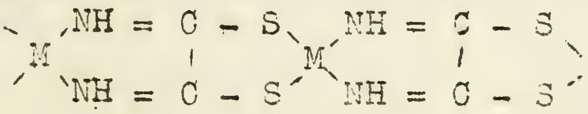




The thermal stability of these polymers was not determined, however, they were only slowly hydrolyzed by acid. The cobalt polymers prove to be the most stable.

Thio-Amide Type

A patent has been obtained by Amon and Kane[7] on polymerized copper and nickel salts of dithio-oxamide. It has not been determin whether a "head to tail", "head to head", or mixture of these structures is present:

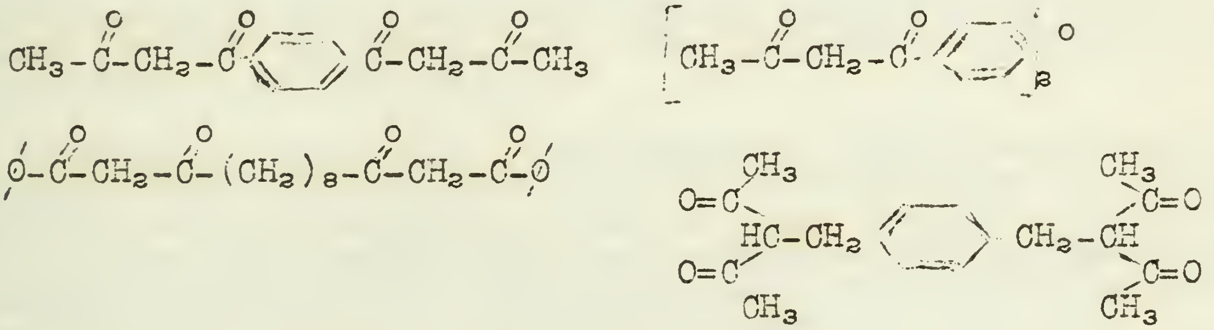


("head to tail")

This polymer may be incorporated into a plastic sheet to give a transparent material which, when stretched, becomes molecularly oriented, importing light polarizing ability to the sheet.

Bis-β-diketone Polymers

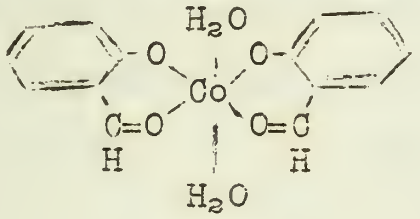
Wilkins and Wittbecker[8] have been granted a patent on transition metal chelate polymers with the tetra-ketone type ligand. Divalent ions of coordination number four were used, thus producing inner complex polymers by a melt polymerization technique. The following tetra-ketones were investigated as ligands.



By the choice of suitable conditions, polymers may be prepared which are suitable for coatings, moldings, fibers or films.

Bis-β-Carbonyl-hydroxyl Ligands

The formation of a polymeric material from 4-hydroxy-5-formyl-salicylaldehyde and cobaltous acetate was reported by Bailes and Calvin.[9] The following structure (II) was postulated on the basis of the known structure of the salicylaldehyde-cobalt (II) coordination compound (I).



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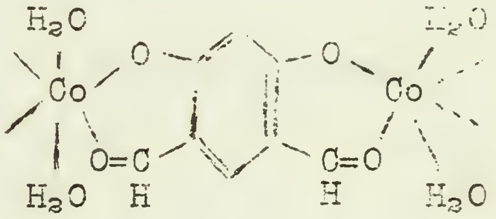
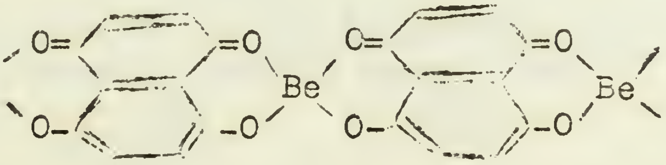


II

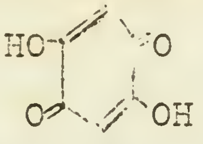
A cobalt-napthazarin polymer was also reported in this paper.

Underwood and Taribora[10] report the formation of a beryllium-napthazarin polymer.



This complex was found to be insoluble in all common solvents, and failed to sublime.

Similar polymers have been formed from 2,5-dihydroxy benzoquinone (I) and polyporic acid[11] (II).



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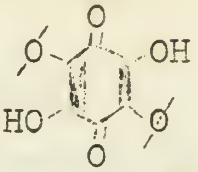
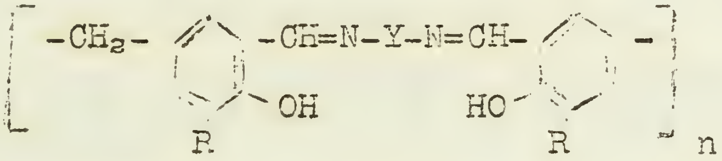


II

Schiff Base Coordination Polymers

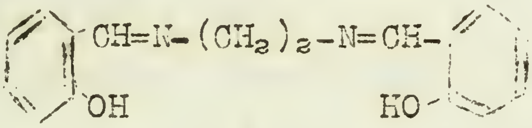
Sacconi[12] prepared a nickel coordination polymer of the schiff base derived from salicylaldehyde and the hydrazide of either beta or gamma pynidine caroxylic acid. This polymer is stable at 350°C, and is inert to boiling alkali.

A different type schiff base polymeric complex was synthesized by Aspey,[13] who first prepared polymeric schiff bases, then chelated these with several transition metal cations. Thus the coordinated cation is not incorporated into the backbone of the polymer chain, b is pendant from the chain. The poly-schiff bases were composed of tetra-dentate monomers of the following type.



Resinous materials were produced by coordination; however, analysis indicated that incomplete chelation had taken place.

Marvel and Dudley[14] have studied the thermal stability of the Cu (II), Ni (II), Zn (II) and Fe (II) chelates of the following tetra-dentate schiff bases.



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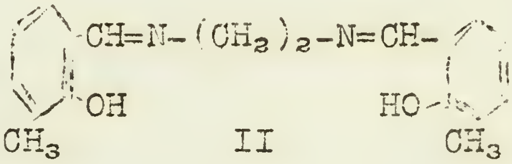

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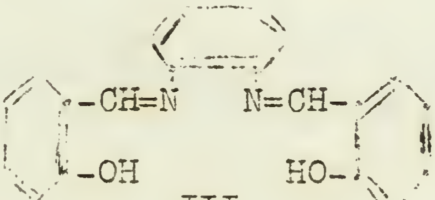
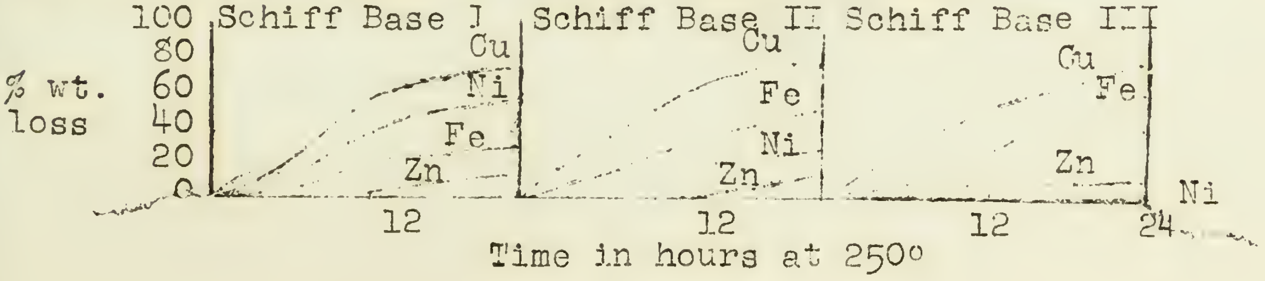


III

The results are plotted on the following graph.



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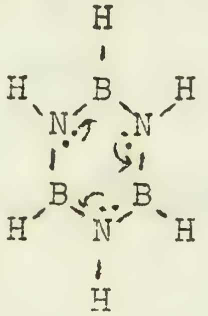
SOME RECENT DEVELOPMENTS IN THE CHEMISTRY OF BORAZOLE

J. K. Stille

November 13, 1956

Borazole has been previously prepared by the action of heat on the diammoniate of boranes, (1,2) or by mixing ammonia and diborane at 250-300° under 1 atm. (3-5) Borazole was earlier reported to be more stable than could be expected for this type compound and its unusual stability was attributed to its "aromatic" character. The planar structure of this six membered ring with alternating boron and nitrogen atoms is supported by electron diffraction data. (6,7) The bond angle is 120° and the B-N bond distance (1.44A°) lies between that of a single bond (1.54A°) and a double bond (1.36A°). Thus the structure may be written:



Infrared and Raman analysis support this resonating structure. (8) From this information, it is not surprising that borazole analogs of benzene have a striking similarity in their physical properties. (9)

Although borazole has been a laboratory curiosity for almost twenty-five years, recent developments in the preparative methods and the unusual thermal stability of substituted borazoles have given them increased importance as possible [illegible] lubricants and polymers.

Schaeffer and Anderson (10) have succeeded in preparing N-trimethylborazole in relatively large amounts by the action of $LiBH_4$ with methyl ammonium chloride.

$$3\ CH_3NH_3Cl + 3\ LiBH_4 \xrightarrow[Et_2O]{Rm.T} + 6H_2 + 3\ LiCl + \left[\ 3\ CH_3NHBH_2\ \right] \xrightarrow[2\ \ 25]{1\ Remov.\ \ ethe}$$

$$3\ H_2 + (CH_3)_3\ N_3\ B_3H_3\ (98\%)$$

Advantages in a similar procedure for the preparation of borazole (11) are in avoiding the preparation and handling of diborane as well as making it possible to carry out the reaction under nitrogen at 1 atm.

$$3\ NH_4Cl + LiBH_4 \xrightarrow[290°-300°]{ground\ glass} B_3N_3H_6 + 9H_2 + 3\ LiCl\ (35\%)$$

Wiberg and Bolz (4) first prepared B-trichloroborazole by the thermal decomposition of the addition compound of borazole and hydrogen chloride. In further studies of derivatives of borazole, Wiberg and Hertwig (12) prepared N-trimethyl-B-trichloroborazole by the reaction of boron chloride and monomethyl amine at 250°C.

Similarly Jones and Kinney (13) thermally decomposed the addition compound of aniline and boron chloride to obtain the corresponding substituted borazole. Previous workers

$$3\ BCl_3 + 3\ RNH_2 \rightarrow R_3N_3B_3Cl_3 + 6\ HCl$$

had obtained a variety of solid products when the reaction was run at low temperatures. (14,15) A new approach to the preparation of borazole was suggested by Laubengayer and Brown (16) who found that B-trichloroborazole may be prepared by the action of BCl_3 on NH_4Cl suspended in chlorobenzene,

$$3\ NH_4Cl + 3\ BCl_3 \xrightarrow[\substack{\text{reflux} \\ \text{pyrex glass}}]{\Phi Cl} N_3H_3B_3Cl_3 + 9\ HCl \quad (40\%)$$

Using this reaction scheme, Schlessinger worked out a procedure for the preparation of B-trichloroborazole and its subsequent reduction by use of $LiBH_4$ (17).

$$B_3Cl_3N_3H_3 + 3\ LiBH_4 \xrightarrow[\text{ether}]{\text{di-n-butyl}} 1\ 1/2\ B_2H_6 + 3\ LiCl$$
$$+ B_3N_3H_6 \quad (65\%)$$

Brown and Laubengayer (18) have described two methods for the preparation of B-trichloroborazole. In either case, boron chloride and ammonium chloride are allowed to react at elevated temperatures. The easier of the two methods consists of passing BCl_3 gas over dry NH_4Cl in a combustion tube at 165-175°C. The B-trichloroborazole produced is collected in the cooler portion of the tube in a 50% yield.

N-methylborazoles are obtained when diborane is heated with the amine. (3,19) The best method of preparation of N-substituted borazoles has already been described. Recently a number of N-trialkyl borazoles have been prepared and characterized. (20) The general procedure can be represented by the following equations

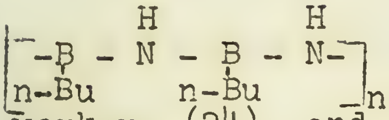
$$LiBH_4 + RNH_3Cl \xrightarrow{Et_2O} LiCl + BNH_5R + H_2$$

$$BNH_5R \xrightarrow[\text{2.}\quad 250°]{\text{1. remove } Et_2O} 1/3\ B_3N_3H_3R_3 + 2\ H_2$$

B-methylborazole is formed when borazole is treated with boron trimethyl (3) or when ammoniates of mono-, di-, or trimethy diboranes are heated in a closed tube. (21) The reaction of boron trimethyl with ammonia, followed by heating the addition compound $(CH_3)_3B \leftarrow NH_3$ gives B-trimethyl borazole. (19) The hexamethyl derivative is obtained when the compound $(CH_3)_3B \leftarrow NH_2CH_3$ is heated. (12)

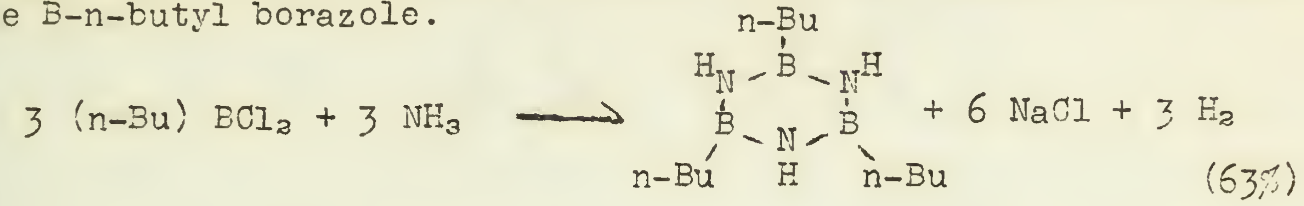
Recently B-trialkyl substituted borazoles have been investigated for their possible use as high temperature lubricants and polymers. (22) Booth and Kraus (23) reported a very stable polymeric boron-nitrogen compound which they described as "n-butyl boronimine" resulting from the reaction of di-n-butyl boron chloride and ammonia.

The structural formula of the polymer was assumed to be

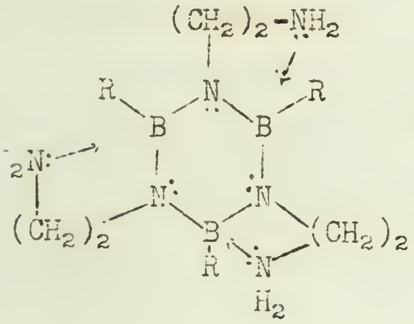


$$\left[-\underset{\text{n-Bu}}{B}-\overset{H}{N}-\underset{\text{n-Bu}}{B}-\overset{H}{N}-\right]_n$$

The work was repeated by a different set of workers (24), and the product obtained from the reaction was found to be B-n-butyl borazole.



This borazole evaluation was of interest since hexamethyl borazole is thermally stable to 500°C. B-triphenyl borazole was also prepared in the same manner. It is the intent to form polymeric borazoles by using aromatic, aliphatic and heterocyclic di-amines in place of ammonia. With ethylene diamine, the following products might be expected:



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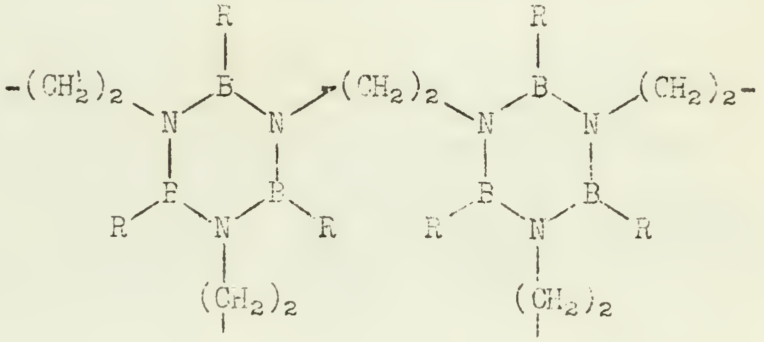

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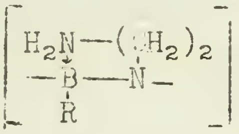
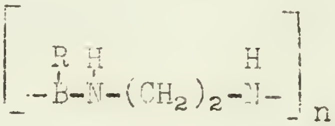


$$\left[\begin{array}{c} H_2N—(CH_2)_2 \\ —\underset{R}{B}——N— \end{array}\right]_n$$

III

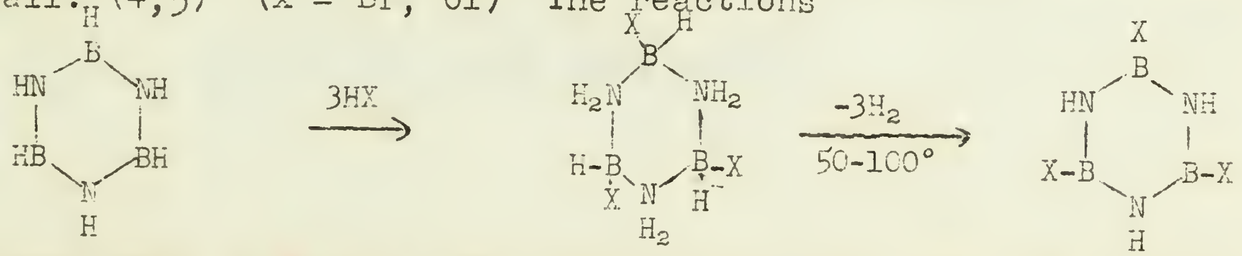


$$\left[-\overset{R}{B}-\overset{H}{N}-(CH_2)_2-\overset{H}{N}-\right]_n$$

IV

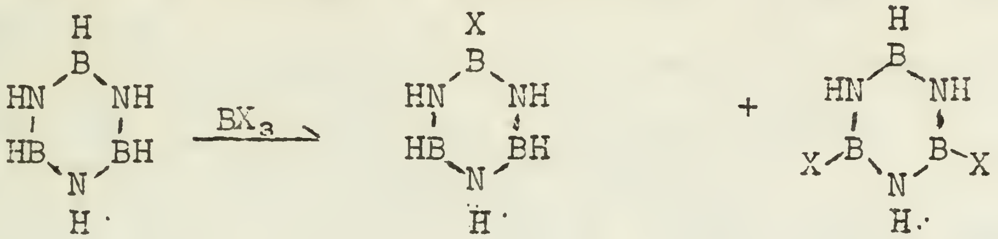
Structure I could be further polymerized with a dibasic acid to give a polyamide or, if 2-hydroxyethylamine were used, a polyester could be made by treatment with a dibasic acid.

Reactions of borazole with hydrohalides have been studied in detail. (4,5) (x = Br, Cl) The reactions



of hexamethyl borazole with hydrohalides were found to be more complicated, the ultimate product of which was B-trichloro-N-trimethylborazole. (5,12) Borazole will also add two moles of

bromine at 0°C, decomposing to dibromo borazole at 60°C. (4) Schlessinger (11) has described the reactions of borazole with boron halides (chloride and bromide).



Borazole reacts with water to form B-trihydroxy borazole (19). Reactions with methanol are like those of water, while ammonia and amines add to borazole. Borazole is somewhat less stable than seems to be generally recognized. This misinformation is probably due to statements made by Stock and Pohland (1) about gaseous borazole. Schlessinger (17) found non-volatile solids formed even at -30°C. Decomposition of B-trichloroborazole at room temperature is slight, but when in contact with water, HCl is evolved. Methyl and ethyl alcohols react similarly.

Ultraviolet absorption studies (25) and x-ray diffraction analysis (26) have also established the cyclic structure of B-trichloroborazole. The heats of formation and other physical properties for borazole and B-trichloroborazole have been measured (27,28). Measurements show that the principle molecular species in the vapor state are monomeric. The infrared absorption maxima of some borazoles are composed in table I (8,24).

I

Borazole	B-trichloroborazole	B-tri-n-butylborazole	Assignments
717	705	712	arom. ring [illegible]s.
756			ring rocking
778		(775)	ring rocking
790		(797)	ring rocking
917		893	ring rocking
1098	1037	1090	N-H bending
--		1351 S	B-C abs.
--		(1408)	--
1465	1440-1472	1475	--
--		2900 S	C-H str.
3050-90	3125	3430	N-H str.
	3435		

(S) absorption due to side chain
( ) minor maxima

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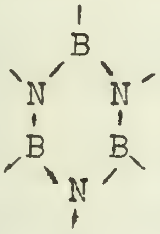
SOME DERIVATIVES OF BOROSULFOLE

Grant White November 27, 19

Numerous types of inorganic compounds which contain six-membered ring systems are known. Work on borazole (I)--the topic of a recent seminar--and boroxole (II) has been extended to the analogous borophosphole (III) and borosulfole (IV) structures. (1) Most of the work on the borosulfoles has been carried out by E. Wiberg and W. Sturm. (1-11)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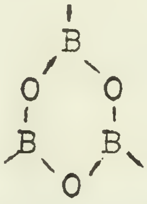
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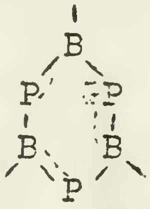
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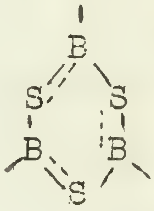
IV

Earlier investigators probably obtained derivatives of borosulfole but designated their products as addition compounds: "$B_2S_3 \cdot H_2S$" (12) and "$B_2S_3 \cdot BBr_3$" (13).

The borosulfoles have been prepared by two general procedures. The reactions are usually carried out in carbon disulfide.

1. From H_2S and "borines":

   a) $3\ BX_3 + 3\ H_2S \rightleftharpoons (BXS)_3 + 6\ HX$

   b) $3\ BRX_2 + 3\ H_2S \rightleftharpoons (BRS)_3 + 6\ HX$

2. Substitution reactions on the borosulfole ring:

   a) $(BYS)_3 + BX_3 \rightleftharpoons (BXS)_3 + BY_3$

   b) $(BYS)_3 + 3\ HX \rightleftharpoons (BXS)_3 + 3\ HY$

Compounds with the general formula $(BXS)_n$ have been prepared with n equal to 2, 3, and higher. Experimental findings are summarized in the following tables.

