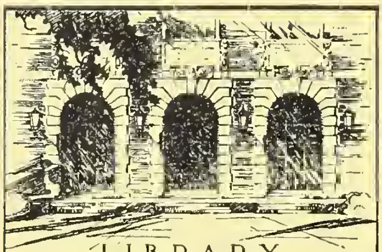

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THE STRUCTURE OF MICAS AND CLAY MINERALS

E. P. Horwitz February 15, 1955

The present concepts concerning the structures of micas and clay minerals are based on the generalizations of Pauling (1).

Two structural units are involved in the lattices of these minerals. One consists of two sheets of closely packed oxygens or hydroxyls in which Al^{+3} or Mg^{+2} are embedded in octahedral coordination, so that they are equidistant from six oxygens or hydroxyls. The formula for the unit cell is $Al_4(OH)_{12}$ in the case of the aluminum ion and $Mg_6(OH)_{12}$ in the case of the magnesium ion. The second unit is built of silica tetrahedra arranged to form a hexagonal network, which is repeated indefinitely to form a sheet of unit cell composition $Si_4O_6(OH)_4$. The tetrahedra are arranged so that the tips of all of them point in the same direction, and the bases of all tetrahedra are in the same plane.

Grim (2) classifies the clay and mica minerals into the following types: two layer types, three layer types, and regular mixed layer type.

Two layer types. The mineral kaolinite is representative of the two layer type. The revised and presently accepted structure of kaolinite was worked out by Brindley. (3, pp. 32-75). The structure consists of a single silica tetrahedral sheet and a single alumina octahedral sheet combined in a unit so that the tips of the silica tetrahedra and one of the layers of the octahedral sheet form a common layer. In the layer common to the octahedral and tetrahedral groups, two-thirds of the atoms are shared by the silicon and aluminum atoms; then they become oxygen atoms instead of hydroxyls. These sheet units are continuous in the a and b directions and stacked one above the other in the c directions. Figure 1 gives the charge distribution in the layers.

Three layer types. The generally accepted structure for the montmorillonite minerals follows the original suggestions made by Hofmann, Endell, and Wilm (4). According to their concept, montmorillonite is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet; the tips of the tetrahedra of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The lattice of montmorillonite is always unbalanced by substitutions of Mg^{+2} for Al^{+3} and Al^{+3} for Si^{+4}. The substitution of Mg^{+2} for Al^{+3} can be one for one, or three Mg^{+2} for two Al^{+3}, with all possible octahedral positions being filled in the latter case. Layer minerals of the three layer type in which all the possible octahedral positions are filled are called trioctahedral, and those in which only two-thirds of the possible positions are filled are called dioctahedral. The netcharge deficiency is balanced by exchangeable cations adsorbed between the unit layers and around the edges. Figure 2 gives the charge distribution of montmorillonite.

The basic structure of mica was worked out by Pauling (1). The structure of mica is the same as that of montmorillonite except that approximately one-fourth of the silicon atoms are replaced by aluminum atoms and the resultant charge deficiency is balanced by potassium ions. Muscovite mica is dioctahedral, whereas biotite mica is trioctahedral with the octahedral positions populated by Mg^{+2} or Fe^{+2}. The illite clay minerals differ from the micas in that only one-sixth of the silicon atoms are replaced by aluminum atoms. The charge distributions of these minerals are given in figure 3.

Regular mixed layer type.. Chlorite is the only member of this group. Its structure was first suggested by Pauling (5) and additional information on its symmetry and dimensions have been worked out by McMurchy (6) and Brindley (3, pp. 172-198). The structure consists of alternate mica-like and brucite-like layers. The mica-like layers are trioctahedral and the brucite-like layers have Al^{+3} substituting for Mg^{+2}. Figure 4 shows the charge distribution in chlorite.