Trimeric Forms, $(BXS)_3$

X	Preparation and Properties		
F	Unknown, probably due to extreme ease of disproportionation.		(
Cl	2a, Y=SH;	Disproportionates to $BCl_3 + B_2S_3$. Sensitive to water.	
Br	2a, Y=SH;	m.p. 132-5, sealed tube	
I	2b, Y=SH; m.p. 122 d.	Crystals and solutions yield I_2.	(
OMe	2a, Y=SH; m.p. 27.5 Oxidation of $(BMeS)_3$;	Vacuum distils at 85°, but disproportionates above 100 . Sensit to oxygen-containing solvents.	(4,
SH	1a, XS H_2S, Δ;		(
SEt	2a, Y=SH;	Dimerizes. Decomposed by oxygen-containing solvents.	(11
NMe_2	2a, Y=SH; m.p. 118.	Slowly hydrolyzed at room temperatu Forms salts with HBr.	(4,
NHMe	Dropping a benzene solution of $(BBrS)_3$ into a benzene solution of CH_3-NH_2.	Empirical analysis: BSNHMe·HBr	(1
Me	2a, Y=SH; m.p. 56.	Oxidizes to X=OMe. Polymerizes readily.	(1,9
-Bu	1b; b.p. 89-94 at 0.8 mm.	No tendency to disproportionate. Decomposed by oxygen-containing solvents.	(
-Bu	1b; b.p. 116-9 at 0.8 mm. 234 at 720 mm.	Polymerizes. Otherwise same as i-Bu.	(
ϕ	1b, $B\phi Br_2$; m.p. 232-3, sealed tube.	No disproportionation even on stro heating. Unaffected by brief conta with the atmosphere.	(1,1

Dimeric Forms, $(BXS)_2$

X	Preparation and Properties	
SH	1a at 50c;	Trimerizes on heating to 90
SEt	2a, Y=SH produces trimer.	Dimer (m.p. 4) formed on dis[illegible] in high vacuum.

Higher Polymeric Forms, $(BXS)_{n>3}$.

X	Preparation and Properties	
Me	2a, Y=SH, $CHCl_3$ solv., N_2 atmosphere, yields trimer. On standing at room temperature, the compound increases in molecular weight with n approximating 4 in one hour.	(1,
n-Bu	1b; Polymerizes to give a high polymer, insoluble in organic solvents, but slowly solvolyzed by water and alcohol.	(
H	1a, BH_3; or $(B(SH)S)_3 + LiBH_4$ or $LiAlH_4$; or $(BBrS)_3 + LiAlH_4$ or $B_2H_6 + H_2S$ (sealed bulb) (14). Polymer formed directly.	(

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Clathrate Compounds

Robert D. Vest December 4, 1956

The clathrate type of molecular compound is formed by the imprisonment of one molecular specie in the cage structure of another component. In such a compound a) there is no apparent means of linking the two components, b) the including host component must somehow be capable of cage formation, c) the included component can be replaced by other molecules that fit into the cage structure but not by chemically similar compounds if these are of unsuitable size, and d) there is a limiting composition which depends upon the number of cavities available in the host compound. The composition of such inclusion compounds may vary since some of these holes may not be occupied (1). The spatial "fitting in" of these molecules has been compared to the positive and negative parts of a relief (2).

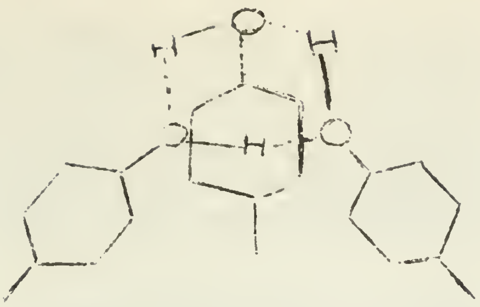
Four forces of interaction are important in such inclusion compounds (3). These are a) London dispersion forces, b) dipole-induced dipole forces, c) dipole-dipole forces which are important in the inclusion of HCl and HBr but are relatively unimportant in the A, Kr, and Xe complexes, and d) repulsive forces due to the distortion of the crystal lattice.

The energies of interaction of gaseous molecules with the β-quinol lattice have been measured (3). The data show that the stability of these complexes is strongly dependent on the polarizability of the included molecule. A major part of the change in free energy of the inclusion compound going to its components is attributable to changes in translational entropy and, for polyatomic gases, in rotational entropy.

Inclusion compounds may be divided into two classes: a) cage structures in which a three dimensional enclosure traps the included molecule and b) channel structures in which layers of host molecules wrap themselves around the included molecule.

Quinol Clathrates

Caspari, in 1927, noted a difference in the crystalline structure of quinol depending upon the solvent from which it was crystallized. The crystals obtained from aqueous solution were characterized as the α-quinol form and those obtained from methanol designated the β-quinol form. More recently, Powell (5,6), has shown that β-quinol is a clathrate compound of quinol in addition to being a different crystalline modification. In the presence of H_2S, CH_3OH, SO_2, A, Kr, Xe, and other molecules of similar size, quinol crystallizes as the strongly hydrogen bonded structure I.



I

Two of these structural units are joined in an inverted manner generating a void in which the included molecule resides. The ideal formula for a resulting clathrate is 3 $C_6H_4(OH)_2 \cdot M$. The actual composition may vary from very small amounts of M to 0.99M for methyl cyanide (6). In order that the crystal lattice accomodate certain larger molecules it is necessary to distort the crystal lattice in one direction.

The adducts of quinol and A, Kr, and Xe are generally prepared by slowly cooling a saturated aqueous or ethanolic solution of quinol under a pressure (ca.25-40 atm.) of the gas in a steel bomb. Adducts of HBr and HCl are prepared by passing the dry gas through a saturated ethereal solution of quinol (10). The products are stable crystalline solids which have no odor of the inclosed gas. They are easily decomposed by heat or by dissolution. The argon compound, 3 $C_6H_4(OH)_2 \cdot 0.8A$, corresponds to an argon content equivalent to a pressure of 73 atmospheres. Based on calculations by Powell (7) a 100 cc. sample of this compound would contain over 7000 cc. of argon at standard conditions. This suggests a possible source of pure noble gases. All attempts to prepare the helium compound have failed indicating that the effective size of the helium atom is such that it can escape readily from the cage structure (8,9). In general these compounds are colorless although the quinol-oxygen and the quinol-sulfur dioxide compounds have been reported as being slightly yellow (10).

The inclosed molecules are essentially isolated, that is, there can be no interaction of the gas molecules with themselves. These compounds offer a means by which the included gases may be studied at very low temperatures. For example, the magnetic susceptibilities of oxygen and nitrous oxide have been studied in the liquid helium range (11).

Gas Hydrates

Methane, carbon tetrafluoride, chlorine and argon form stable compounds with water. These are believed to be inclusion compounds (12, 13).

Ammonia - Nickel Cyanide Complex

Benzene, thiophene, furan, pyrrole, aniline and phenol form inclusion compounds when allowed to react with ammoniacal [illegible]

nickel cyanide solutions. Their structures are best pictured as a two dimensional array of -Ni-CN-Ni- groups which form flat networks. It is thought that every other nickel atom has two ammonia groups projecting above and below this network. Such an arrangement yields a structure in which voids are available for the inclusion of smaller molecules (1,14).

Cyclodextrins (15,16)

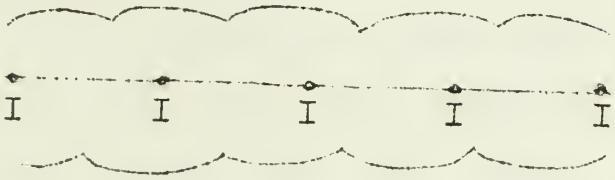
Cyclodextrins are large cyclic organic molecules which are capable of including a variety of other molecules. The following table summarizes their properties.

Cyclodextrin	No. of glucose units	Diameter of hole (Å)	Forms adducts with
α	6	6	Cl_2, Br_2, I_2, hydrocarbo substituted benzenes
β	7	8	Br_2, I_2, many organic molecules
γ	8	10-11	I_2, only large organic molecules

Since the voids in the cyclodextrins are within the molecule in contrast to the voids in a crystal lattice, these compounds include other components in solution.

The void in the center of the cyclodextrin molecule has been described as "basic" due to the high electron density in that space (17). This basic character has considerable effect on certain included molecules.

Included iodine was found to exist in polymeric chains with a constant distance (3.06Å) between iodine atoms (18). Structurally this has been depicted as follows:



This has been termed a "metallic modification" of iodine in that the electrons can move freely along the molecular axis (19). Infra-red analysis supports the polymeric chain structure (20).

X-ray analysis of the V-amylose-iodine compound indicates that other starch iodine complexes are of the same nature (21). Starch in neutral or acidic solutions forms a helical structure in which each turn has about 6 glucose units similar to α-cyclodextrin.

The high electron density in the cyclodextrin voids has effects on systems other than iodine. This high electron density enolizes α-hydroxy ketones, thus facilitating oxidation to α-diketones (17).

Cramer has shown that the activity of iodine in cyclodextrin solutions is greatly decreased as observed in the decrease in the E.M.F. of reduction-oxidation potential $I_2/2I^-$ (17).

Urea and Thiourea

Urea and thiourea complexes represent inclusion compounds which are formed as a result of the channel nature of the crystal lattice. These channels in urea have a diameter of about 5A and will thus accomodate straight chain compounds with more than six carbon atoms; the channel diameter in the crystal lattice of thiourea is larger and will include some branched chain and ring compounds (22). Such inclusion compounds have found application in the separation of hydrocarbons. The process has been termed "extractive crystallization" (23).

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THE CHEMISTRY OF THE NITROSYL ION

C. W. Kruse December 11, 1956

The nitrosyl cation, $:N\equiv\overset{+}{O}: \longleftrightarrow :\overset{+}{N}=\ddot{O}:$, is isosteric with nitrogen and carbon monoxide molecules and with cyanide ion. The attainment of an even number of electrons and resonance stabilization account in part for the low ionization potential of nitric oxide (NO, 9.3 e.v.) in comparison with corresponding values for other diatomic molecules (O_2, 12.2 e.v.; N_2; 15.6 e.v.). The existence of the nitrosyl ion in salts and in solution has been confirmed in a number of ways which include freezing point determinations, conductance experiments, spectroscopic measurements, and comparisons with isomorphic salts.

The ionic nitrosyl salts are limited to those of strong acids. The anions of weak acids are strong enough bases to give covalent nitroso derivatives. Nitrosyl acetate (acetyl nitrite) is therefore a nonelectrolyte whereas nitrosyl hydrogen sulfate is an ionic salt, m.p. 73.5°C. The following equations illustrate various preparative methods:

(a) $N_2O_3 + 3\ HX \xrightarrow[\text{liq. } SO_2]{\text{abs. HX}} 2\ NOX + H_3OX$; ($X=ClO_4^-$, HSO_4^-)

(b) $SO_3 + RONO \longrightarrow NOSO_3OR$

(c) $SO_2 + HNO_3 \longrightarrow NOHSO_4$

(d) $Al + 4\ NOCl \longrightarrow NOAlCl_4 + 3\ NO$

(e) $BF_3 + NOF \longrightarrow NOBF_4$

Liquid sulfur dioxide and nitrosyl chloride do not undergo solvolysis reactions with nitrosyl salts and are useful solvents for carrying out metathetic reactions. The nitrosyl salts of monobasic chloroacids are very soluble, whereas the salts of dibasic chloroacids, of fluoroacids, and of oxygen acids are insoluble or difficulty soluble. The precipitation of nitrosyl perchlorate from a solution of nitrosyl chloroantimonate in liquid sulfur dioxide upon addition of tetramethylammonium perchlorate is analogous to the precipitation of potassium perchlorate from water.

$$NO^+ + ClO_4^- \xrightarrow{\text{liq. } SO_2} NOClO_4$$

$$K^+ + ClO_4^- \xrightarrow{H_2O} KClO_4$$

Liquid sulfur dioxide cannot be used as a solvent for reactions in which nitrosyl compounds are to be reacted with basic substances since sulfur dioxide, which is an acid anhydride, reacts preferentially. For such reactions pyridine is a useful solvent.

Precipitation reactions can even be carried out in absolute sulfuric or nitric acids:

$$NOHSO_4 + KClO_4 \xrightarrow{H_2SO_4} NOClO_4 + H_2SO_4$$

$$NO^+\ NO_3^- + R_4N^+BF_4^- \xrightarrow{HNO_3} NOBF_4 + RN_4^+ + NO_3^-$$

Solutions of nitrosyl salts in absolute sulfuric acid and in absolute nitric acid behave as solutions of nitrosyl sulfuric acid and of dinitrogen tetroxide, respectively, in accordance with the following equilibria:

$$NO^+ + H_2SO_4 \rightleftharpoons NOHSO_4 + H^+$$

$$NO^+ + HNO_3 \rightleftharpoons N_2O_4 \; (\rightleftharpoons NO^+NO_3^-) + H^+$$

The nitrosyl ion is solvated in nitrosyl chloride (as hydrogen ion is in water), and the high transport number of NO^+ (0.88 for $NOFeCl_4$) suggests a transport mechanism which is analogous to that proposed for hydrogen ion. The similarity between NO^+ ion and H^+ ion is recognized in the reaction of metallic sodium with each,

$$Na + NO^+ \xrightarrow{\text{liq. } SO_2} NO + Na^+$$

$$Na + H^+ \xrightarrow{H_2O} 1/2\, H_2 + Na^+$$

Several chemical reactions are available for detection of the nitrosyl ion. Reaction with azide ion reveals concentrations which are too low to be detected spectroscopically,

$$NO^+ + N_3^- \longrightarrow N_2O + N_2$$

Precipitation of the insoluble perchlorate is suitable for detection at higher concentrations. The formation of the blue to blue violet "nitric nitrosyl" cation ($N_2O_2^+$) with nitric oxide under pressure has been demonstrated to be a property of the nitrosyl ion. The existence of this blue cation leads us to speculate that the blue compound reported by Lehner and Mathews to be $(NO)_2SeO_4$ may have been $N_2O_2^+\ HSeO_4^-$ instead (4).

Nitrosyl salts react with water (or alcohols) to give nitrous acid (or alkyl nitrite) and the conjugate acid of the anion. Ammonia (or primary amines) react with the salts to yield nitrogen, the ammonium (or quaternary ammonium) salts, and water. Aromatic amines are diazotized by nitrosyl salts in liquid sulfur dioxide,

$$ArNH_2 + NOHSO_4 \longrightarrow ArNN^+\ HSO_4^- + H_2O$$

Nitrosyl salt solutions are remarkably stable toward many oxidizing agents, but the nitrosyl ion can be oxidized electrolytically or by chlorate ion. The nitrosyl ion is easily reduced to nitric oxide and functions as an oxidizing agent in many reactions. The reactions of nitrous acid are more easily explained if an equilibrium which involves nitrosyl ion is assumed, as

$$HONO + H_2O \rightleftharpoons OH^- + H_2ONO^+$$

In aqueous medium the NO^+ ion is an unsolvated acid. The solvated ion, H_2ONO^+, gives by protolysis first nitrous acid then nitrite ion,

$$H_2ONO^+ \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} HONO \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} NO_2^-$$

Nitrous acid is therefore an amphoteric substance, as illustrated by the following equations:

$$HONO + H_2SO_4 \longrightarrow NOHSO_4 + H_2O$$

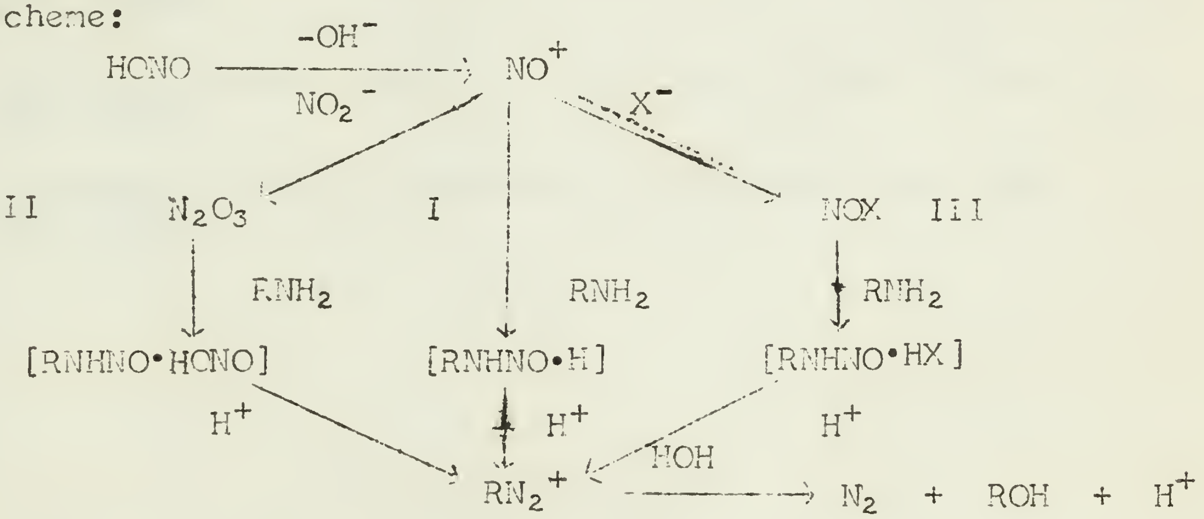
$$HONO + KOH \longrightarrow KNO_2 + H_2O$$

The displacement of carbon monoxide or cyanide ion from complexes by the action of nitrous acid is believed to be a displacement by nitrosyl ion.

$$Co(CO)_4^- + NO_2^- + 2\ H^+ \longrightarrow Co(NO)(CO)_3 + CO + H_2O$$

$$Fe(CN)_6^{-4} + NO_2^- + 2\ H^+ \longrightarrow Fe(NO)(CN)_5^{-2} + CN^- + H_2O$$

Kinetic data from various nitrous acid reactions can be interpreted in terms of the nitrosyl ion. The formation of nitrosyl ion is considered to be the rate determining step for the reactions of nitrous acid with azide ion, with hydrogen peroxide, with sulfite ion, and with labeled nitrite ion, since in each case, rate= $k[HONO][H^+]$. The reactions of nitrous acid with derivatives of ammonia (RNH_2) give a variety of different kinetic expressions, but these reactions, which lead to nitrosations, diazotizations, and cleavage of nitrogen, can be interpreted in terms of the following reaction scheme:



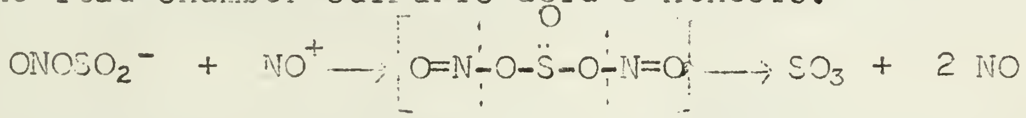
Path I: rate = $k\ [HONO][H^+][RNH_2]$
Path II: rate = $k\ [HONO]^2$ or $k[HONO]^2[RNH_2]$
Path III: rate = $k\ [HONO][H^+][X^-]$ or $k\ [HONO][H^+][X^-][RNH_2]$

Path I is followed at low nitrous acid concentration and high acidity. Path II is followed at high concentration of nitrous acid, whereas path III is followed when the halide ion concentration is high.

Nitrosyl ion is a strong antibase by Bjerrum's concept. The oxidation of an anion by nitrosyl ion can be represented by an antibase-base reaction followed by homolytic cleavage of the resulting bond.

$$NO^+ \quad + \quad :I^- \longrightarrow NO{-}I \longrightarrow NO \quad + \quad I$$

The oxidation of the nitrosyl sulfite ion is postulated to be a step in the lead chamber sulfuric acid synthesis.



$$ONOSO_2^- \quad + \quad NO^+ \longrightarrow \left[O{=}N{-}O{-}\overset{O}{\ddot{S}}{-}O{-}N{=}O \right] \longrightarrow SO_3 \quad + \quad 2\ NO$$

In conclusion, the reactions of nitrosyl cation in nonaqueous solvents are comparable to those of metallic or hydrogen ions in water. The formation of nitrosyl ion from nitrous acid appears to be a step in the majority of the reactions of this acid. The lead chamber process for sulfuric acid, oxidations with nitric acid, the Raschig hydroxylamine synthesis, and diazotizations proceed directly or indirectly by way of the nitrosyl cation.

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RECENT DEVELOPMENTS IN THE CHEMISTRY OF THE SULFANES

H. D. Frame January 8, 1957

Since sulfur-sulfur bonds exist in the S_8 ring in elemental sulfur with a bond energy (63.8 kcal/mol) greater than that of the carbon-carbon bond (58.5 kcal/mol) (1), one might expect thermodynamic stability among the chain-like sulfur compounds.

Nomenclature:

A consistent nomenclature has been proposed by Franz Feher (2) for compounds containing the S-S linkage. The parent hydrides are known as the sulfanes and thus are to be compared with the alkanes, germanes, boranes, azanes, etc.

H_2S_n	Sulfane
$M^1_2S_n$	Alkali Sulfane
X_2S_n	Halo Sulfane (X=F, Cl, Br, CN
R_2S_n	Dialkyl-(or Diaryl-) Sulfa
$(HSO_3)_2S_n$	Polythionic Acid

M. Schmidt has proposed that the polythionic acids be designate "sulfonated sulfanes" (3).

Preparative Methods:

The principal methods which have been used for the preparation of these compounds are illustrated by the following type reaction.

I. $Na_2S_x(aq.) \xrightarrow{HCl} H_2S_x\ (x=4,5,6) \xrightarrow[\text{or crack}]{\text{dist.}} H_2S_n\ (n=2,3,4,5,6$

II. $M^1_2S_n\ (M=Na,K,NH_4) \xrightarrow{HCOOH} H_2S_n\ (n=2,3,4,5)$

III. Cathodic reduction of aqueous SO_2 solutions:

$x\ SO_2 + (4x+2)\ H^+ + (4x+2)\ e^- \rightarrow H_2S_x + 2x\ H_2O\ (x=7,8,9,10,11,1$

IV. $2H_2S_x + S_yX_2 \rightarrow H_2S_{2x+y} + 2HX$ (X=halogen) (x=1,2,3,....;
y=0,1,2,....)

I. This long-known method (4) depends upon the acid decomposition of aqueous alkali sulfide solutions. A crude water-insoluble sulfane mixture is obtained which has been shown to contain H_2S_x (where x=4,5,and 6), and some dissolved sulfur (5). The di- and tri- sulfanes result in the final step from the thermal cracking of the higher homologs.

II. Earlier workers used $(NH_4)_2S_5$ to prepare H_2S_5 (6). This reaction entails operation in anhydrous formic acid. Feher (7) has

shown that the fairly pure sulfanes (H_2S_2, H_2S_3, H_2S_4, and H_2S_5) can be more readily obtained from the corresponding sodium and potassium poly-sulfides. The genetic relationship of such "poly-sulfides" to the corresponding sulfanes has thus been established.

III. Electrolysis is effected in a compartment cell in which the catholyte consists of $3\underline{N}$ H_2SO_4 saturated with SO_2. If the anolyte consists of ammonium sulfate accidified with sulfuric acid, simultaneous production of peroxydisulfate can be effected. The cathodic reaction is assumed to entail initial formation of dithionous acid, $H_2S_2O_4$:

$$2SO_2 + 2H^+ + 2e^- \rightarrow H_2S_2O_4.$$

The latter undergoes "hydrolysis" and disproportionation to reform sulfurous and polythionic acids (sulfonated sulfanes) which decompose to yield the higher sulfanes (8,9).

IV. If equivalent quantities of the halosulfane or the halog are allowed to react with the sulfane, the hydrogen halide and sulfur are the only products. If an excess of the "hydrogen conta ing component" is used, higher sulfanes with chain length from 6-30 sulfur atoms are produced (10,11). Reaction is carried out at low temperatures in presence or absence of solvent and with high mole ratios of sulfane to halosulfane or halogen. Mixtures of sulfanes are obtained when lower ratios of the reactants are employed. Thes reactions can be considered as examples of thiosolvolysis.

Other methods include acid decomposition of thiosulfate solutions, which is claimed to lead to sulfanes as high as H_2S_{354} (12, 13), reduction of SO_2 solutions with nascent hydrogen or phosphorous acid, and oxidation of H_2S with H_2O_2 (7).

Properties:

The color of the sulfanes increases with molecular weight fr a clear pale yellow in the case of H_2S_2 to brown in the higher sulfanes. No sharp melting points can be obtained, for the sulfanes behave much like glasses upon cooling, gradually hardening. However, when the solids are warmed, a momentary halt occurs in the heating curve. The odor of the sulfanes is comparable with camphor or S_2Cl_2 and the vapor has a disagreeable effect on the eyes and nose. The viscosity increases from water-like for H_2S_2 to an olive-oil consistency for the higher mixtures (which could arise from the longer chains or dissolved S_6).

Physical properties are given in Moeller (14).

Structure:

Although various structures have been suggested in the past, the following evidence has been presented to support the contention that sulfur chains characterize the linkages in these compounds:

1. Parachors. Earlier work on ethyl sulfanes (15) led Baroni to the assumption that branched-chain structures were capable of existence. More recent work (16,17) on chloro- and bromo-sulfanes [illegible] by constant increments thus

supporting a straight chain structure. Since parachor work is known for its extreme sensitivity to impurities, Feher has suggested that impurities are responsible for the earlier discrepancies.

2. Molecular volume. The molecular volume of a series of alkali sulfanes varies linearly as a function of the number of S atoms for the M_2S_x compounds (M= Na, K, Rb, Cs) (18).

The molecular volume of the sulfanes as a function of the number of sulfur atoms can also be expressed by a straight line relationship. The data are given in the following table (7):

Molecular Volume

Sulfane	Observed	Predicted
H_2S_2	49.58	-----
H_2S_3	65.86	65.96
H_2S_4	82.34	82.34
H_2S_5	98.73	98.72
H_2S_6	115.09	115.10

The theoretical values in the second column are calculated from the equation:

$$V_m = 49.58 + (x-2)\ 16.38,\ \text{where x=number S atoms.}$$

3. Molecular refraction. Values for R_m as a function of the number of sulfur atoms can be represented by the equation:

Molecular Refraction

Sulfane	Observed	Predicted
H_2S_2	17.65	-----
H_2S_3	26.24	26.24
H_2S_4	34.92	34.83
H_2S_5	43.58	43.42
H_2S_6	52.00	52.01

In both (2) and (3) above the two increments may be thought of as serving for the end -SH group (and hence, a constant after H_2S_2) and the inner -S- atom. Only dissolved sulfur interferes with these values.

4. Raman spectra. Perhaps the best evidence for the chain structure is found here. Below are listed the observed Raman frequencies for various sulfanes (19):

Crude Sulfane*	H_2S_2	H_2S_3	H_2S_4	H_2S_5	H_2S_6	Soln of S in H_2S_x
148(2)					148(1)	152(8)
183(2)			183(4)	182(00)	183(2)	184(1)
215(2)		207(5)			215(1)	217(8)
242(0)					246(0)	245(2)
[illegible]					467(6)	434(2)

	H_2S_2	H_2S_3	H_2S_4	H_2S_5	H_2S_6	Soln of S in H_2S_x
485(7)	508(9)	484(8)	484(7)	485(7)	485(7)	473(8)
882(1)	882(3)	882(2)	882(1)	882(0)	882(0)	520(0)
2513(2)	2513(2)	2513(4)	2513(2)	2513(2)	2513(2)	

*approximate composition $H_2S_{5.5}$

Derivaqives and Reactions:

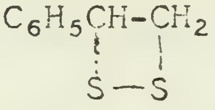
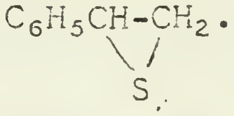
1. Sulfanes react with halosulfanes to produce either higher sulfane or higher halosulfane homologs.

a) with xs halosulfane

$$aH_2S_n + bS_mX_2 \rightarrow (b-a)X_2S_x + 2aHX$$

b) with xs sulfane

$$aH_2S_n + bS_mX_2 \rightarrow (a-b)H_2S_x + 2bHX \quad (10,11)$$

2. Sulfanes have been shown to add to double bonds (20). The action of crude sulfane on styrene in liquid H_2S gives a product containing 37.4% sulfur. This finding has been explained by assuming formation largely of  $C_6H_5\underset{S-S}{CH-CH_2}$ with some  $C_6H_5\underset{S}{CH-CH_2}$.

Hydrazobenzene is formed from azobenzene. Dry benzenediazonium chloride reacts explosively; in CS_2 solution the reaction takes plac more slowly.

3. Some miscellaneous reactions of trisulfane with inorganic compounds are summarized in the following table (21).

	violent reaction	ignition	rapid decomposition	slow decomposition	no or incomplete rx.
metal oxides	PbO, SnO_2 Fe_3O_4	Ag O, CuO PbO_2, HgO		ZnO, BaO_2 MnO_2	
non-metal oxides				As_2O_3, As_2O_5	P_2O_5, B_2O_3 HCl-washed SiO_2
oxidizing agents		$KMnO_4$	$K_2Cr_2O_7$		
salts*			anhyd. $CuSO_4$ $Pb(NO_3)_2$ Ag NO_3 Cu NO_3	$FeSO_4$, $Al_2(SO_4)_3$ $NiSO_4$, $ZnSO_4$ $MnSO_4$ $Al(NO_3)_2$ $CdCl_2$, NH_4Cl $PbCl_2$, $CuCl_2$ $Cu(O\ Ac)_2$, Cu Br_2 Cu oleate	
Metals			powdered As, Sb, Zn, Fe		massive became coated with sulfide and non-reactive

*$Fe(NO_3)_3$ slowly, then violently reacting-suggests autocatalytic rx.

4. Mercaptans react with halosulfanes in CS_2 solvent (in presence of sulfur) in a closed tube (100°) to yield the alkyl sulfanes (22):

$$S + RSH + XS_nX + HSR \xrightarrow[\Delta]{CS_2} R_2S_{n+3}.$$

The action of Ag powder on Cl_3CSCl under reflux at 85-90° for 72 hours followed by purification gives $Cl_3CSSCCl_3$. Disulfane, H_2S_2, reacts with Cl_3CSCl when heated at 85° for 20 hours, to give $Cl_3CSSSSCCl_3$ (23).

5. The metal sulfane salts are prepared by the reaction of the metal with sulfur in liquid NH_3 (K_2S_2, K_2S_4), boiling toluene ($K_2S_{4.7}$ mixture) or by addition of the calculated amount of S to a K_2S solution in absolute alcohol followed by precipitation of the insoluble product (K_2S_3, K_2S_5). K_2S_6 results from melting K_2S_5 and S in vacuo (24).

High (β) and low (α) temperature modifications of Na_2S_2 have been reported (25).

6. The polythionic acids have been shown to be sulfonated sulfanes (3). Interaction of thiosulfate in ether suspension at -50° with dry HCl leads to formation of the etherate of free thiosulfuric acid:

$$Na_2S_2O_3 \xrightarrow[\substack{\text{dry HCl} \\ -50^\circ}]{Et_2O} H_2S_2O_3 . xEt_2O.$$

The latter decomposes into H_2S and SO_3, suggesting that thiosulfuric acid is a monosulfonated monosulfane:

$$H_2S_2O_3 \rightarrow HSO_3 \cdot SH \rightleftharpoons SO_3 + H_2S$$

This finding has been used to synthesize higher polythionic acids,

a) by reaction of H_2S_n (in xs) with SO_3 to give $HSO_3 \cdot S_nH$

b) by reaction of H_2S_n with SO_3 (in xs) to give $HSO_3 \cdot S_n \cdot SO_3H$

c) by action of oxidizing agents (I_2) upon mono-sulfonated sulfanes

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IONIC REACTIONS IN ETHER

J. L. Fedrick

February 19, 1957

Diethyl ether has been used as a solvent for inorganic reactions for many years. Although Walden (1) was the first investigator to study reactions in anhydrous ether, more detailed investigations have been undertaken recently by Gerhart Jander of the "Anorganisch-chemisches Institut der Technischen Universitat" at Berlin-Charlottenburg (2).

PHYSICAL PROPERTIES

Ether is a liquid from -116° to 35.5° (3). Its low freezing point makes it an excellent solvent for low temperature reactions. The fact that it is a good solvent for covalent compounds is apparent from the comparison of its specific conductance of 14.7×10^{-1} with that of water which is 6×10^{-8}. Although its low boiling point and low heat of vaporization make it an easy solvent to eliminate, this volatility also has its disadvantages since ether forms a combustible mixture with air.

SOLUBILITY

An attempt was made to gather data and correlate the solubilities of inorganic compounds in ether. Data was collected from Chemical abstracts, Beilstein, Walden (1) and Jander (2). Compounds were listed by the periodic group of the cation. Attempts to correlate solubility with ionic size, polarizability and electronegativity were unsuccessful. Walden has made the following generalizations concerning the solubilities of binary halides. (1) For the same cation the solubility increases with increasing atomic weight of the halogen. (2) For a series of cations with the same halogen anion, the solubility increases with decreasing atomic weight of the metallic ion. (3) The lower oxidation state of an element forms less soluble compounds than does the higher oxidation state. (4) Hydrated compounds are more soluble than anhydrous compounds. (5) The temperature coefficient of solubility is always small. These statements were found to be valid; however, it is difficult to extend these rules due to lack of information. The relative solubilities of binary compounds from the same two families can be determined by Fajans' rules, if Lewis acid strength, proton bonding and other factors are taken into account.

ETHERATES

Many substances, notably Lewis acids, become strongly bound to one or more molecules of ether. These etherates lose ether of solvation stepwise when heated, as illustrated by the changes which the magnesium bromide etherates undergoes (4). The stability of the

etherates varies widely

$$MgBr_2 \cdot 3\ Et_2O \xrightarrow{10^{0}} MgBr_2 \cdot 2\ Et_2O \xrightarrow{30^{0}} MgBr_2 \cdot Et_2O \xrightarrow{190^{0}} MgBr_2$$

but formation of such solvates should be expected whenever reactions are carried out in ether.

IONIC REACTIONS IN ETHER

The limited conductance of ether is presumably due to dissociation in accordance with the following equilibrium. According to the solvent system concept the $C_2H_5^+$ ion should be the acid

$$(C_2H_5)_2O \longrightarrow C_2H_5^+ + C_2H_5O^-$$

species and $C_2H_5O^-$ the base species of this system. The specific conductances of a series of ethyl compounds in ether suggests that the same order of acid strength holds for these acid analogs as for the hydrogen halodes in water.(2).

$$C_2H_5I > C_2H_5NO_3 > C_2H_5Br > C_2H_5Cl$$

From these considerations it should be possible to titrate ethyl bromide with lithium ethoxide; however, no reaction was observed. Lithium ethoxide is only slightly soluble and ethyl bromide is not dissociated to any appreciable extent. This reaction may be compared to the inertness of boric acid in the presence of the strong insoluble base, Ag_2O.

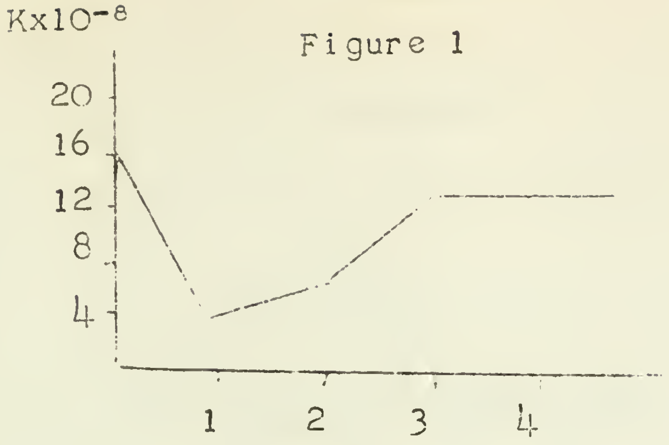
In an attempt to find a strong acid which could be titrated with lithium ethoxide the relative strength of a number of Lewis acids was determined conductometrically. The following order of acid strength was observed. The fact that BBr_3 is a weaker acid

$$AlI_3 > Al(ClO_4)_3 > AlBr_3 > TiBr_3 > AlCl_3 > GaBr_3 > BBr_3$$

than $GaBr_3$ and $AlBr_3$ would not have been expected.

The possibility of an acid-base reaction between BBr_3 and $LiOC_2H_5$ was next investigated and successfully carried to completion. The course of this ionic reaction could be followed by potentiometric methods since BBr_3 forms a highly conducting complex ion in ether. The titration

Figure 1



curve depicted in Figure 1 suggests that the following reaction sequence may be postulated.

$$C_2H_5\ [B\begin{smallmatrix}Br_3\\ (OC_2H_5)\end{smallmatrix}] + LiOC_2H_5 \rightarrow Li[B\begin{smallmatrix}Br_3\\ (OC_2H_5\end{smallmatrix}] + (C_2H_5)_2O$$

$$Li[B\begin{smallmatrix}Br_3\\ (OC_2H_5)\end{smallmatrix}] + (C_2H_5)_2O \rightarrow C_2H_5[B\begin{smallmatrix}Br_2\\ (OC_2H_5)_2\end{smallmatrix}] + LiBr$$

$$C_2H_5[B\begin{smallmatrix}Br_2\\ (OC_2H_5)_2\end{smallmatrix}] + LiOC_2H_5 \rightarrow Li[B\begin{smallmatrix}Br_2\\ (OC_2H_5)_2\end{smallmatrix}] + (C_2H_5)_2O$$

$$Li[B\begin{smallmatrix}Br_2\\ (OC_2H_5)_2\end{smallmatrix}] + (C_2H_5)_2O \rightarrow C_2H_5[\begin{smallmatrix}Br\\ (OC_2H_5)_3\end{smallmatrix}] + LiBr$$

$$C_2H_5[B\begin{smallmatrix}Br\\ (OC_3H_5)_3\end{smallmatrix}] + LiOC_2H_5 \rightarrow Li[B\begin{smallmatrix}Br\\ (OC_2H_5)_3\end{smallmatrix}] + (C_2H_5)_2O$$

$$Li[B\begin{smallmatrix}Br\\ (OC_2H_5)_3\end{smallmatrix}] + (C_2H_5)_2O \rightarrow C_2H_5[B(OC_2H_5)_4] + LiBr$$

Thirteen analogous reactions between $TlOC_2H_5$, $NaOC_2H_5$, $LiOC_2H_5$ and such acids as $AlBr_3$, BBr_3, $ZnBr_2$, $SnBr_3$, $GaBr_3$, $Al(ClO_4)_3$ were studied by the same experimental procedure. It was necessary to postulate similar intermediate lithium complexes in the reaction schemes to explain the shapes of some of the titration curves.

Similar results were obtained for the reaction between $LiAlH_4$ and $GaBr_3$ (5). Figure 2 suggests that the bromide ions of $GaBr_3$

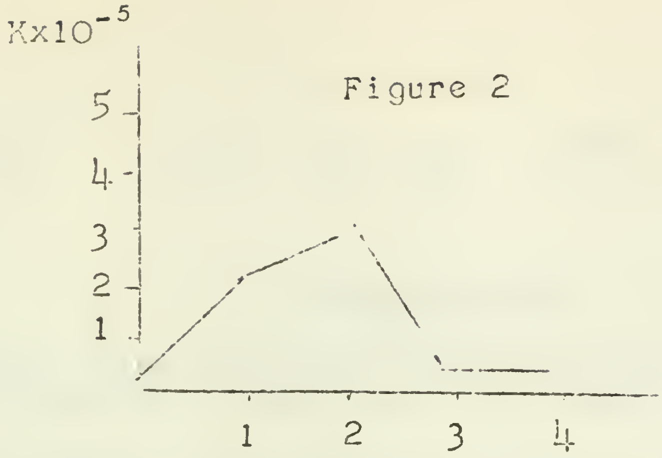


Figure 2

moles of $LiAlH_4$ to one mole of $GaBr_3$

are replaced one at a time. Similar curves are obtained when $ZnBr_2$ and $AgClO_4$ are permitted to react with $LiAlH_4$.

HYDRIDES

Hydrides of the group A elements of most of the group B elements and many of their complex metal hydrides have been prepared(6). Some of these compounds exist only at low temperature. The preparation of these compounds has been made possible by carrying out the reactions of metal chlorides with $LiAlH_4$, $LiBH_4$, $LiGaH_4$ and LiH at low temperatures in ether. Indium aluminum hydride has recently been made by this method (7,8).

$$LiAlH_4 + InCl_3 \xrightarrow{-70} In(AlH_4)_3 + 3\ LiCl$$

$$\xrightarrow{-40} In + 3/2\ H_2 + 3\ AlH_3$$

In general the hydrides and borohydrides are more stable thermally than the gallium and aluminum hydrides. The stability of the metal hydrohalides increases with the number of halogens present in the molecule. $Cd(BH_4)_2$ decomposes at 25° while $CdClBH_4$ is stable up to 85°.

REACTIONS IN ETHER

The reactions of inorganic compounds in ether are so numerous that only a few examples need be mentioned (6). Reactions are frequently run in ether when anhydrous products are desired or whenever reactants or products are unstable in the presence of moisture.

1. $4\ HN_3 + LiAlH_4 \rightarrow LiAl(N_3)_4 + 4\ H_2$
2. $LiAlH_4 + N_2O_4 \xrightarrow{Ag^+} Ag{-}O{-}N{=}N{-}O{-}Ag$
3. $2\ LiAlH_4 + 5\ NH_3 \rightarrow [LiAlH(NH_2)_2]_2NH + 6\ H_2$
4. $(C_6H_5)_2NK + ClN(C_6H_5)_2 \rightarrow (C_6H_5)_2N{-}N(C_6H_5)_2 + KCl$

5. $HCN + Li \rightarrow H_2 + LiCN$

6. $Na_2S_2O_3 + 2\ HCl\ (dry) \xrightarrow[-40^\circ]{} 2\ NaCl + H_2S_2O_3 \times Et_2O$

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MOLECULAR CHARGE TRANSFER COMPLEXES

C. D. Schmulbach February 26, 1957

Introduction:

Chemical and spectroscopic evidence furnish confirmation of the hypothesis that in brown solutions of I_2 the solute is solvated to varying degrees, while in the violet (inert) solutions the solute consists solely of diatomic molecules.

Several theories have been proposed to account for the observed color change and for the bond formation in these molecular charge-transfer complexes (1). The Mulliken theory, a quantum-mechanical treatment, appears to be most consistant with the observed spectroscopic evidence.

Mulliken's Theory: (2,3,4,5,6)

The theory applies to the interaction of electron donors and acceptors to form 1:1 or 1:n molecular species ranging from loose complexes to stable complexes. The utility of the donor-acceptor representation is borne out by the experiments of Andrews and Keefer (7) who showed, that for any given acceptor molecule, increased methylation on the benzene ring (increased basicity) resulted in a substantial increase in the equilibrium constant.

Mulliken represents the ground state of the complex as composed predominantly of a no-bond structure (DA) mixed with a small amount of the dative bond structure ($D^+.A^-$) in resonance with a small amount of the no-bond structure. In addition to the individual spectra of D and A, which are somewhat modified by their interaction there exists a band corresponding to an electron jump from the ground state to the excited state. *This new band is characteristic of the complex as a whole.*

Mulliken's theory suggests that resonance may take place "between structures differing in the occupation of *molecular* rather than *atomic* orbitals and even between non-bonded structures and those produced from them by charge transfer."

Iodine-complexes:

The most common iodine complexes include complexes with simple benzene derivatives (8,9), ethers, alcohols and water (10) ketones (4,11), pyridine (12,13) and olefins (14).

For a review of iodine solutions see reference 15.

Other Molecular Complexes:

U.V. Sprectrum of various acceptor molecules such as SO_2, Cl_2, oxalyl-chloride, $AlCl_3$ and ICl in aromatic solvents show strong [illegible] (1).

McConnell, Ham and Platt (16) noticed a linear relationship between the ϵ_{max} of the charge transfer band versus the wave length of the maximum absorption for a number of complexes of benzene (donor) with acceptor molecules such as I_2, Br_2, SO_2 and $Cl-\overset{O}{\overset{\|}{C}}-Cl$. A linear relationship between the lowest observed ionization potentials of D molecules versus the charge-transfer absorption frequencies of D•A complexes (where $A=I_2$) was also plotted. The intensities of the charge transfer transitions between I_2 and various donors shows no strong correlation with the ionization potentials of the D molecules, the equilibrium constants of the complexes or with the wave lengths of the transition.

Problems and Developments: (1,6)

With respect to its ability to form soluble complexes, $HF-BF_3$ is very sensitive to changes in substituents on aromatic donor molecules. This property affords a possible means of selectively extracting alkyl benzenes.

The charge transfer theory may be used to predict the stereochemistry of complexes.

The anomolous intensity problem of the alkylbenzene-iodine complex band, the blue shift of the iodine visible band in iodine complexes and the absorption of I_2 and Br_2 in "inert" solvents are explained, at least in part, by the charge transfer theory.

In the light of recent infra-red studies on the benzene•Br_2 complex (17) and x-ray structural studies by Hassel on the dioxane•ICl complex (18) one may reasonably question the utility of Mulliken's theory in predicting the stereochemistry of these complexes.

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Chemical Consequences of Nuclear Decay

J. A. Chandler March 5, 1957

The use of radioactive materials in tracer experiments for the study of structures and the kinetics of reaction has become widespread. Hence, the preparation of materials of high specific activity, which minimizes counting errors, has become increasingly important.

There are usually several means of producing any given radioactive species. The method chosen is often dependent upon the availability of the starting material and the yield obtainable by a given nuclear reaction. The (n, γ) reaction is often used because of the "high" yields obtained (10^{-6}-10^{-8}%) conversion being typical). However, the product nucleus of the n,γ reaction is isotopic with the target material, and this complicates chemical separations. For this reason, the chemical form of the target must be chosen to enable separation of the product.

Due to the small numbers of atoms formed in nuclear reactions, there are two necessary conditions for study of the chemical behavior of atoms so produced.

1) Atoms must be radioactive for high sensitivity experiments.
2) The various possible chemical forms of the atom must not exchange, or their exchange behavior must be known.

Energy Considerations: The discussion here will be limited to the n,γ reaction of the halogens. The energies involved in most nuclear reactions are of the order of 10^5ev for greater per nuclear process which is far greater than the energies of chemical reactions.

The kinetic energy is divided among the nucleus and the gamma emitted and the distribution is governed by conservation of momentum (1). Often the momentum imparted to the nucleus is sufficient to break one or more bonds. In all cases, excited atoms or molecules may be expected. If one gamma of energy is emitted, the recoil energy available to the nucleus $E_m = 536 \frac{E_\gamma^2}{M}$ ev (E_γ in Mev, M in amu). If the molecule is not immediately dissociated, the whole molecule may recoil. The internal energy (E_i) available for bond rupture is then given by (2) $E_i = E_m(\frac{M'}{M + M'})$. Thus bond rupture may be relatively improbable when the newly formed atom is attached only to a very light atom such as hydrogen (Mass M').

The impact of thermal neutrons, having a kinetic energy of about 0.025 ev, cannot be responsible for bond rupture. Therefore, any bond rupture accompanying thermal neutron capture must be due to liberation of the binding energy or to electronic excitation (if internal conversion occurs).

Table 1 (3)

Element	E_{γ}(max) Mev	Em(max) ev	E_{C-X} ev
Cl	6.2	543	2.9
Br	5.1	174	2.3
I	4.8	96	2.0

Thus C-X bond rupture appears very likely when RX is bombarded with thermal neutrons; the resulting halides should have different chemical properties than the halogen in RX since bond rupture is invariably accompanied by changes in electronic configuration.

Inorganic Considerations: The first experimental test of the above was the irradiation of C_2H_5I (with a trace of I_2) by thermal neutrons (4). A large fraction of the radioiodine formed was extractable by aqueous reducing agent. Since the energetics of the reaction indicate that nearly all of the radioiodine atoms should be ejected from the molecule and hence be extractable, (recombination being very improbable) further experiments were performed to determine why this is not found.

A. Effect of free halogen present (5): The presence of free halogen increases the amount of extractable activity. The increase in inorganic radiohalide is attributed to exchange between inactive X_2 and X^* or newly formed but still excited RX molecules (6).

B. Effect of added organic base (5): The increase in extractable halogen is attributed to the reaction of the free organic radical and the halogen recoil atom with aniline $R+X+\phi NH_2 \rightarrow \phi NH_2R^+ + X^-$. Alternately, if R and X have recombined, this molecule could retain enough vibrational energy to react $(RX)+\phi NH_2 \rightarrow \phi NH_2R^+ + X^-$.

C. Dilution effect (7): Dilution of the reacting material generally leads to an increase in extractable activity.

D. Phase effect: Essentially all of the radiohalide formed in gas phase reactions is inorganic (8,9). The amount of extractable halide formed when the target is solid is usually considerably less than when the target is liquid (10-12).

Table 2
Extractable halide (%)

Target	Liquid	Solid	Ref.
L-C_3H_7Br	68	6-12	10
n-C_3H_7Br	61	11.6	10
CH_3I	43	44	11
CCl_3Br	58	28	12
CCl_2Br_2 as Cl	49	19	12
CCl_2Br_2 as Br	60	25	12
CBr_4	12	7	12
CCl_4	56	25	12
CCl_4 + 1 mol % Br_2	73	50	12

Organic Considerations: Also experimentally studied was the form in which the organically bound radiohalogen appears. Some typical results are as follows (6):

Table 3

Target	Chemical Fraction	Liquid	Solid
i-C_3H_7Br	i-C_3H_7Br	10.0%	11.2%
	n-C_3H_7Br	23.7	23.5
	1,2-dibromopropane	3.8	20.0
	1,3-dibromopropane	4.6	11.5
n-C_3H_7Br	i-C_3H_7Br	12.0	11.3
	n-C_3H_7Br	30.6	28.5
	1,2-dibromopropane	3.8	20.2
	1,3-dibromopropane	4.5	18.2

Careful investigation of the effect of changing the target material from one isomeric form to another, of varying isotopic composition, and varying neutron energies has led to the conclusion that none of these have any significant effect on the total retenti of radiohalogen in pure liquid RBr (and presumably RCl and RI). Any apparent variations are probably due to trace quantities of impurities (13-15).

Theory of Retention: The basic points of Libby's theory of retention are (16-17):

1) High energy of recoil atom assures its quick removal from the original molecular fragments.
2) Collisions of recoil atom with carbon and hydrogen only slightly decrease its energy.
3) Collision of recoil atom with another halogen atom may lowe the energy sufficiently to trap the recoil atom in a reaction "cage" with secondarily formed molecular fragments, and the recoil atom may combine with these fragments
4) If, as a result of collision described in 3, the energy the recoil atom falls below the energy necessary to break a C-X bond, it will not be retained.
5) Retention should be essentially zero for gas phase reactions since no reaction cage can be postulated here.
6) Substitution may occur when the energy of the recoil atom is below "escape value", but when it still has sufficient energy to provide activation energy for a reaction of the type $Br^{82} + C_nH_mBr^{81} \rightarrow C_nH_{m-1}Br^{82}Br^{81} + H$ or exchange of X.
7) Since the radiohalides usually have a considerable positive charge at birth [e.g. $Br^{80m} \xrightarrow{IT} Br^{80}$ gives rise to a charge of +10+2(18)], electronic excitation energy arising from partial charge neutralization may be responsible for some of the substitution reactions.

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SEPARATIONS OF RARE EARTHS BY ION EXCHANGE PROCEDURES

G. Giffin March 12, 1957

The use of ion exchange materials for the separation of the rare earth elements was reported for the first time in 1943 by Russell and Pearce (1). Some enrichments were obtained but adjacent rare earths were not separated into pure components.

The occurrence of rare earth elements in fission products provided great impetus to the development of ion exchange separations within the Manhattan Project. Two separate ion exchange projects were carried out: the development of methods for separating fission products on a radio-tracer scale, and the development of methods whereby macro quantities of the pure rare earths could be separated. The use of a complexing agent in the eluant was a major feature of these methods. The advent of synthetic high capacity organic resins greatly aided both projects.

Any separation that is achieved by ion exchange results from the repeated application of the equilibria described by the simplified equations:

$$(1) \qquad Ln_s^{+3} + 3M_r^{+} \rightleftharpoons Ln_r^{+3} + 3M_s^{+}$$

$$(2) \qquad Ln^{+3} + NY^{-1} \rightleftharpoons LnY^{-1} + N^{+3}$$

where N and Ln are rare earth elements, M is the cation on the resin and Y is the ethylenediaminetetraacetate ion. Equation (1) represents the simple exchange of a cation in solution for a different cation on the resin. Equation (2) represents the exchange of one rare earth ion in solution for a different rare earth ion in a chelate complex which is also in solution. (The EDTA complex is given as an example.)

Numerous experimental factors must be determined for the best separation by any one method. These factors include particle size of the resin, flow rate of the eluate, column size (diameter, length), ionic strength of the eluant, pH, and concentration of the eluant.

The first successful separation of adjacent rare earth elements was developed simultaneously and independently at the Ames Laboratory (2) and at Oak Ridge (3) during World War II. The eluant used was 5% citric acid, buffered with ammonium hydroxide to a pH of 2.5 to 3.2. This method was best suited for radio-tracer scale separations. This work led to the isolation and identification of about 15 different radioactive isopotes, which are by-products of uranium fission, and to the first conclusive evidence for element 61, promethium.

Elution with 5% citric acid at a low pH was impractical for the separation of macroscopic quantities of the rare earths. Spedding and co-workers (4) developed a method of elution with 0.1% citric acid buffered with ammonium hydroxide to a pH between 5.0 and 8.0. Under these conditions the rare earth band spreads out initially as it moves down the resin bed, until it reaches an equilibrium value. If several individual rare earth species are present in the originally adsorbed band, they tend to separate into individual bands which follow one another head to tail as the total band is eluted down the column. The rare earths appear in the eluate in reverse order of atomic numbers (i.e., Lu first and La last). Sizeable quantities of most of the rare earths have been separated by this method with a purity of 99.9% or better.

Several amino-polyacetic acid chelating agents have been used in attempting to separate the rare earths by ion exchange. Holleck and Hartinger (5) compared the effectiveness of EDTA, o-diaminocyclohexanetetraacetic acid, bis (2-aminoethyl)ether tetraacetic acid, and ethylene glycol bis(2-aminoethyl) ether tetraacetic acid. Efficiency of separation increases in the order named at equivalent pH values of the eluant.

Ethylenediaminetetraacetic acid has been applied to enriching rare earth fractions rapidly (6). This process consists of complexing part of the rare earths in a mixture with EDTA, then separating the complexed from uncomplexed rare earth ions by passing the solution through an ion exchange column resin bed in the ammonia cycle. The complexed ions pass through the column while the uncomplexed ions are adsorbed on the resin. This technique is particularly used to separate ore concentrates into light and heavy rare earth fractions.

A logical extension of the use of EDTA was to find a method that would allow the rare earths to be continually readsorbed onto the resin from the rare earth complex as the rare earth band moves down the column (7, 8). In the citric acid systems, this mechanism is provided by the acid-form of the resin ahead of the rare earth band. Acid-cycle resin cannot be used with EDTA because, unlike citric acid, the acid form of the chelating agent is quite insoluble. Consideration of the stability constants for the EDTA complexes with the rare earths and other metal ions shows that iron (III), copper (II), nickel (II), and lead (II) should serve to retain a number of rare earth ions. The stability constant of the iron (II)-EDTA complex is much larger than the rare earth constants and therefore an iron (III) bed ahead of the rare earth band should serve much the same function as a hydrogen bed for citric acid elutions. A fair degree of separation is attained, but there are several disadvantages in using iron (III), e.g., limited pH range, trailing of iron into the rare earth bands, etc.

A copper (II) resin bed ahead of the rare earth band is superior to iron (III). The operating conditions for the copper (II)-EDTA method must be carefully controlled, but the pH range is considerably broader than that for the iron (III)-EDTA system. Rare earth

concentration in the eluate is about ten times as great as it is when citric acid procedures are used. Groups of rare earths difficult to separate, lutetium-ytterbium, dysprosium-yttrium-terbium, and gadolinium-europium-samarium, have been separated with excellent success by the copper (II)-EDTA procedure.

A method of "gradient elution" has been described by Nervik (8). An eluant of continuously changing pH effected in 5 hours separation that took 40 hours with an eluant of constant pH. This work was done on a radio-tracer scale.

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ELECTRODEPOSITION OF METALS FROM NON-AQUEOUS SOLVENTS

Grant White March 19, 1957

The known metals, listed in Table I with several non-metals of interest from the standpoint of electrodeposition, can be classified as follows: (adapted from Lowenheim (1))

Class 1: Metals so rare as to discourage study or render their employment impractical at present. This class includes many of the lanthanides, the trans-uranium elements, francium, technetium, and yttrium.

Class 2: Metals which have not been plated successfully, in spite of many attempts, including molybdenum, tantalum, tungsten, and strontium. Twenty-five years ago, chromium would have been in this class.

Class 3: Metals which probably can never be electrodeposited from aqueous solutions, such as the alkali and alkaline earth metals.

Class 4: Metals which are readily plated, but which at present lack utility. This group includes arsenic, antimony, and bismuth.

Class 5: Metals which can be plated from aqueous solutions. Some of these -- gallium, germanium, iridium, manganese, mercury, osmium, polonium, ruthenium, and thallium -- have found no great technical use in the plated form, but others -- class 5T in Table I -- are plated on a large scale. The 5T metals are: cadmium, chromium, cobalt, copper, gold, indium, iron, lead, nickel, palladium, rhodium, silver, tin, and zinc.

While a number of class 5 metals can be plated from non-aqueous solutions (2), it is doubtful whether these processes will ever become important since plating from aqueous solution is usually more convenient (3). Classes 1 and 4 will not be of much interest until the metals become more available and/or until important new uses have been found. Electrodeposition from non-aqueous solvents is of the most interest in the cases of metals of classes 2 and 3, corresponding with Brenner's "NQ" metals (3), and it is with these metals that the remainder of the seminar will deal. Although a number of these metals have been deposited as alloys, such mixtures will not be discussed comprehensively.

There are several reasons why less than half of the known metals can be deposited from aqueous solution:

(a) The most obvious circumstance occurs when the metal is less noble than hydrogen, which therefore tends to be discharged preferentially. Some metals which exhibit this behaviour are the alkali metals, and probably titanium, molybdenum, zirconium, beryllium, and aluminum. Zinc is an exception

for although it is less noble than hydrogen, zinc can be plated from aqueous solution because of the high "overvoltage" of hydrogen on zinc -- another way of saying that zinc plates out on zinc more readily than hydrogen discharges on zinc (3). Preferential discharge of hydrogen may be eliminated by the use of highly basic solvents (4).

(b) It is less obvious why some metals which have about the same E_o as hydrogen (for example, tungsten, molybdenum, and germanium) do not electrodeposit from aqueous solution. This phenomenon has been attributed to "some kind of non-reactivity of their lower valent ions with electrons at the cathode" (3), a circuitous way of confessing ignorance.

(c) Hydrolysis effects complicate deposition from aqueous solution if compounds with covalent character are used as solutes. Such effects may be avoided by the use of highly acidic solvents (4).

Thus non-aqueous solvents may provide ways of circumventing the above difficulties encountered with aqueous solutions:

(a) The use of solvents in which the hydrogen is "bound" or absent eliminates the possibility of its preferential discharge.

(b) Non-aqueous solvents may permit the formation of complexes nonexistent in aqueous solution, and permit the use of higher potentials, making non-reactive ions more reactive.

(c) Undesirable solvolysis may be avoided.

A common type of non-aqueous bath is the fused salt bath. Nearly any metal can be deposited from one or more of its fused salts, but often the procedure does not yield a coherent plate (3). Even when it does not, the fused bath may be useful in electrowinning the metal. The obvious disadvantage of the fused salt bath is the high operating temperature required. Solutions melting at a lower temperature (say below 100° C.) are desirable.

Among the inorganic solvents, hydrazine, liquid ammonia, and liquid sulfur dioxide have been studied as possible solvents for the deposition of the NQ metals (classes 2 and 3), and have been found to be ineffective (3). A report of the deposition of beryllium from liquid ammonia has not been substantiated (3). Much work has verified an early statement that it is questionable whether the use of liquid ammonia would yield metal deposits which have not already been discharged from aqueous solution (5).

In the field of organic solvents, an empirical approach has been used for several reasons:

(a) For the deposition of a given metal, several hundred compounds, several thousand solvents, and practically an infinite variety of experimental conditions could be tested.

(b) Classical concepts of the nature of solutions have not been fruitful. It was formerly thought that a solvent with a high dielectric constant, and a solute with ionic bonds in the crystal, would be most likely to form a good plating solution. However, ethyl ether, with a very low dielectric constant of 4.3, has been found to be the best solvent for the deposition of some NQ metals. Moreover, conductivity has been found to be an insufficient criterion of a potentially good plating solution.

It has been suggested that the nature of the bonding between the solvent and the solute is the prime factor in determining whether plating will take place. According to this hypothesis, there is no conduction if the ion complex is too weak, and there is no metal deposition if the ion complex is too strong. Solutes studied have been metal hydrides, halides, and borohydrides, and organometallic compounds with small organic radicals. There has been found to be no deposition if there is a metal-oxygen or a metal-nitrogen bond in the solute.

Solvents reactive enough to form a not-too-stable coordination compound with the solute include:

(a) Oxygen-containing: alcohols, ketones, acids and anhydrides, and ethers.

(b) Nitrogen-containing: amines, amides, and nitriles.

(c) Unsaturated: benzene and toluene.

Ether and aromatic hydrocarbons have been reported to be the only solvents useful in the deposition of magnesium, aluminum, beryllium, titanium, and zirconium (3). However, magnesium has been plated on platinum from solutions of the bromide in pyridine (6), and magnesium and aluminum have been deposited from solutions of their salts in ethanolamine (4).

A recent innovation in electrodeposition has been the plating of aluminum from a "hydride bath". Ethyl ether was the solvent, and a mixture of aluminum chloride and either lithium aluminum hydride or lithium hydride served as the solute (3,7). Any of these aluminum compounds alone dissolves in ether to give a non-conducting solution. An aluminum anode may be used, but bath life depends on the amount of solute aluminum chloride rather than on the aluminum content of the solution. The function of the hydride is unknown. Addition agents permitted deposition of layers 1.5-2.0 mm. in thickness.

Except for lanthanum and cerium, little work has been done on plating the pure lanthanide metals (1). Some of the rare earths have been deposited as amalgams from solutions of the anhydrous chlorides in ethanol. Neodymium, lanthanum, and cerium were obtained from the amalgams by vacuum distillation of the mercury and by thermal decomposition of the amalgams, while samarium and yttrium were obtained only as dilute amalgams (8).

At present, the most challenging area in the field of electrodeposition is probably that of the "refractory metals", titanium, zirconium, molybdenum, and tungsten. The difficulties involved in working with these metals, none of which have been deposited in a satisfactory plate, are discussed by Brenner (9).

TABLE I

Name	Class	Remarks *1
Actinium	3?	Ac or Th halide, EtOH-acetone, Ag anode (10)
Aluminum	3	"Hydride bath" (3,7)
Americium	1	
Antimony	4	Refining; "explosive" form; brittle plate.
(Arsenic)	4	Winning
Barium	3	Iodide or thiocyanate in acetone (11)
Berkelium	1	
Beryllium	3	Aq. reported, doubtful; acetamide
Bismuth	4	
Cadmium	5T	
Calcium	3	Chloride from aq. MeOH
Californium	1	
Cerium	3	Analgam; see discussion
Cesium	3	
Chronium	5T	
Cobalt	5T	
Copper	5T	
Curium	1	
Dysprosium	1	
Erbium	1	
Europium	1	
Francium	1	
Gadolinium	1	
Gallium	5	"easily"
Germanium	5	
Gold	5T	
Hafnium	3?	References rare; probably similar to Zr
Holmium	1	
Indium	5T	
Iridium	5	Little work
Iron	5T	
Lanthanum	3	Amalgam; see discussion
Lead	5T	
Lithium	3	LiCl from various ROH (12); see Rb
Lutetium	1	
Magnesium	2	No practical method; some success from Grignard. Powder from ethylenediamine (13)
Manganese	5	Winning
Mercury	5	Analytical application; dip to plate.
Molybdenum	2	"self-polarization"; "sometimes" from chloride in EtOH (14)
Neodymium	3	
Neptunium	1	
Nickel	5T	
Niobium	5	Reports await verification
Osmium	5	Little work
Palladium	5T	

TABLE I (continued)

Name	Class	Remarks *1
Platinum	5T	
Plotonium	5	Thin films on Pt as α standards (15)
Polonium	5	(16)
Potassium	3	KI ethylenediamine, K:Hg anode (13); see Rb.
Praseodymium	1	
Promethium	1	
Protoactinium	5	(17)
Radium	3?	Amalgam (18); Ba and Ra salts acetone → alloy (11)
Rhenium	5	
Rhodium	5T	
Rubidium	3	Li, K, and Rb halides + $AlBr_3$ in Ø-NO_2 (19)
Ruthenium	5	Little work
Samarium	3	See discussion
Scandium	3?	
(Selenium)	5	Rectifiers; Brightener, e.g. for Ni.
Silver	5T	
Sodium	3	(13), see K; Sat. Na or Sr iodide/ acetone (20).
Strontium	3	See Na, (20).
Tantalum	2	Aqueous literature not very convincing.
Technetium	1	
(Tellurium)	5	Impractical for plating, brittle.
Terbium	1	
Thallium	5	
Thorium	3	See Ac, (10).
Thulium	1	
Tin	5T	
Titanium	(5?)	Ambiguous results
Tungsten	2	Much effort expended: Deposition from liq. NH_3, alc., Et_2O but not repeated
Uranium	3	Efforts usually fail; dep. reported from UBr_3 or UBr_5/ ethanol, formamide, acetamide, and gl. HOAc.
Vanadium	2	
Ytterbium	1	
Yttrium	3	Amalgam; see discussion.
Zinc	5T	
Zirconium	2	V. thin plate/aq. reported; unlikely; oxychloride in butanol. Brenner says no method practical (9).

*1 Unreferenced remarks from (3)

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MECHANISM OF ELECTRON TRANSFER REACTIONS IN SOLUTION

J. R. Larson March 26, 1957

Introduction:

Most electron transfer reactions fall into one of the following three groups. (1)

1. Reactions between oppositely charged ions:

   $$A^+ + B^- \rightarrow (A^+ \cdots\cdots B^-)^* \rightarrow A + B$$

   These reactions are rarely slow since the electrostatic attraction makes it easy to acquire the activation energy necessary for electron transfer.

2. Reactions between a neutral particle and an ion:

   $$A^+ + B \rightarrow (A^+ \cdots\cdots B)^* \rightarrow A + B^+$$
   or
   $$A + B^- \rightarrow (A \cdots\cdots B^-)^* \rightarrow A^+ + B$$

   Reactions such as these are not common in solution and will not be discussed in this seminar.

3. Reactions between like ions:

   $$A^p + B^q \rightarrow (A^p \cdots\cdots B^q)^* \rightarrow A^{p-1} + B^{q+1}$$

   This third type of reaction, where p and q are positive has been studied extensively and will be the basis of this seminar.

Types of Mechanisms:

The mechanisms of reactions between cations can be divided into two general groups, and each will be discussed separately.

Electron Jump Theories:

Libby (2) calculated the probability of electron exchange between nuclei as a function of distance, and reported that the frequency of exchange should still be great at separations of 10 Å and larger. Since the actual electron transfer is always a fast process, the rate determining step must be a rearrangement of the environment to accommodate the electron transfer.

The Frank-Condon principle (2,3), which states that the motion of nuclei during electron transfer is negligible, implies that the rearrangement of coordination spheres takes place before electron transfer. These facts suggest that the reaction will be fast when little rearrangement is necessary. Two such fast reactions are the electron exchanges between MnO_4^- and $MnO_4^=$ (4) and between $Fe(CN)_6^{\equiv}$ and $Fe(CN)_6^{\overline{\overline{=}}}$. A typical slow reaction is that between $AsO_4^{\equiv}$ and $AsO_3^{\equiv}$ (5).

The Electron Tunnelling Hypothesis is another factor which could be important in determining the rate of electron transfer reactions. This idea, first recognized by Libby (2), and developed more fully by Weiss (6) and by Marcus, Zwolinski, and Eyring (3) refers to the probability of an electron penetrating an energy barrier. In general, it can be said that the closer two bodies approach, the higher the probability of electron transfer. An opposing factor is that of the energy required for the approach of the two bodies. The reaction will be most rapid when the probability of transfer is maximized and the energy of repulsion of minimized. The overall free energy of activation of a series of reactions has been calculated by Marcus and the results are in fair agreement with thos observed experimentally.

Mechanisms Involving Intermediates:

Zwolinsky (1) has shown by calculation that the coulombic repulsion between a ferrous and a ferric ion at a separation of 2 A is approximately 1000 kcal./mole. If a negative ion such as chloride is placed between the two cations so that it is 2 A from each, the force becomes attractive and with a magnitude of about 300 kcal./mol. These calculations are admittedly inaccurate, but do show the tremendous change in repulsive force when a suitable anion is introduced into the activated complex.

Taube and his associates (7,8) have introduced the concept of a bridged activated complex in an effort to provide a more detailed mechanism for the process of electron transfer between an oxidant and a reductant. This mechanism involves the coordination of an added group between the oxidant and reductant which provides a more "accessible path for the flow of electrons". By the careful selection of oxidant and reductant, Taube has proven that bridges do exist in certain systems. The oxidation of Cr(II) with oxidizing agents of the type $Co(NH_3)_5X^{+2}$ was studied; a quantitative transfer of X to the reducing agent was found to occur. Although Cr(II) is labile to substitution, the Cr(II) complex formed in the reaction is stable for periods of time which are long compared to the rate of oxidation of Cr^{+2}. It was shown that where $X=Cl^-$ the transfer takes place without exchange with radioactive Cl^- in solution.

In a more recent work Murmann, Taube, and Posey (9) have shown that H_2O and OH^- can function as bridging ligands, and that at least partial oxygen transfer takes place. The reaction between $Co(NH_3)_5H_2O^{+3}$ and Cr^{+2} is illustrative.

In reactions which go by way of a bridged intermediate, the bridging group may or may not transfer, depending on the substitution lability of the products. In the reaction between $Co(NH_3)_5Cl^{+2}$ and Cr^{+2}, the activated complex after electron transfer can be pictured as shown below:

$$[(NH_3)_5Co^{II}\cdots\cdot Cl\cdots\cdot Cr^{III}]^{+4}$$

Since Co(II) complexes are fairly labile to substitution (10), and Cr(III) complexes are relatively inert, one would expect the cobalt-chlorine bond to rupture. This would result in transfer of the chloride from cobalt to chromium, which is observed.

In general the reaction rates parallel the complexing ability of the ions, with the exception that the bridging group must have two pairs of electrons available for complexing. An example is ammonia which is a good complexing agent, but a poor bridge former.

Some common cations which are fairly labile to substitution and for which bridged activated complexes should be considered in electron transfer reactions involving them are: Ti(II), Ti(III), Ti(IV); V(II), V(III). V(IV); V(V); Cr(II), Cr(IV); Mn(II), Mn(III); Fe(II), Fe(III); Co(II), Co(III); Cu(I), Cu(II); Ag(I), Ag(II); Eu(II), Eu(III); Ce(III), Ce(IV); Ti(I), Ti(III).

Another type of reaction which must involve an intermediate has been observed by Duke (11) and his associates. In the postulated mechanism the oxidant takes an electron from the solvent or from an anion or other base which in turn regains its electron from the reducing agent. Examples cited are the reactions between Ce(IV) and Tl(I) in presence of chloride (12), and between Fe(III) and Sn(II) in presence of iodide (13).

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THEORY AND APPLICATIONS OF NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

John Dismukes

April 2, 1957

Fundamentally the phenomenon of Nuclear Magnetic Resonance (or NMR) is an absorption of energy in quantized amounts, and in this manner it is similar to Infrared, Ultraviolet, or Microwave absorption spectroscopy. The basic difference between NMR and other spectroscopic absorption processes is that the energy quanta ($hf = hc/y = E$) effect transitions between distinct energy levels of the nucleus instead of between energy levels of atomic or molecular electrons. The separation of these nuclear energy levels is much smaller than in the case of electrons, and the absorption takes place in the radiofrequency region (from about 0.1 to 40 mc/sec.) of the electromagnetic spectrum. In 1952 Bloch and Purcell jointly received the Nobel Prize in Physics for discovery of this phenomenon. References 1,2,3,10,28, and 29 by these two workers discuss the basic theory and the early applications of their discovery. References 6,22,23,24,25,26, and 27 treat the theory and applications of NMR in more detail and summarize the work in the field through 1955.

Any nucleus with non-zero spin ($I \neq 0$) has an associated magnetic moment (u). When such a nucleus with spin I is placed in a stationary magnetic field (H_z), a set of $(2I + 1)$ nuclear Zeeman energy levels is established corresponding to quantized nuclear angular momentum values $Mh/2\pi$ (M varies from $+I$ to $-I$) in the direction of the stationary magnetic field H_z.(17,18) Any nucleus with a dipole moment (u) is a magnetic dipole (equivalent to a small magnet); consideration of a magnetic dipole in a stationary magnetic field(24) shows that the dipole is precessing about the stationary field H_z with a "Lamor" frequency $w_o = gH_z$, where (g) is the "magnetogyric" ratio $u/(h/2\pi)I$. If a small sinusoidal field $H_x = H_{xo} \sin wt$) is applied by means of a coil perpendicular to the direction of H_z, transitions between the nuclear Zeeman energy levels take place if the frequency of the sinusoidal field H_x is equal to the "Lamor" frequency w_o. The separation of the nuclear Zeeman energy levels, between which M varies by one unit, shows that the sinusoidal frequency of H_x must be equal to w_o for energy absorption to occur.(23)

$$E = uH_z \cos e = uH_z(M/I)$$

$$(\Delta M = 1) \quad \Delta E = (u/I)H_z = h(w/2\pi)$$

$$w = uH_z/(Ih/2\pi) = gH_z$$

Therefore: $w = w_o$

Figure (1) illustrates the precession of the nucleus about the stationary field H_z; it also shows the spatial arrangement of the field H_z, the radio transmitter coil, and the radio receiver coil along three mutually perpendicular axes. Figure (2) is a schematic diagram of the experimental equipment.

Figure (1)

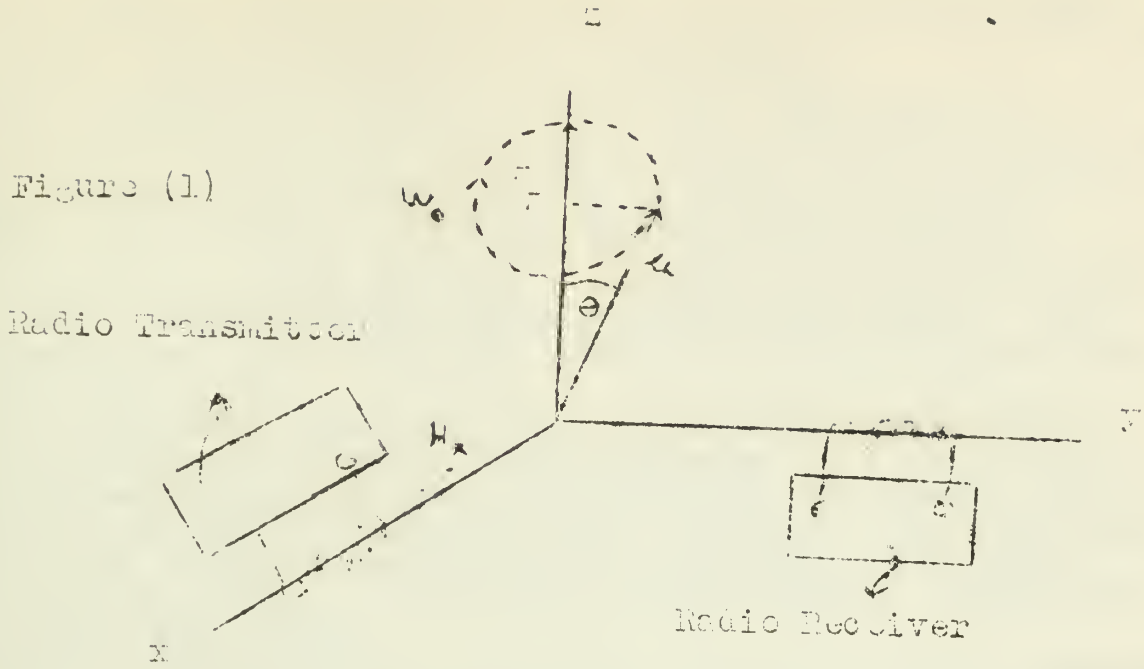
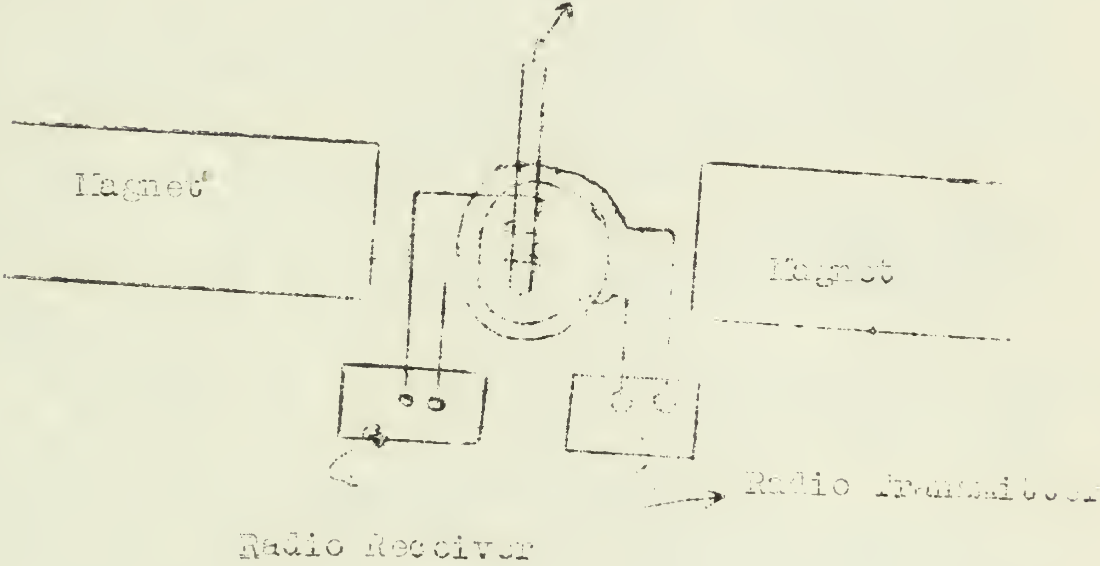


Figure (2)



During the shift of the nuclear dipole between Zeeman energy levels, a voltage is induced in the receiver coil. This voltage is recorded to give a picture of the resonance.

When the external field is turned on, the numbers of nuclei in each Zeeman level are equal. For resonance absorption to occur thermal relaxation with the lattice must establish a Boltzmann distribution of nuclear energy levels $(N_M/N_{M-1} = e^{-\Delta E/kT})$ with an excess of nuclei in lower energy states. The references in paragraph (1) may be consulted for other relaxation effects, which broaden the absorption line width. From the standpoint of line width and detail, liquids or gases are preferable to solids.

To an excellent approximation, at constant field H_z the absorption frequency of each nuclear species is a constant value, independent of the chemical compound (see Varian Associates Table, pp. 840-3, reference 24.) However, the main value of NMR to the chemist lies in the fine structures of these main absorption lines, as evidenced in (1) Chemical Shift and (2) Spin-Spin Splitting.

Chemical Shift refers to a variation of absorption frequency with chemical compound; the magnitude of this shift increases with atomic number and varies from a few parts per million in the case of ^1H compounds to as much as 13,000 parts per million in the case of certain ^{59}Co complexes.(32) The shift is due to a variation of the local shielding field of the atomic electrons with chemical environment. Since H_z = applied field - shielding field, the absorption is shifted to higher applied fields for greater shielding of the nucleus. Chemical shift may be distinguished from spin-spin splitting on the basis that the former is field and temperature dependent, while the latter is field and temperature independent.

Spin-Spin or "multiplet" splitting is the separation of an absorption line of nucleus A into (2I + 1) groups, where (I) is the spin value of a nucleus B covalently bonded to A. In some cases splitting still occurs if the nucleus B is further removed, but is still connected by covalent bonds to A. Ogg(8) has suggested that spin-spin splitting is a criterion of covalent bonding. If the two nuclei A and B are the same (e.g. F in BrF_5) no splitting is observed unless the nuclei are in structurally non-equivalent positions.

Chemical shift and spin-spin splitting have been applied to (1) Qualitative Analysis, (2) Quantitative Analysis, (3) "Gross" structure determinations (positioning of atoms), and (4) Electronic Structure and Bonding. For other applications consult the reviews listed in paragraph (1).

One of the best examples of the use of chemical shift for qualitative analysis occurs in the case of phosphorus compounds, on which there is much recent work.(17,18,21,30) Hydrogen (mostly in organic compounds) and fluorine have also been studied; phosphorus was chosen here because of the large number of compounds listed in the recent literature.

The following are two examples of quantitative analysis. Rapid quantitative analysis of the volume percent H_2O in D_2O can be made(31) by comparing the ^1H signal intensities of unknown and control samples of H_2O and D_2O. An accuracy of ± 0.2% is claimed for the determination. A recent study has been made of the rate of isomerization of the insecticide systox to isosystox, in which the concentration of the two isomers as a function of time was measured by their NMR absorption.(16)

The "gross"structure (positioning of the fluorine atoms) of ClF_3, BrF_3,(15) BrF_5, IF_5,(5,15,19) IF_7,(19) and PF_5,(5) has been studied by means of chemical shift and spin-spin splitting. Some interesting determinations of inorganic hydrogen by spin-spin interaction include borohydride ion and diborane,(9) phosphorous and hypophosphorous acids,(5) and ammonia.(7,8) The NMR data agree with the accepted structures of these compounds. The work of Packard on hydrogen resonance in the first five primary aliphatic alcohols(4) is one of the earliest and simplest examples of chemical shift and spin-spin splitting applied to chemical structure. To date, however, the most concise and easily understood evaluation of structure by NMR is the determination of the fluorine positions in SO_3F_2, SOF_4, and SOF_6.(11)

Since the discovery of the chemical shift correlations of the shift of one atom with (1) the electronegativity of another attached atom, (2) the position of the attached atom in a given periodic group, (3) the valence of the atom exhibiting the shift, and (4) the bond hybridization of the atom exhibiting the shift have been pointed out. At present only compounds of H, F, and P have been studied in detail.(19,20,21,17,18) A recent article by Wertz(14) discusses some bonding considerations of chloride ion in aqueous solutions. Much additional study of chemical shift, however, must be carried out before accurate predictions can be made on the basis of the known correlations.

References 12 and 13 list chemical shifts for ^{14}N and ^{17}O in various compounds. It is noteworthy that ^{17}O can be measured in its natural abundance.

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STRUCTURES OF THE INTERHALOGEN COMPOUNDS

R. D. Archer April 9, 1957

The interhalogen compounds have the general formula XX'_n where X and X' are different halogens and n is 1, 3, 5, or 7 (25). Only eleven of the many possible combinations have been isolated (38).

XX'. Five of the six possible diatoric interhalogen compounds have been isolated (38). The sixth, IF, has been detected (12). They are simple linear molecules with interatomic distances approaching, but not equal to the sum of the radii of the two elements (3,15). Correction for differences in electronegativities (35) still does not give exact results (17).

Observed Interatomic Distances of Diatomic Interhalogens

XX'	Observed IAD	References
ClF	1.63 A	(16, 30, 51)
BrF	1.76 A	(44)
BrCl	2.14 A	(45)
ICl	2.30 A	(49, 52)
IBr	. . .	. . .

In contrast to the other interhalogens, ICl exhibits polymorphism (38), and has therefore been subjected to more detailed structural investigation (1, 7, 13, 49, 52).

XX'₃. Only ClF_3, BrF_3, and ICl_3 have been characterized (38). Evidence for the existence of IBr_3 has been adduced (14). Several possible geometric configurations have been proposed; actual structures have been found to differ from those postulated as most probable. Pauling (29) as well as Sidgwick and Powell ([illegible]) have suggested that unshared electron pairs tend to occupy spatial positions as though other atoms were present. This theory is in agreement with experimental work (26) on the polyhalides and suggests structures for ICl_2^-, ICl_4^-, and the XX'_3 interhalogens as shown in figures 1, 2, and 3, respectively. The X's of figure 3 correspond to d^2s and sp^2 bonding (25).

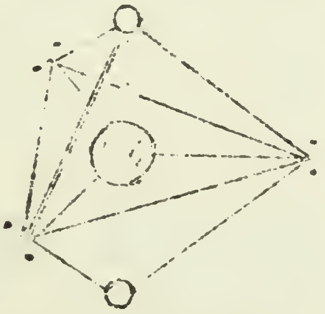


Fig. 1 -- ICl_2^-

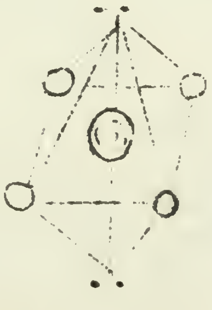


Fig. 2 -- ICl_4^-

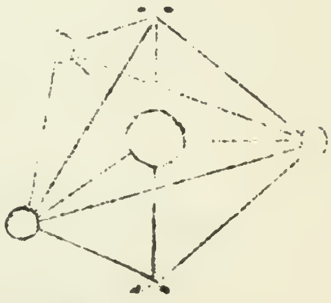
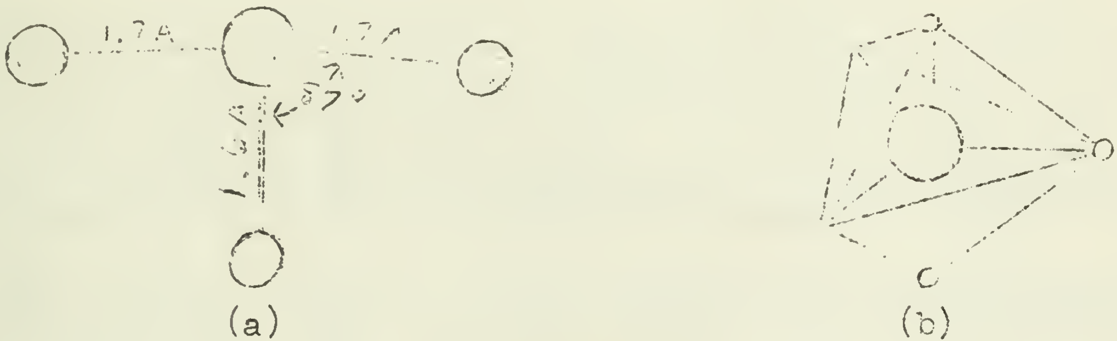


Fig. 3 -- XX'_3

ClF_3. Electron diffraction measurements (30), Raman work (34), and application of the Zachariasen rule (15,48) support a pyramidal structure.

The Raman spectrum of the liquid (21) indicates either that association occurs as has been shown for the gas (35), or possibly that the molecules are asymmetric. A dipole moment of 0.554 Debye (24) would rule out the "logical" planar symmetric model.

A "T" structure for ClF_3 (46) has most recently been proposed; calculated thermodynamic data (39) agrees quite well with experimental values. Recalculation of values for the microwave spectrum (47) for ClF_3 gas leads more logically to a distorted "T" structure. X-ray data (8) for the solid ClF_3 makes such a structure seem more reasonable (see figure 4).



(a) (b)

Fig. 4 -- ClF_3

Raman analysis at Argonne (10) also supports this structure.

ICl_3. This interhalogen is depicted as being built up of planar I_2Cl_6 molecules (5) (see figure 5). The conductance of ICl_3 (50) does show discontinuity at its melting point (98.5°) by a factor of 10^2 to 10^5, in contradiction to results reported by Emeléus and Greenwood (13).

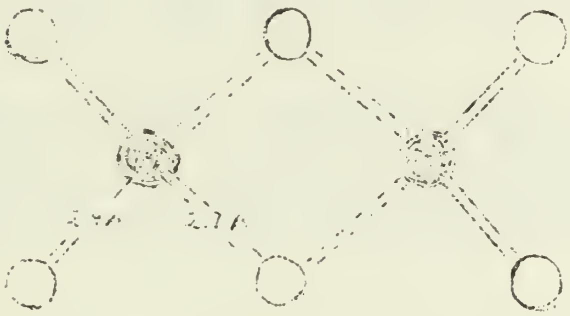


Fig. 5 -- $ICl_3(I_2Cl_6)$

BrF_3. The structure of this interhalogen has never been completely determined. Muetterties and Phillips (27) have found that the magnetic resonance of F^{19} gives only one peak with no structure or breadth, which indicates a very rapid fluorine exchange if BrF_3 has the same structure as ClF_3. Infrared data (10), although incomplete, indicate a structure similar to that of ClF_3. Rogers, Pruett, and Spiers (32) have also indicated

this possibility. However, conductivity values indicate partial dissociation into BrF_2^+ and BrF_4^- ions (2).

XX'_5. Only BrF_5 and IF_5 are known. Braune and Pinnow (6) concluded twenty years ago and the I - F bond distances in IF_5 are all equal, but when they assumed a trigonal bipyramid structure the bond lengths became over 2.5 A. whereas the sum of the covalent radii of iodine and fluorine is less than 2 A. Kimball (22) showed that IF_5 should have p^3d^2 bonding and should therefore possess a tetragonal pyramidal structure. As in the case of ClF_3, the pair of unshared electrons is useful in justifying this structure. Rogers (30) showed that IF_5 is not a trigonal bipyramid and that the I - F bond distance is not 2.56. Although Lord, Lynch, Schumb, and Slowinski (23) considered a tetragonal pyramid more likely than a planar pentagon, they did not rule out the latter on the basis of their work.

Nine Raman frequencies have been found (9) in accord with a tetragonal pyramid. Nuclear magnetic resonance measurements (18, 19, 27) have confirmed such a structure for both IF_5 and BrF_5. The high electric moment for IF_5 (31, 32) also excludes the planar pentagon and the trigonal bipyramid structures. Infrared studies on BrF_5 (20) yielded no definite conclusions. Both compounds have been found to be diamagnetic (33).

The I and Br atoms in these molecules have been assumed to be both above and below the plane of the four coplanar fluorine atoms (15, 31, 43, 48).

XX'_7. A pentagonal bipyramid structure has been considered a more likely configuration than a planar heptagon (23) for IF_7, the only known interhalogen of this type. Bonding may be either sp^3d^3 or f^2sp^3d (37). Gutowsky (18) has found that the seven fluorine atoms are not equivalent.

Work on the structures of interhalogens is far from complete. Palmer (27) points out that neutron diffraction may help in the elucidation of structures that have not been determined with electron and x-ray diffraction methods.

A seminar paper by Musker (March 13, 1956), several reviews (4. 38, 40), as well as books on inorganic chemistry (25, 42, 43, 48) may be consulted for information concerning methods of preparation, and the physical and chemical properties of these compounds.

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Tetrasulfur Tetranitride (N_4S_4)

S. K. Madan April 23, 1957

The literature lists three sulphides of nitrogen, namely NS_2, nitrogen disulphide, N_4S_4 tetranitrogen tetrasulfide and N_2S_5, dinitrogen pentasulfide. The compound N_2S_4, dinitrogen tetrasulfide has been isolated recently and its absorption spectrum found to be identical with that of nitrogen disulfide and of dinitrogen pentasulfide which would indicate that the latter are actually dinitrogen tetrasulfide (1).

Tetrasulfur tetranitride was first made by Gregory in 1835 (2). Although subsequent investigations have contributed a tremendous amount to our present knowledge of tetrasulfur tetranitride the exact nature of this coupound with respect to many of its properties and reaction is still under investigation.

Physical Properties

Tetrasulfur tetranitride, N_4S_4, is an orange-red crystalline substance, insoluble in water, but soluble in benzene, carbon disulfide, and liquid ammonia. In powder form it readily explodes.

Molecular Weight	Melting Point	Specific Gravity	Dipole-Moment	Crystal System
184	178-80°	2.2 (20°)	0.72 x 10^{18} e.s.u.	Monoclinic

X-Ray diffraction data (3); Space group $C^5.2h$ $P2_1/n$;

Cell constants: a_o 8.74°A b_o 7.14A° c_o 8.645A°

92°21 Z 4(N_4S_4).

Preparation

The preparation of tetrasulfur tetranitride depends on the reaction of ammonia with various sulphur compounds, S_2Cl_2, SCl_2, $SOCl_2$, CS_2, and sulphur itself. Gregory (2) first prepared the compound by dropping S_2Cl_2 slowly into an excess of aqueous ammonia and allowing the mixture to stand until the red product became yellow. The yellow substance was extracted with boiling alcohol. This method yielded an impure compound for which he reported an analysis corresponding to the composition NS_6.

Subsequent workers have improved the methods of preparation by utilizing dry ammonia, in reactions with the above sulphur compounds either directly or dissolved in various solvents such as benzene, ether, chloroform, etc. (4-13).

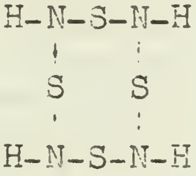
Constitution

The structure of tetrasulfur tetranitride has been investigated by a number of workers. Chemical investigation (14-16) has shown that the average oxidation number of sulphur in this compound is 3. Hydrolysis always gives ammonia or ammonium ions and sulphur oxy-acids. This is in agreement with the fact that nitrogen is more electronegative than sulphur (17). In weakly alkaline solution the hydrolysis occurs according to equation (i) but in strongly alkaline solution according to equation (ii):

$$2S_4N_4 + 6OH' + 9H_2O \rightarrow 2S_3O_6^{-2} + S_2O_3^{-2} + 8NH_3 \qquad \text{i -- (15)}$$

$$S_4N_4 + 6OH' + 3H_2O \rightarrow 2SO_3^{-2} + S_2O_3^{-2} + 4NH_3 \qquad \text{ii -- (17)}$$

Reduction of tetrasulphur tetranitride with tin II chloride (18, 19) or with dithionate, $S_2O_4^{-2}$ (20) yields tetrasulphur tetrimide, $S_4(NH)_4$. Tetrasulphur tetrimide is easily oxidized back to tetrasulphur tetranitride -- for example by chlorine (20). It is therefore reasonable to assume that N_4S_4 has formula II (23), (15) which is nicely in line with the results of reduction and of hydrolysis.



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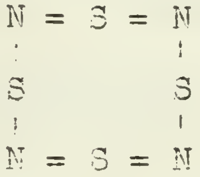
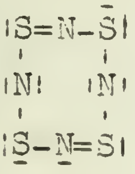
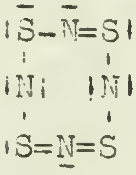


II

Formula II depicts sulphur bound in two different ways and does not correctly reproduce the valency states of the components. It has been shown that the sulphur atoms cannot be differentiated (24) by labelling with ^{35}S. The sulphur atoms cannot be differentiated as S^{+4} and S^{+2} atoms, as formula II would demand, but that an equalization of valency must take place in the molecule. This conclusion is supported by investigation of the K∝ X-ray emission spectrum of the sulphur in N_4S_4 suggesting the electronic formulae (II a-f). Resonance between the limiting formulae would account for the impossibility of differentiating between the sulphur atoms. Other formulae such as (IIg-i) could be brought into the resonance system, although (IIk) appears less likely from the K ∝ spectrum.

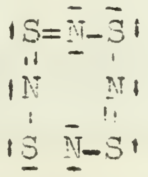


IIa



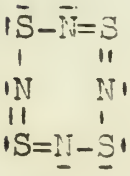
IIb

IIc

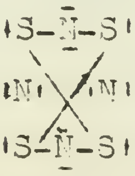


IId

IIe



IIf



IIg

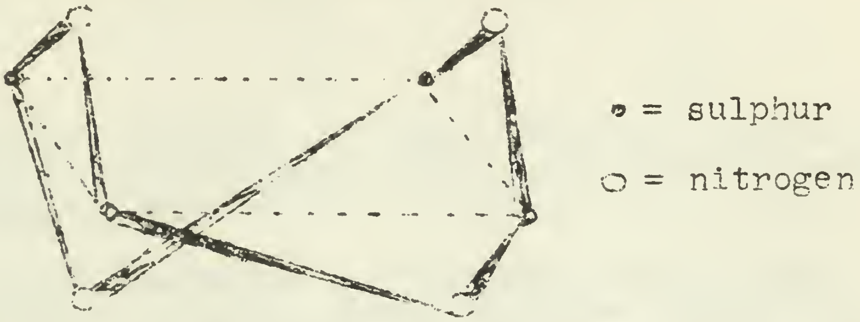
IIh

IIi

IIk

Chia-Si Lu and Donohue (25) proposed the formulae (IIa-i) as the result of a study of electron difraction of N_4S_4 in the vapor state.

Von Hassel and Viervoll (26) suggest that the sulphur atoms be in a plane and that the nitrogen atoms are tetrahedrally disposed towards each other. Formula IIk is therefore suggested as a consequence of infrared and Raman spectra (27).



Reactions

1. On heating tetrasulphur tetranitride vapor at 300°/0.01 mm and cooling rapidly, depolymerization to disulfur dinitride occurs. The dimer is soluble in organic solvents and stable only at low temperatures. At room temperature it polymerizes to form $(SN)_x$ which is brass-colored in mass, dark blue in thin layers, insoluble in organic solvents. In presence of atmospheric moisture N_2S_2 dimerizes to S_4N_4.

2. An ammoniate is formed by dissolving N_4S_4 in liquid ammonia. An ammoniate is also obtained from N_2S_2.

$$N_2S_2 \xrightarrow[NH_3]{liq.} S_2N_2NH_3 \qquad (23)$$

$$N_4S_4 \xrightarrow[NH_3]{liq.} S_4N_42NH_3 \qquad (9)$$

X-ray diffraction studies and absorption spectra shows that these two products are identical.

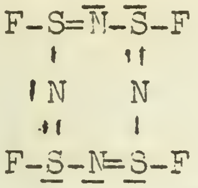
3. Thionitrosylates are prepared from the ammoniate of S_4N_4 by way of imide III

$$\underset{I}{H_2\underline{N}-\underline{S}=\underline{N}-\overline{\underline{S}}-\overline{\underline{N}}-H} \longrightarrow \underset{II}{H-\overline{\underline{N}}-\underline{S}=N-H} + \underset{III}{\overline{\underline{S}}=\underline{N}=H}$$

Thus, reaction with lead iodide gives the red $Pb(NS)_2$ (29) with thallium nitrate the brown-red $Tl(NS)_3$ or the ochre-colored $Tl(NS)$, $5Tl(NS)_3$ with silver nitrate the red-brown $Ag(NS)_2$, and with cuprous chloride, the brown $Cu(NS)_2$ (29). For preparation of these thio nitrosylates one can use solutions of the imide I in liquid ammonia or in alcohol.

4. Complex compounds with transition group elements have the composition $M(NS)_4$ where M = Ni, Pd, Pt, Co and Fe. (30,31)

5. Halogenation gives thiazyl halides. The ring system of tetrasulphur tetranitride remains intact on cautious fluorination with silver fluoride. $S_4N_4F_4$ (I) is a colorless solid (32).



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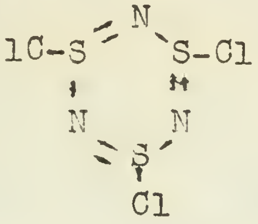

II

$[\mathrm{Br} - \mathrm{S} \overset{-}{=} \mathrm{N}]_x$

III

Chlorination yields the chloride II (33). Finally bromination gives a brown-colored solid bromide III whose molecular weight has not yet been determined. (34)

6. Thiotrithiazyl compounds derived from tetrasulphur tetranitride belong to a peculiar group with the composition S_4N_3X, where X may be a halogen, HSO_4 or NO_3. More accessible is thiotrithiazyl chloride S_4N_3Cl, which is obtained as yellow solid, S_4N_4 with HCl (35) or by reaction with sulphur monochloride (36).

Uses

1. Insecticide (37, 38, 39, 40, 41, 42, 43).
2. Fungicide (37, 38, 44, 45).
3. Ignition promoter for diesel fuels (46, 47).
4. Indicator in the titration of acids in non-aqueous solvents (48, 49).
5. Accelerator in the vulcanization of rubber (50).

The utilization of tetra sulfur tetra nitride as an insecticide and fungicide is by far its most important practical application.

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An Introduction to Electron Spin Resonance

Robert D. Vest April 30, 1957

Electron paramagnetic resonance, or electron spin resonance is a phenomenon first observed in 1945 in $CuCl_2 \cdot 2H_2O$. Several reviews are available on the subject (2,3,4) and a recent seminar covers the applications for organic chemistry.

Theory (2,3,4,5)

Free electrons spin about their own axis (in addition to their orbital motion) and possess a magnetic moment . If these electrons are placed in a magnetic field H, they experience a torque which causes them to precess about an axis parallel to the applied field. This situation is analogous to a spinning top precessing or wobbling in the earth's magnetic field. The frequency of precession, sometimes called the Larmor frequency is directly proportional to the field strength and independent of the angle of inclination Θ. See Figure I.

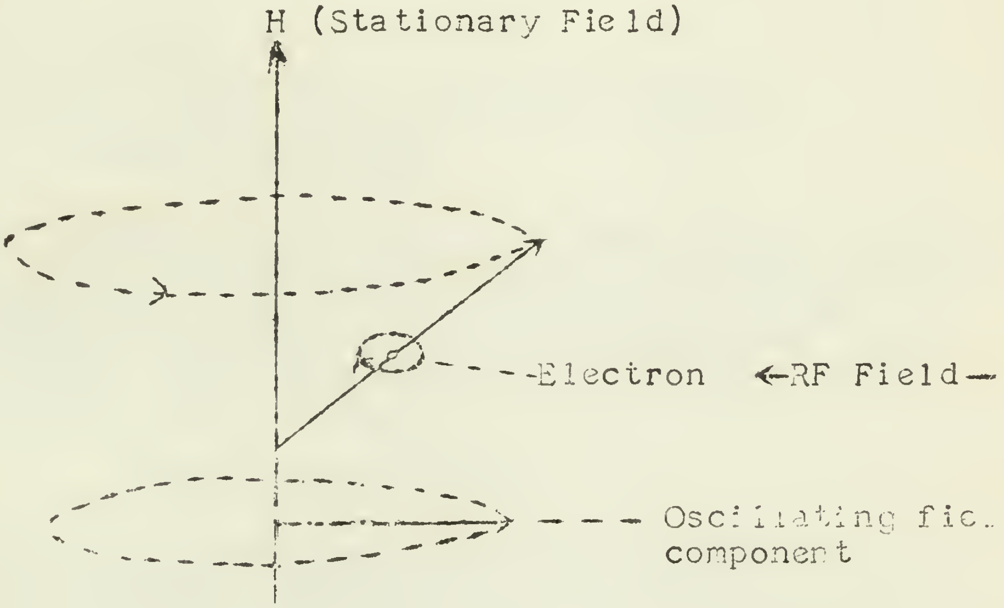

Figure I

If now a radiofrequency (r-f) field is beamed perpendicular to the magnetic field, it is possible to determine the Larmor frequency in the following manner. The r-f field is equivalent to two counter-rotating fields, one of which will be rotating in the same direction as the precessing dipole. When this field rotational frequency equals the precessional frequency, the ends of the two vectors will move in unison and the latter will be attracted toward the field vector. There will be an accompanying absorption of energy from the radiant field which can be detected.

The resonance condition is described by the equation

$$E_2-E_1 = h\nu = g\beta H$$

where E_1 and E_2 are the energy levels, β is the Bohr magneton and H is the strength of the applied field. The term "g" is known as the spectroscopic splitting factor and for free electrons is equal to 2.0023. If orbital motion is present it is some value other than this. It should be noticed that the splitting between the energy levels is determined by the field strength.

Hyperfine Structure

Many atomic nuclei have an inherent spin and consequently a magnetic moment which influences electrons in its vicinity. This nuclear magnetic moment will act in conjunction with the applied fie to produce hyperfine splitting. In general, if the spin of the neighboring nucleus is I, then each electronic transition will be split into 2I + 1 electronic levels resulting in that number of resonance peaks in the spectrum. In particular, electrons associated wit divalent cobalt ions (I = 7/2) will have eight peaks, those associate with N^{14} (I = 1) will have three, etc. The multiple splitting observed in many cases resulting from the odd electron extending over many nuclei is conclusive experimental evidence for delocalization of electrons.

Line Widths and Heights

Resolution of the spectrum is limited not by instrumental effects but by the width of the lines themselves. The line widths are dependent on three factors; spin-lattice interactions, spin-spin interactions and exchange interactions all of which are mechanisms by which the electrons may lose energy. The last of these is a complicated phenomenon (see ref. 6) and will not be discussed here

except to say that it may be avoided by dilution of the sample with some diamagnetic-material.

The distribution of electrons between two energy states at ordinary temperatures is such that there is a slightly higher population in the lower state. The signal intensity is greatest at very low temperatures because of a much higher population in the lower energy state.

If at the resonance condition, the transitions up and down become equal, there is no net absorption and the sample is magnetically saturated. However, the electrons in the higher energy state may lose a quantum of energy to the lattice (spin-lattice interaction) or to another electron (spin-spin interaction) and return to the lower energy state. The time required for the dissipation of such energy is termed the relaxation time. If the relaxation time is short, the spectral line will be broadened, since by the Heisenberg Uncertainty Principle $\Delta E \cdot \Delta t = \hbar$

By utilizing suitable standards and operating under similar conditions one can obtain quantitative results since the area under the curve is directly proportional to the concentration of free electrons. The measurements are very sensitive in that free radicals in concentrations as low as 10^{-11} molar have been studied. The theoretical limit is 10^{-14} molar.

A simplified representation of the apparatus is given in Figure 2

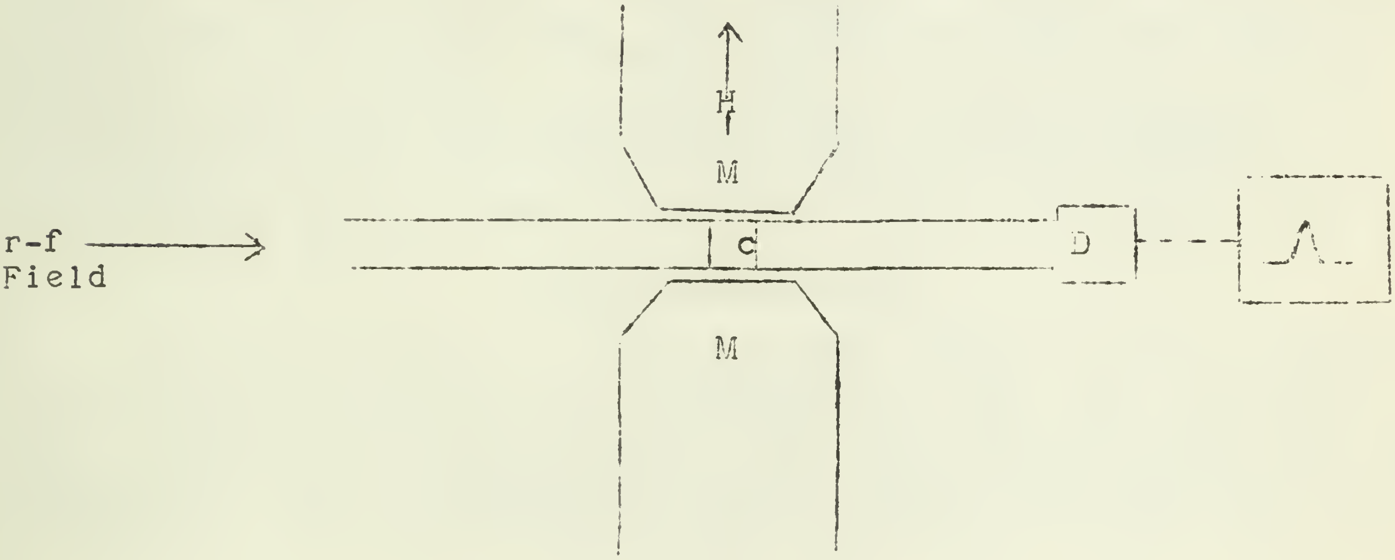

Figure 2.

The sample is placed in the cavity "c" located between the pole pieces of the magnet "m". The oscillating field (r-f) is transmitted by means of a rectangular wave guide through the cavity, detected at "D", amplified, and recorded. H is measured in kilogauss and the wavelength of the r-f field is of the order of a few centimeters.

Applications

Several selected applications of ESR techniques will demonstrate the principles presented in the previous section and will show the usefulness of these measurements. No attempt has been made to cover all of the applications and the reader is referred to the several reviews for a more complete coverage.

Liquid Sulfur (7)

It has been thought for some time that sulfur, at temperatures above 160^0, exists in an equilibrium mixture of S_8 rings and polymeric chains. The chain molecules should possess unpaired electrons on the terminal sulfur atoms but this was not detectable with ordinary magnetic measurements. Frankel (8) proved conclusively by ESR techniques that this polymeric form of sulfur existed with a number average chain length of 1.5×10^6 at 171^0C. He further calculated the concentration of unpaired electrons to be $6 \pm 3 \times 10^{-4}$ m/l, at 300^0C. The observed broadening of the line width was attributed not to a physical phenomenon as discussed in the theory section but to the chemical exchange reaction

$$\text{----S-S-S}\cdot\text{+---S-S-}\rightarrow\text{--S-S--+---S}\cdot \ .$$

Ammonium hexachloroiridate (9)

Studies on $(NH_4)_2[IrCl_6]$ diluted with an isomorphous diamagnetic platinum salt at 20^0K show a hyperfine structure consisting of many lines, 16 of which are resolvable. Since Ir^{191} and Ir^{193} ($I = 3/2$) should yield only four lines, this spectrum can only be explained by assuming the odd electron interacts appreciably with the Cl^{35} or Cl^{37} ($I = 3/2$) orbitals. In other words, the "electronic hole" is described by unequal mixtures of 3p (Cl) orbitals with the $5d_{xy}d_{yz}d_{zx}$ of Ir. The time that the electron spends in the chlorine orbitals has been estimated to be about 18% of the time.

Copper Acetate (10)

The ESR spectrum of copper ($I = 3/2$) acetate is quite anomalous. It resembles that of an ion of spin equal to one. This spectrum (See Figure 3) is indicative of an exchange interaction or coupling of isolated pairs of copper atoms. The two electron spins would then interact to form a paramagnetic triplet state (spins parallel) and a diamagnetic singlet state (spins anti-parallel). At low temperatures

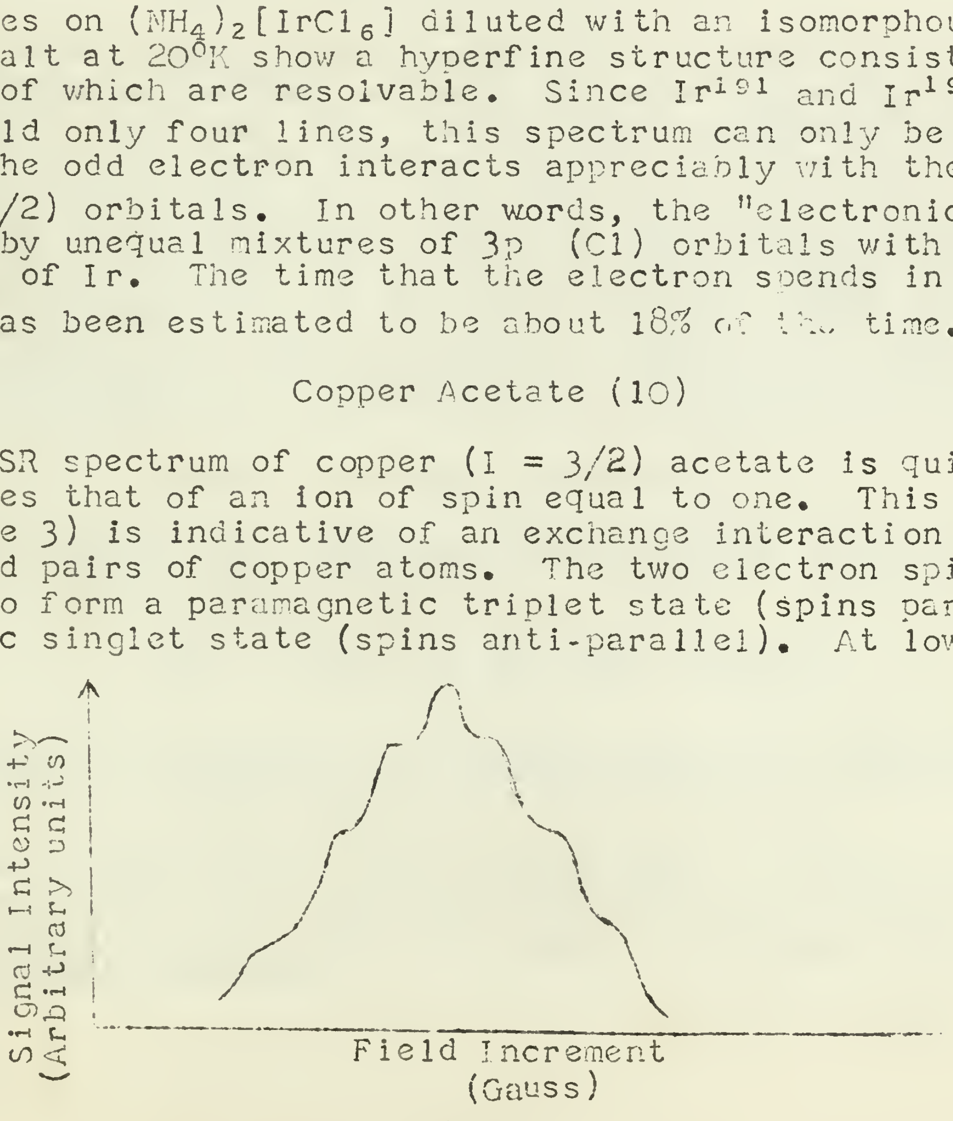

Figure 3.

the copper ions are drained out of the paramagnetic state (higher energy) to the singlet state with the consequent diminishing paramagnetism which is observed. At 20°K no absorption spectrum is observed.

The two interacting copper ions have an equivalent spin of $3/2 + 3/2 = 3$. There would then be $2I + 1$ or seven resonance lines in the spectrum.

Iron Group Fluorides (11)

Another example of delocalization of electrons over several nuclei is afforded by a study on single crystals of ZnF_2 containing small amounts of either MnF_2, FeF_2, or CoF_2. Since the cations of the crystal are surrounded by an octahedron of F^- ions (spins = 1/2) the hyperfine structure of the spectrum is a direct means of measuring the charge transfer or delocalization.

Symmetry considerations reduce the number of theoretical lines to 15 which is actually observed and it is estimated that the magnetic electron spends 12% of its time on the fluorine. The spectrum of Cr^{+3} under these conditions shows no hyperfine structure because the magnetic electrons are not directed toward the F nuclei.

Copper Porphine Complex (12, 13)

The infrared absorption frequency of the C-Cl bond in tetra-(p-chlorophenyl)-porphine is found at lower frequency than the same absorption in the metal (Cu, Co, Ni, etc.) complexed porphines. This is indicative that there is some double bond character in the C-Cl bond in the metal complexes. The ESR spectrum of these complexes shows a hyperfine structure similar to that of the chloro-iridate complex indicating that the magnetic electron spends part of its time in the neighborhood of the chlorine atom. This is somewhat remarkable because the Cu-Cl distance is about 9-10A° and the phenyl rings are not coplanar with the rest of the molecule. An intramolecular interaction is discarded on the basis of g values.

Hydrocarbon Negative Ions (3, 15)

Sodium reacts with naphthalene and similar hydrocarbons in ethers to produce negative ion radicals.

$$Na + C_{10}H_8 \xrightarrow[THF]{} Na^{\oplus} + C_{10}H_8^{\ominus}$$

The electron on the negatively charged specie is distributed throughout the ring and can be observed by ESR techniques.

If now an equal quantity of anthracene is added, the two organic species compete for the electron. This process has been used to set up an electronegativity scale for aromatic hydrocarbons and may find use in inorganic systems.

Color Centers (3, 16, 17)

The F-center of the alkali halides is presumably an electron trapped in an anion vacancy. This electron should be associated with the six alkali metal atoms surrounding it. This has been found to be the case by E.S.R. techniques.

Copper Chelates (18)

The ESR spectrum of copper acetylacetonate shows the existence of strong π bonds and weak σ bonds. The results are in disagreement with Pauling's covalent theory of copper compounds in that the unpaired electron is not in a $4\ p_z$ orbital.

Alkali Metals in Liquid Ammonia (3)

A very narrow absorption line appears in the ESR spectra of liquid ammonia solutions of sodium or potassium. The g value is 2.0012 and the signal amplitude decreases when the sample is cooled. Presumably the electrons removed from the metal atoms reside in cavities of radius about 4 - 5 Å. (19)

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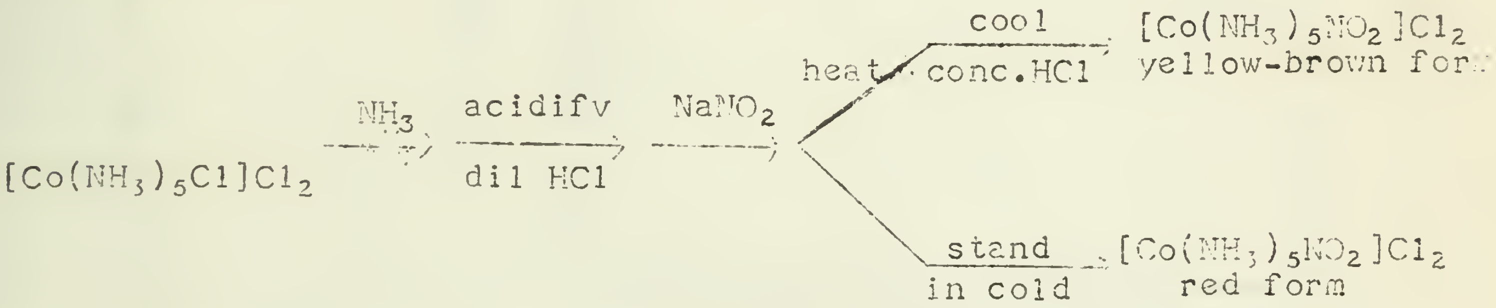
Structural Isomerism in Coordination Compounds

Bruce R. Karstetter May 7, 1957

The existence of structural isomerism in inorganic complexes is limited to a very few cases, foremost of which are the nitro-nitrito compounds. In the case of the nitro compounds, the nitrite ion is bonded to the metal ion through the nitrogen ($M-NO_2$) whereas, in the nitrito compounds, the bonding is through oxygen ($M-ONO$).

If chloropentamminecobalt(III) chloride is treated in the following manner (1)



two seemingly different compounds with the same composition are found. The red form can be changed to the yellow-brown form by heating in solution and by adding concentrated HCl. It will even change slowly in the solid phase. On the basis of the colors of these complexes we would expect the red compound to be the nitrito form and the yellow-brown the nitro form.

Lecompte and Duval (2) studied the Debye-Scherrer X-ray patterns, the infrared absorption, and the ultraviolet absorption bands of both of these compounds. They concluded that the nitrito form does not exist and that the red color is due to unreacted starting material.

However, these conclusions are not supported by kinetic studies. The rate of conversion of the red form to the yellow-brown form has been studied photometrically and was found to follow a first order rate law (3). If the conclusion of Lecompte and Duval were correct, the conversion of the highly ionized salt, chloropentamminecobalt(III) chloride-nitrite, $[Co(NH_3)_5Cl]ClNO_2$, to the nitro complex in solution should follow a second order rate law, unless the rate determining step is a slow rearrangement which takes place subsequent to the collision of a chloropentamminecobalt(III) ion and a nitrite ion.

The problem has now been resolved by further infrared and tracer studies.

The infrared work was done by Quagliano et. al. (4). They have reported the infrared spectra of both forms in the solid state, changes in the infrared spectra associated with the rearrangement of the nitrito complex to the corresponding nitro compound, and have made assignments of the infrared bands in both the nitro and nitrito isomers in the sodium chloride region.

Figure 1 gives the infrared spectra of freshly prepared nitritopentamminecobalt(III) chloride, the same material aged for five days, and pure nitropentamminecobalt(III) chloride.

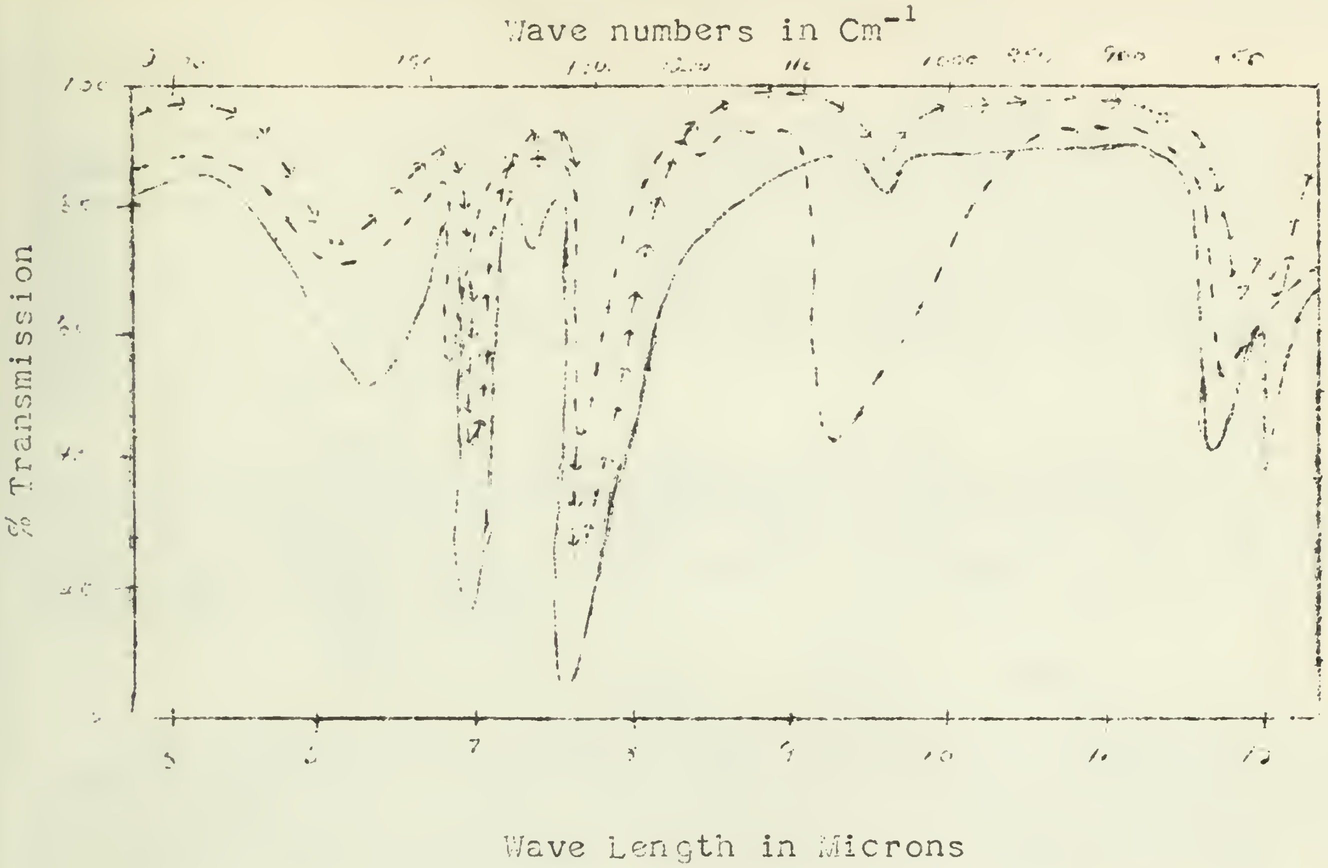


Figure 1.

-, nitropentamminecobalt(III) chloride; --- nitritopentamminecobalt(III) chloride, fresh; →→, nitritopentamminecobalt(III) chloride, aged.

Both isomers have absorption maxima at 1595, 1315 and 850 cm^{-1}. These absorption bands correspond to those observed in the spectrum of $[Co(NH_3)_6]Cl_3$ and have been identified with the degenerate deformation vibration, symmetric deformation vibration and rocking vibration of NH_3 ligands respectively.

The remaining bands in the region from 2000-650 cm^{-1} are associated with vibrations of the NO_2 and ONO ligands for it has been shown that cobalt-nitrogen stretching frequencies are not expected to appear in this region (6). The spectrum of the nitrito isomer has additional peaks at 1460 and 1065 cm^{-1}. Upon aging of the sample, these bands decrease in intensity and, simultaneously, two new bands appear at 1430 and 825 cm^{-1}. The bands which increase in intensity are characteristic of the nitro complex as seen by comparison with the spectrum of sodium hexanitrocobaltate(III) (5). The strong bands which decrease in intensity can be assigned to the nitrito ligand. Thus, the bands of decreasing intensity in the spectrum of the nitrito isomer at 1460 and 1065 cm^{-1} may be assigned to the two ONO stretching vibrations.

This work shows that the nitrito isomer, on standing for several days at room temperature, gives rise to an absorption spectrum almost identical with the spectrum of the pure nitro compound. This can be explained as a change in the coordinating group from (Co-ONO) to ($Co-NO_2$).

Even more conclusive proof for the existence of the nitrito isomer is given by the work of Murmann and Taube (7). On the basis of isotope and kinetic studies reported in the literature (8, 9, 10) they felt that the nitrito compound might be formed from the aquo complex without breaking the original cobalt-oxygen bond. In order to elucidate the mechanism of the formation of nitrito compounds of Co(III) and Cr(III) ammines and of the nitrito-nitro conversion, they used O (18) as a tracer.

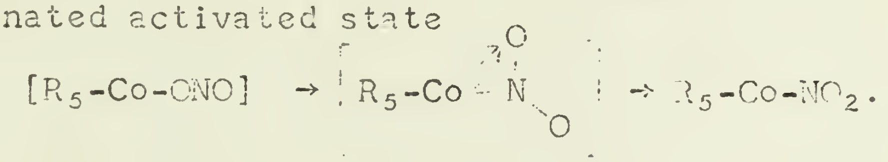
Since $[Co(NH_3)_5OH_2]^{+3}$, (ROH_2), exchanges its water with the solvent only slowly at room temperature, the preparation of O_{18} enriched $[Co(NH_3)_5ONO]^{+2}$, (RONO), from normal H_2O, NO_2^- and enriched (ROH_2) was thought possible <u>if</u>, during the reaction, the cobalt-oxygen bond is <u>not</u> broken.

$$(R\overset{*}{O}H_2) + NO_2^- + H_2O \rightarrow (R\overset{*}{O}NO) + 2H_2O$$

The experimental results showed almost 100% retention of the cobalt-oxygen bond, indicating that the nitrosating agent substitutes on the complex ion oxygen. The identity of the nitrosating agent is not clear, but in solutions containing large amounts of NO_2^- it is probably ($NO^+NO_2^-$).

Under slightly alkaline conditions the nitro complex is formed rather slowly and does not involve the nitrito intermediate. The most likely path is dissociation followed by entry of a nitrite ion; a displacement reaction is less likely.

Similar tracer studies on the nitrito to nitro conversion were also made. Experimental results indicated that in at least two cases, $[Co(NH_3)_5ONO]^{+2}$ and cis$[Co(en)_2(NO_2)(ONO)]^+$, the rearrangement is certainly an intramolecular one. Murmann and Taube postulate a heptacoordinated activated state



$$[R_5\text{-}Co\text{-}ONO] \rightarrow \left[R_5\text{-}Co \leftarrow N\begin{matrix} \nearrow O \\ \searrow O \end{matrix} \right] \rightarrow R_5\text{-}Co\text{-}NO_2.$$

This conversion is found to be slower in slightly acid solution than in neutral solution. It is suggested that the slower rate is due to an equilibrium which removes a portion of the nitrito complex with the reaction going to completion by a shift of the equilibrium concentrations on depletion of the nitrito complex.

$$[R_5CoOH_2] + HONO \xrightleftharpoons{H^+(H_2O)} [R_5Co\text{-}ONO] \rightarrow [R_5CoNO_2]$$

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Chemistry of the Bis-Cyclopentadienyl Metal Compounds

Donald J. Casey May 14, 1957

Preparation

a) By the reaction of a cyclopentadienyl organometallic compound (C_5H_5MgBr in C_6H_6 or C_5H_5Na in T.H.F.) with metal halides or acetylacetonates.

1. Grignard Plus Metal Halide: Cr(II), V(II) (1); Co(III)(2); Mn(II)(3); Ti, Zr, and V in (IV) state, Nb, Ta in (V) state (4); Fe(II) (5).
2. Grignard Plus Acetylacetonate: Co(III)(6); Ru(II)(7); Rh(III), Ir(III)(8).
3. C_5H_5Na Plus Metal Halide: Fe(9); Ti(10); Cr, Mo(IV), W(V)(11); U(IV), Th(IV) (12); Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Dy (13).

b) Reaction of cyclopentadiene vapor with a metal carbonyl

$$Cr(CO)_6 + C_5H_6 \xrightarrow{280-340^\circ} (C_5H_5)_2Cr \quad (14)$$

c) Reaction of C_5H_5K in liquid NH_3 with a metal thiocyanate: Co(II)(15); Ni(II)(16); Cr(II)(17).

d) Reaction of metal halide with C_5H_6 in presence of R_2NH (39).

Reactions (18)

It is theoretically possible that $(C_5H_5)_2M$ compounds can undergo an ionic dissociation such as:

$$(C_5H_5)_2M \rightleftharpoons (C_5H_5)M^{\oplus} + C_5H_5^{\ominus} \rightleftharpoons M^{++} + 2C_5H_5^{\ominus}$$

Unless the dissociation is small (indicating a largely covalent bond) two types of reactions should be possible: (1) Cationic exchange, (2) Reactions which consume the $Cp^{\ominus}$ ion.

(a) Exchange Reactions

It has been found that ferrocene undergoes no isotopic exchange over a period of 12 months. With $FeCl_2$, $Mg(Cp)_2$ and $Mn(Cp)_2$ react rapidly to give quantitative yields of ferrocene; $Co(Cp)_2$ and $Ni(Cp)_2$ yield no ferrocene while the vanadium compound forms $(Cp)_2VCl$ and a trace of $Fe(Cp)_2$.

(b) Hydrolysis

The $M(Cp)_2$ compounds of Mg and Mn have been found to hydrolyze instantly while the compounds of V, Cr, Fe, Co and Ni give no reaction. $Co(Cp)_2$ is slowly oxidized to $[Co(Cp)_2]^{\oplus}$.

(c) Reaction with Aldehydes, Ketones and Dienophiles

$Fe(Cp)_2$ and $Ru(Cp)_2$ failed to react with benzophenone, m-nitrobenzaldehyde and maleic anhydride. The Mg and Mn compounds form diphenylfulvenes with $(Ph)_2CO$ while the V, Cr,

and Co compounds form unidentified products. With maleic anhydride the $M(Cp)_2$ compounds of Mg, Mn, V, Cr, Co, and Ni react in an unknown manner.

(d) Solvation and Conductance

In liquid NH_3 the V, Cr, and Mn compounds show evidence of forming ammoniates, the exact nature of which is unknown. Conductance measurements demonstrate the Fe, Co, and Ni compounds are non-conducting while the Mg, Mn, V, and Cr compounds show conductances of 10^{-4}, 10^{-5}, 10^{-4}, and 10^{-4} ohm^{-1} respectively.

Physical Properties

With the exception of $Mn(Cp)_2$ and $Mg(Cp)_2$, the bis-cyclopentadienyl compounds behave as typical covalent materials. They are soluble in organic solvents and readily volatile. The V, Cr, Mg, Fe, Co and Ni compounds are isomorphous forming monoclinic crystals and having similar cell dimensions with a unit cell containing two molecules (19, 20). In contrast, $Mn(Cp)_2$ forms rhombohedral crystals and possesses a unit cell containing 16 molecules (21). The results from crystal studies indicate a pentagonal antiprism structure (20) confirming the early proposals of a "sandwich" type structure (22,23). Electron diffraction studies on ferrocene in the vapor phase indicate the rings rotate freely about the common orthogonal axis (24). This is contrasted with the observation of a staggered configuration in the crystal state (25) and restricted rotation in solution (26). The infrared spectra of the $M(Cp)_2$ compounds are remarkably similar showing one C-H band at 3.23-3.27μ (7,11,22,27). The mass spectra of the $M(Cp)_2$ compounds provide additional evidence for the similarity of their structures. Relative yields of the main ions $(Cp)_2M^{\oplus}$, $CpM^{\oplus}$, and $M^{\oplus}$ are similar for the covalent bonded V, Cr, Fe, Co, Ni, and Ru compounds. For the ionic Mn and Mg compounds the $CpM^{\oplus}$ ion predominates and greater yields of ions of lower mass are obtained (18,28).

Bonding

Octahedral Theory

The original concept of bonding in the $M(Cp)_2$ compounds suggested that the three pairs of electrons of each $Cp^{\ominus}$ ring were used in bonding to the metal so that all available metal orbitals were filled to produce the configuration of an inert gas. The three electron pairs of each ring were considered to be arranged around the ring in the form of an equilateral triangle giving a total of six dative bonds with the d^2sp^3 orbitals of the metal (23,29).

Molecular Orbital Theory

A number of attempts have been made to interpret the bonding of these compounds in terms of molecular orbital theory. Jaffe (31) constructed molecular orbitals from the

A.O.'s of iron and the M.O.'s of the Cp radicals. He then assumed the 18 valence electrons were distributed so that 16 occupied bonding orbitals and 2 occurred in a non-bonding M.O. The metal atom was assumed to be bound to each Cp ring by four covalent bonds. Dunitz and Orgel (32) and Moffitt (33) considered the 3d orbitals of the metal which are of three types according to their quantum numbers: $m_l = 0$, $m_l = \pm 1$, and $m_l = \pm 2$. Theory shows that only the pair $m_l = \pm 1$ have both the same transformation properties and approximate energy as one of the available orbitals on each Cp ring. Each one of the latter metal orbitals can combine with a ring orbital to give a bonding M.O. (E_{1g}). The result will be a single covalent bond from the metal to each ring delocalized equally among all five carbon atoms of the ring. Moffitt regards the orbital with $m_l = 0$, which has the same transformation properties as the 4s orbital, as combining with the latter to produce a pair of orbitals. (designated ha_g and ka_g) one of which has an energy of the order of the 4p orbitals while the other is in the region of the 3d orbitals. This interpretation provides a satisfactory explanation for the aromatic properties of the rings since only one electron from each ring is involved in C-M binding. The theory postulated by Jaffe leads to the prediction of diamagnetism for $Cr(Cp)_2$ whereas magnetic measurements indicate the presence of 2 unpaired electrons (34,35). The ideas proposed by Dunitz and Orgel are also inadequate since they incorrectly predict the magnetic moments of $Fe(Cp)_2$ and $Ni(Cp)_2$ (36). Moffitt's inovation in the formation of the hybrid ha_g and ka_g orbitals leads to correct predictions of the magnetic properties of these compounds. His conclusions may be summarized: There are four approximately degenerate d levels in the metal; two of these have E_{1g} symmetry and are used for bonding. The other two have E_{2g} symmetry. In addition there are the two hybrid orbitals ha_g and ka_g. In the $M(Cp)_2$ molecules the levels are filled as follows. For $Cr(Cp)_2$ the four non-bonding electrons are disposed two paired in the ha_g orbital and two unpaired in the doubly degenerate E_{2g} orbitals. The additional two electrons in ferrocene enter the remaining E_{2g} orbitals leading to diamagnetism (36). For $Co(Cp)_2$ the additional electron over the configuration of ferrocene may occur either in a 4 p orbital or in the ka_g orbital resulting in one unpaired electron.

Among the major objections to the octahedral (d^2sp^3) theory are the following (36). (1) The exact symmetry conditions required by the octahedral theory are only approximated by the $M(Cp)_2$ molecules. (2) It does not explain the aromatic character of the rings. (3) Dative bonding required by the octahedral theory would result in accumulation of negative charge on the metal atom and it has been shown that the metal is electrically neutral (37). (4) The existence of stable derivatives of transitional elements of Groups IV and V suggests that the attainment of a rare gas configuration is not critical.

Unusual Cyclopentadienyl Metal Compounds

The preparation of a biscyclopentadienyl compound of rhenium by the reaction of $ReCl_5$ with NaCp has been reported (38). The diamagnetism of the product precludes $Re(Cp)_2$ as a possibility for its composition. N.M.R. studies have shown two peaks; one with a shift relative to H_2O of -1.17 ppm attributable to the cyclopentadienyl hydrogens and a second with a shift of +17.2 ppm which has been assigned to a hydrogen directly attached to the rhenium atom, thus establishing the product as $(Cp)_2ReH$.

The $Mn(Cp)_2$ compound previously mentioned has been shown to possess ionic properties. Magnetic measurements indicate the presence of 5 unpaired electrons whereas M.O. theory for covalent type molecules would predict the possibility of one unpaired electron. The ionic properties of this compound have been attributed to the stability of the half filled 3d shell in Mn^{++} (18).

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QUALITATIVE ASPECTS OF THE CRYSTAL FIELD THEORY

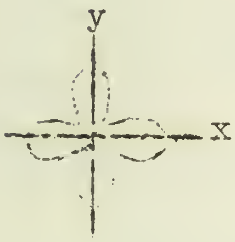
N. Koertge May 16, 1957

According to crystal field theory, the interaction of cation and ligand in transition metal complexes may be regarded as consisting entirely of electrostatic forces of the ion-ion or ion-dipole variety. (1,2,3) This admittedly crude and oversimplified point of view makes possible explanations and calculations of such physical properties as magnetic susceptibility, paramagnetic resonance absorption, visible spectra, and heat of complexation.

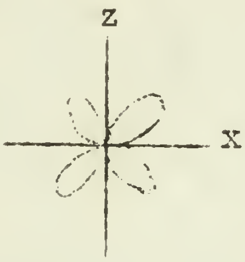
The quantum mechanical basis for the crystal field theory was laid in 1929 by Bethe. (24) It was first applied by Schlapp, Penny, and Van Vleck in 1932, (15,16,18) and it has since been a common tool of physicists, although its acceptance among chemists has been slow until recently.

Although applications to compounds where the degeneracy of *p* or *f* orbitals is affected by a crystal field have been made, the greatest success has been achieved with the complexes of the transition metals where the outer electrons move in *d* orbitals. It is the latter which will be discussed here.

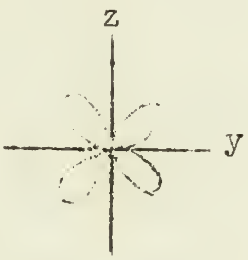
A convenient representation of the *d* orbitals is: (7)



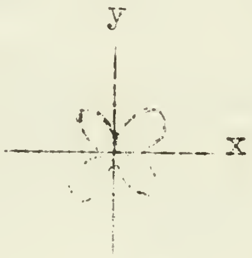
$d_{x^2-y^2}$



d_{xz}



d_{yz}



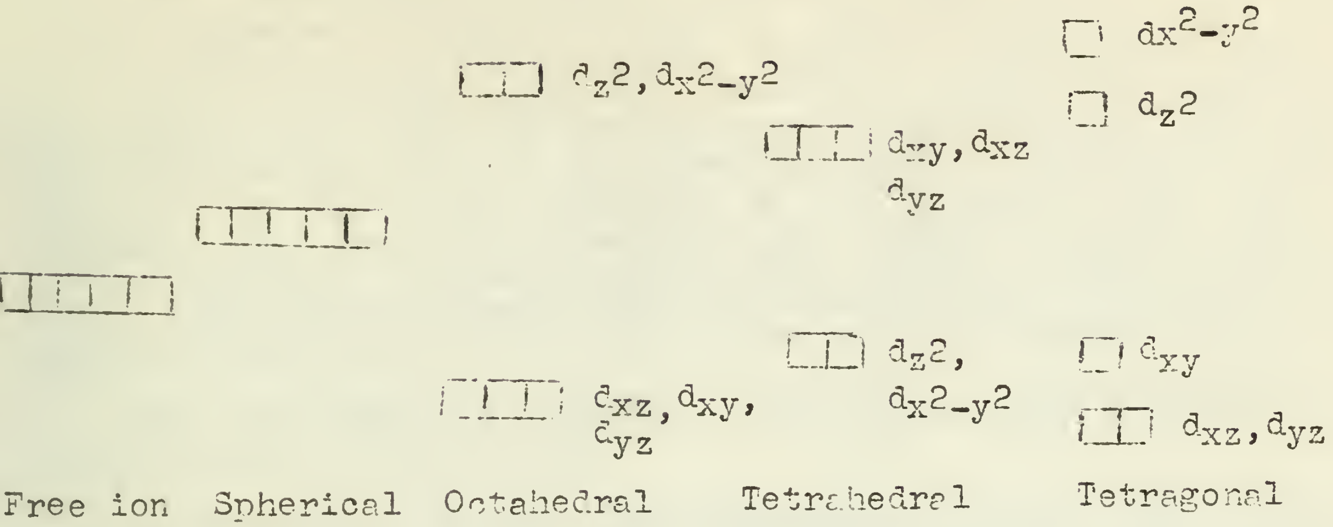
d_{xy}

d_{z^2}

For an isolated atom or ion these orbitals are degenerate. However, the introduction of electron-rich ligands along the x, y, and z axes would effect a repulsion of any electrons in the d_{z^2} or $d_{x^2-y^2}$ orbitals. In octahedral complexes, therefore, the net result is an increase in the energy of the orbitals directed along the axes and, since the center of gravity of the *d* levels must remain unchanged in a purely octahedral field, a compensating decrease in the energy of those orbitals directed in the areas between the axes.

In tetrahedral complexes the ligands take positions between the coordinate axes and the d_{xy}, d_{yx} and d_{xz} orbitals assume a higher energy. The tetragonal configuration may be regarded as a distorted octahedron and the resultant splitting is of a more complex nature. The Jahn-Teller theorem predicts that octahedral

complexes with orbital degeneracy will distort into a tetragonal configuration.



Many of the bands in the visible spectra of complexes can be attributed to electronic transitions occurring in the d orbitals. The frequency of the absorption band depends on the magnitude of the splitting caused by the coordinated groups. Thus, the color of $Ti(X^{-n})_6^{+3-6n}$ complexes varies from purple to green depending on the field strength of the particular ligand. (2) From various spectra a general spectrochemical series like the following can be set up:

$I^- < Br^- < Cl^- < OH^- < F^- < H_2O < py < NH_3 < en < ophen < CN^-$, where CN^- is associated with the greatest energy difference in the d orbitals. The exact order of such a list depends on the dipole moment and polarizability of the ligands, possibility of π bond formation, and other factors which are as yet less clearly defined.

The quantitative value of the crystal field strength is measured in terms of a parameter--D_q, the difference in the energies of the split d levels being arbitrarily designated as 10 D_q. The crystal field stabilization is expressed in terms of D_q and varies with the number of d electrons present. D_q values for tetrahedral configurations are about 4/9 of the corresponding octahedral values. (9)

Number of d Electrons	Octahedral Stabilization	Number of d Electrons	Tetrahedral Stabilization
d^0, d^5, d^{10}	0 D_q	d^0, d^5, d^{10}	0 D_q
d^1, d^6	4	d^1, d^9	6
d^2, d^7	8	d^2, d^8	12
d^3, d^8	12	d^3, d^7	8
d^4, d^9	6	d^4, d^6	4

A consideration of ions containing three or more d electrons suggests a distinction between weak and strong crystal fields.(5) In an octahedral field, for example, three d electrons will reside in the lower or t_{2g} energy level. However, a fourth electron can either enter the higher e_{2g} level or, if the value of 10 D_q is prohibitively high due to a strong crystal field, forfeit the Hund stabilization of the state of maximum multiplicity and pair up with one of the electrons in the t_{2g} level. (2) What actually does occur is measured by the magnetic susceptibility of the complex. In some compounds there seems to be a statistical distribution between the two possibilities, leading to unusual temperature dependence of the magnetic moment. (10,12,15)

The following are examples of the qualitative applications of the crystal field theory:

Visible Spectra of $Cu(AA)_2$ Type Complexes: (11,26) The broad band in the visible spectrum of $Cu(AA)_2$'s can be mathematically resolved into three peaks, the position and intensity of which are influenced by the basicity of both the solvent and the diketone.

Spectra of Cis and Trans Isomers:(8) The relative intensities and wavelengths of bands in the spectra of cis and trans isomers can be related to the different symmetry of their crystal field models.

Paramagnetism of Planar $Ni(acac)_2$: (28) As this compound illustrates, the configuration of complexes cannot be infallibly implied from their magnetic susceptibilities.

ESR Spectrum of CrF_3: (25) The ESR spectra of MnF_2, FeF_2, CoF_2 all exhibit a hyperfine structure which is an indication that the paramagnetic electron resides partially on the fluoride ions. The fact that the spectrum of CrF_3 lacks such structure may be related to the absence of electrons in the e_{2g} level.

Heats of Hydration of Divalent Iron Group Ions:(1) The discrepanc between the simple increase in $-\Delta H_{hyd}$ which might be expected in the series Ti(II) - Zn(II) and the irregular relationship which actually exists can be explained in terms of the variance of the crystal field stabilization with the number of d electrons.

Ionic Radii of Transition Elements: (6) The irregular radii of di- and trivalent transition element ions can be attributed to repulsions between d electrons and ligands.

Relative Stability of Hydrates and Ammines of Fe(III) and Co(III): (The instability of $Fe(H_2O)_6^{+3}$ and the relative stabilities of $Co(H_2O)_6^{+3}$ and $Co(NH_3)_6^{+3}$ can be described in terms of crystal field stabilization, dipole moment, and polarizability.

Relative Stability of Fe(II)-Fe(III) Complexes: (4) The molar oxidation potentials of various ferrous complexes

$Fe(H_2O)_6^{+2} = Fe(H_2O)_6^{+3} + e^-$ -0.74 v.

$Fe(CN)_6^{-4} = Fe(CN)_6^{-3} + e^-$ -0.49 v.

$Fe(o\text{-}phen)_3^{+2} = Fe(o\text{-}phen)_3^{+3} + e^-$ -1.14 v.

can be related to π bond formation, electron density on the ligand nitrogen and crystal field stabilization.

Crystal field theory provides a convenient basis for the calculation and correlation of the physical properties of transition metal complexes. It is much less complex than the molecular orbital treatment and allows phenomena to be related to measurable quantities such as dipole moment and polarizability instead of relying on the as yet untestable concepts of covalency and hybridization upon which the valence-bond explanation depends.

It has been shown that calculations based on crystal field theory in its simplest form do not give detailed agreement with experimental measurements. (27) It can be refined, however, by considering the effect of dipoles outside the immediate coordination sphere, and by introducing the concepts of π bonds, partial double bonds, and molecular orbitals.

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SOME PROPERTIES OF ISO- AND HETEROPOLYMOLYBDATES

Valentine Galasyn May 21, 1957

I. Introduction

The weak acids formed by the elements of Groups VB and VIB are characterized by the ease with which they condense to form anions containing several molecules of the acid anhydride. In the case of molybdenum, for example, the molybdates in alkaline solution are represented by the formula R_2MoO_4, but in acid solution the formation of more complex anions takes place. These condensed acids, containing only one type of acid anhydride, are called isopoly-acids. The same anhydrides (MoO_3, WO_3, V_2O_5) can condense with other acids to form heteropoly-acids. This second acid furnishes the central atom or ion of the whole complex anion.

II. Isopolymolybdates

Aggregation processes brought about by the addition of acid to molybdate solutions have been studied by the use of various techniques including diffusion, conductance, spectrophotometry, and light-scattering. The diffusion and conductance techniques of Jander[1] did not give exacting results, but did lay the foundation for future work. Lindqvist[2], using a spectrophotometric method, proposed the following stepwise reactions when solutions of Na_2MoO_4 are progressively acidified:

$$7\ MoO_4^{-2} + 8\ H^+ \rightarrow (Mo_7O_{24})^{-6} + 4\ H_2O$$

$$8\ MoO_4^{-2} + 12\ H^+ \rightarrow (Mo_8O_{26})^{-4} + 6\ H_2O$$

A more recent study by Tyree[3], using the light-scattering method, verified the work of Lindqvist.

Lindqvist has also determined the structures of the para- and octamolybdate anions, using x-ray techniques[4,5]. Six of the MoO_6 octahedra are attached to each other in the same way in both anions, and the remaining octahedra differ only slightly in position.

III. Heteropolymolybdates[6]

A. Typical Properties

1. The molecular weights are high, ranging up to over 300
2. The free acids and most salts are very soluble in water and in many organic solvents.
3. The crystalline free acids and salts are usually highly hydrated, and a given acid or salt often forms several solid hydrates.
4. Many are highly colored, the colors ranging through the spectrum. Others are colorless.
5. Some are strong oxidizing agents and can be changed

easily to fairly stable reduced species.

6. The free acids are fairly strong acids.
7. All anions are decomposed by strongly alkaline solutions.
8. Throughout specific ranges of pH and other conditions, most solutions appear to contain predominantly one distinct species of anion.

B. Principal Species

	No. of Atoms X:Mo	Principal Hetero Atoms	Typical Formulas
1.	1:12	Series A: P^{+5}, As^{+5}, Si^{+4}, Ge^{+4}, Sn^{+4}(?), Ti^{+4}, Zr^{+4}	$[X^{+n}Mo_{12}O_{40}]^{-(8-n)}$
2.		Series B: Ce^{+4}, Th^{+4} Sn^{+4}(?)	$[X^{+n}Mo_{12}O_{42}]^{-(12-n)}$
3.	1:11	P^{+5}, As^{+5}, Ge^{+4}	$[X^{+n}Mo_{11}O_{39}]^{-(12-n)}$ (Possibly dimeric)
4.	1:10	P^{+5}, As^{+5}, Pt^{+4}	$[X^{+n}Mo_{10}O_x]^{-(2x-60-n)}$
5.	1:9	Mn^{+4}, Co^{+4}, Ni^{+4}	$[X^{+n}Mo_9O_{32}]^{-(10-n)}$
6.	1:6	Te^{+6}, I^{+7}	$[X^{+n}Mo_6O_{24}]^{-(12-n)}$
7.	2:18	P^{+5}, As^{+5}	$[X_2{}^{+n}Mo_{18}O_{62}]^{-(16-2n)}$
8.	2:17	P^{+5}, As^{+5}	$[X_2{}^{+n}Mo_{17}O_x]^{-(2x-102-2n)}$
9.	2:12	Co^{+3}, Al^{+3}, Cr^{+3}, Fe^{+3}, Rh^{+3}	$[X_2{}^{+n}Mo_{12}O_{42}]^{-(12-2n)}$
10.	1m:6m	Ni^{+2}, Co^{+2}, Mn^{+2}, Cu^{+2}, Se^{+4}, P^{+3}, As^{+3}, P^{+5}	$[X^{+n}Mo_6O_x]_m^{-m(2x-36-n)}$ (m unknown)

C. Structures

X-ray structural determinations have been made on types 1,5,6,7, and 9. Structural information about the various types mentioned above is summarized as follows:

1. Pauling's structure[7] for the 12-heteropoly anion was modified by Keggin[8], whose model has been substantiated by the work of others[9- A central XO_4 tetrahedron is surrounded by 12 MoO_6 octahedra, each corner of the tetrahedron being shared with three octahedra. Each octahedron has 4 of its remaining 5 oxygens in common with its 4 nearest neighbors, whereas the remaining oxygen is free.

2. The structure here appears to be based on a central XO_6 octahedron. Baker[12] has proposed several structures, two of which are very similar to the Keggin structure. A third possibility may be derived by joining two paramolybdate ions and eliminating the two MoO_6 octahedra that have all six oxygens shared.

3. This structure is unknown, but may be dimeric. These compounds are possible degradation products of (1).

4. These also appear to be degradation products of (1). However, their existence is still controversial.

5. These are built around a central XO_5 octahedron[13]. A middle layer of four octahedra has a group of three MoO_6 octahedra above and below it.

6. The telluro-6-molybdate structure consists of seven octahedra all lying in one plane[14]. The central TeO_6 octahedron is surrounded by a ring of 6 MoO_6 octahedra, each of which shares one edge with each of its two neighboring MoO_6 octahedra.

7. This anion consists of two identical half-units linked together by six common oxygen atoms[15]. The half-unit can be pictured by removing a group of 3 octahedra from the Keggin model.

8. These are degradation products of (7).

9. On the basis of potentiometric titrations and partial x-ray analysis, Baker has postulated a dimeric structure for these anions. It is based on the union of two anions of the paramolybdate type[16,17]

10. The structure, molecular weight, and degrees of polymerization of these compounds are unknown.

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DETERMINATION OF THE STRUCTURE OF COORDINATION COMPOUNDS BY IR MEASUREMENTS

R. H. Hunt May 23, 1957

Studies of directive influences, stabilities, cis-trans isomers, and general structural properties of coordination compounds have been carried out using infrared absorption spectra. Infrared measurements should be considered as auxiliary to other methods, such as X-ray diffraction and magnetic measurements, in obtaining structural information. Common practice is the comparison of observed frequencies with established reference frequencies in an empirical approach to various problems.

The IR absorption spectra of cis and trans-$[Co(NO_2)_2(NH_3)_4]Cl$ and other ammine complexes have been measured to investigate the structural properties of ligands and their directive influences about the central metal ion of the complex (1). As a result of the trans effect and differences in symmetry between the cis and trans-$[Co(NO_2)_2(NH_3)_4]Cl$ isomers, significant differences appear in the infrared and ultra violet regions. Two strong absorption bands at 7.5 and 12 μ are attributed to the deformation of ammonia groups co-ordinated to the metal atom. The configurations which are in accord with the observed spectra are octahedral d^2sp hybridization, angular d^2 hybridization, and a d^2sp irregular tetrahedron.

Evidence has been presented in support of the hypothesis that in thiocyanato cobalt ammines, such as $[Co(NH_3)_5NCS]Cl$, the structure of coordinated thiocyanate may be described by a resonance hybrid of the form (2):

A necessary assumption is that sulfur has expanded its shell to accommodate more than eight valence electrons. Suitable compounds were chosen to establish reference frequencies for the "pure" carbon-to-sulfur single bond and the "pure" carbon-to-nitrogen triple bond. The expected shifts in frequency for these stretching vibrations lend s port to the resonance hybrid structure.

The infrared spectra of copper, nickel, and zinc glycine complexe have been of value in a study of the nature of the chelation bonding i these complexes (3)(4). A comparison with the spectra of potassium glycinate, ethyl glycinate, and glycine hydrochloride was made to assist in assignment of frequencies and obtaining structural information. For example, the N-H stretching vibration frequency is alter considerably on formation of the nitrogen-to-metal bond in the complexes. This is to be expected if the bond is essentially covalent. Absorption in the 6-6.5 μ region indicates that the resonance in the carboxylate ion is preserved in the complexes. The oxygen-to-metal bonds may then be considered essentially electrostatic. From the infrared data, combined with X-ray diffraction and magnetic susceptibility studies, it appears that the metal atoms use sp orbitals in forming linear bonds with the nitrogen atoms of the ligand molecules.

The similarity of the carboxylate frequencies in the glycine complexes and sodium glycinate is in contrast to the change in the absorption characteristics of ions on coordination with a metal ion. In the case of $[Cu(NH_3)_4]SO_4 \cdot H_2O$, for example, normal frequencies of the tetrahedral sulfate ion are present, whereas in $[Co(NH_3)_5SO_4]Cl$ the strongest absorption band characteristic of the free sulfate ion disappears (5). This indicates that the sulfur-to-oxygen bonds in the sulfate ion are no longer equivalent and implies an appreciable covalent character for the oxygen-to-cobalt bond.

The characteristic bands of coordinated water molecules in Ni(II), Cu(II), and Cr(III) aquo complexes are observed only when the water molecules are linked to the metal by fairly covalent bonds, or to the outer ion or the ligand of the neighboring complex molecule by strong hydrogen bonds (6).

Merritt and Wiberly (7) have observed that the cis and trans isomers of ethylenediamine complexes can be distinguished by their IR spectra. There are significant differences in the positions of the absorption maxima in the 6 and 12μ regions.

The effects of coordination in the spectra of rhodanato and azido complexes have been studied (8). An increase in the carbon-to-nitrogen stretching frequency of the rhodanato complexes can be interpreted as an increase in ionic character of a metal-to-nitrogen bond. The antisymmetrical structure of the azido group in azido complexes is evident in that the asymmetrical N_3 stretching frequenc is higher in covalent molecules than in ionic crystals.

A comparison with the normal vibrations of urea has permitted assignment of the absorption bands observed in metal-urea complexes A shift of the carbonyl vibrations in $[Pt(NH_2CONH_2)_2]Cl_2$ and $[Pd(NH_2CONH_2)_2]Cl_2$ to higher frequencies indicates that nitrogen, not oxygen, is coordinated to the central metal atom. This shift occurs for two reasons: the formation of the nitrogen-to-metal bond increases the electron demand by the donor nitrogen and blocks the resonance between this nitrogen atom and the carbonyl group. In addition to the bands for the N-H stretching vibrations for urea, two bands at lower frequencies are in the spectra of the Pt(II) and Pd(II) urea complexes. Since these may be assigned to the N-H stretching vibrations of the coordinated NH_2 group, it is concluded that only one nitrogen atom of each urea molecule coordinates to the metal ion.

N-H stretching vibrations in urea are observed at almost the same frequencies in the spectra of Cr(III) and Fe(III) complexes. This and other evidence from the spectra indicate that osygen-to-metal bonds are present. A similar conclusion may be drawn from the spectra of Zn(II) and Cu(II) urea complexes.

With the infrared spectrum of $Ni(CO)_4$ Crawford and Cross (10) have shown that the carbonyl groups are all identical and that most of the triple bond character of carbon monoxide is retained on coordination. Similar conclusions may be drawn from the work on the structure of $Fe(CO)_5$ (11). The infrared data are consistent with the reported trigonal bipyramid structure. Two distinct types of carbonyl groups, a triply bonded and a doubly bonded species, are seen to be present in $Fe_2(CO)_9$.

The infrared spectrum of chromium hexacarbonyl, $Cr(CO)_6$, indicates only one intense $-C\equiv O$ stretching frequency in the vapor phase (12). This is strong evidence that all the $-C\equiv O$ bonds are equivalent and that $Cr(CO)_6$ and other metal hexacarbonyls possess a regular octahedral structure.

The spectra and structures of cobalt hydrocarbonyl, $HCo(CO)_4$, dicobalt octacarbonyl, $Co_2(CO)_8$, cobalt carbonyl anion, $[Co(CO)_4]^-$, and tetracobalt dodecacarbonyl, $Co_4(CO)_{12}$, have been studied (13). The spectra of cobalt carbonyl anion indicates that the structure is tetrahedral. From the spectra of dicobalt octacarbonyl the structure proposed is a trans configuration of two trigonal bipyramids joined at the edge such that apical and equatorial carbonyls are shared as bridge carbonyls. A structure which contains bridge carbonyls is also indicated for tetracobalt dodecacarbonyl.

The success of infrared in differentiating between $-C\equiv O$ and $>C = O$ frequencies in metal carbonyls led to its application in the analogous problem in cyanide complexes. A study by Sheline (14) has suggested a planar structure involving bridged $C = O$ groups in the complex $[Ni(CN)_6]^{4-}$ ion.

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