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Figure 1 (kaolinite)

$6O^{-2}$	12 −
$4Si^{+4}$	16 ∓
$4O^{-2} + 2OH^{-}$	10 −
$4Al^{+3}$	12 ∓
$6OH^{-}$	6 −

Figure 2 (montmorillonite)

$6O^{-2}$	12 −
$4Si^{+4}$	16 ∓
$4O^{-2} + 2OH^{-}$	10 −
$4Al^{+3}$	12 ∓
$4O^{-2} + 2OH^{-}$	10 −
$4Si^{+4}$	16 ∓
$6O^{-2}$	12 −

Figure 3 (micas)

K^{+1}	1 +
$6O^{-2}$	12 −
$3Si^{+4}, 1Al^{+3}$	15 +
$4O^{-2} + 2OH^{-1}$	10 −
$4Al^{+3}$ (dioctahedral) or 6R (trioctahedral, R = Mg^{+2}, Fe^{+2}	12 ∓
$4O^{-2} + 2OH^{-}$	10 −
$3Si^{+4}, 1Al^{+3}$	15 +
$6O^{-2}$	12 −
K^{+1}	1 +

Figure 4 (chlorite)

$6OH^{-}$	6 −
$(6-2x)Mg^{+2}, 2xAl^{+3}$	$[2(6-2x) + 3(2x)]$ +
$6OH^{-}$	6 −

$6O^{-2}$	12 −
$(4-x)Si^{+4}, xAl^{+3}$	$[4(4-x) + 3x]$ +
$4O^{-2} + 2OH^{-}$	10 −
6R (trioctahedral, R=Mg^{+2}, Mn^{+2}, Fe^{+2})	12 +
$4O^{-2} + 2OH^{-}$	10 −
$(4-x)Si^{+4}, x Al^{+3}$	$[4(4-x) + 3x]$ +
$6O^{-2}$	12 −

ISOMORPHISM AND CHEMICAL HOMOLOGY

W. C. Drinkard February 22, 1955

The term isomorphism is used to indicate the occurrence of different chemical compounds in the same crystalline form. Mitscherlich was the first to recognize the relation between structure and chemical properties. He stated that substances which are similar in crystalline form, i.e. isomorphous, and in chemical properties can usually be represented by similar formulas.

Isomorphism usually demands that the number of atoms be the same in compounds which are isomorphous. For complex ions or molecules a similar arrangement in space is also required. In addition to these steric factors, atomic or ionic size is also of great importance. For isomorphism to occur radii of interchangeable constituents should not differ by more than 10%. When substitution is attempted outside this permissible range a discontinuous alteration of crystalline structure occurs. Such a phenomenon is known as morphotropism. (2)

The property of polarizability is also an important factor in determining isomorphism. Increase in polarizability leads to decrease in crystallographic coordination number, to differences in distances between particles and thereby to a lower degree of symmetry in the crystalline arrangement. (1)

The ability of compounds to form mixed crystals is the best indication of their isomorphism. However, the more complex method of X-ray diffraction analysis has also been used.

Because of the great similarity of isomorphous substances in size and polarizability it is to be expected that they would also resemble each other in thermodynamic and chemical properties. Such properties as molecular volume, coefficient of expansion and compressibility are found to be similar for isomorphous substances.

The similarity of $SO_4^=$ and $BeF_4^=$ has been shown by Sarkar and his coworkers, (3,4,5). Other ions have been added to the isomorphous $XO_4^=$ series, and a group of isomorphous monovalent ions has been reported.

ISOMORPHOUS IONIC SPECIES

$SO_4^=$
$BeF_4^=$
$PO_3F^=$
$BeF_3OH^=$
$PO_3OH^=$
$AsO_3OH^=$

ClO_4^-
MnO_4^-
BF_4^-
$PO_2F_2^-$
SO_2OH^-
CrO_3OH^-

A summary of the ionic radii and electronegativities of the various ions is presented for comparison.

ION	RADIUS A	ELECTRO-NEGATIVITY	ION	RADIUS A	ELECTRO-NEGATIVITY
Be^{+2}	0.34	1.5	Cr^{+6}	0.3-4	2.1
S^{+6}	0.34	2.5	B^{+3}	0.20	2.0
P^{+5}	0.35	2.1	O^{-2}	1.32	3.5
As^{+5}	0.47	2.0	F^{-1}	1.33	4.0
Cl^{+7}	0.26	3.0	OH^{-1}	1.4-1.5	
Mn^{+7}	0.46	2.3			

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SOME METAL FERRATES (VI)

T. Muniyappan March 1, 1955

1. Introduction: Apart from certain abnormal valencies of the iron in the carbonyl and more especially in the nitrosyl compounds (where valencies have a slightly different meaning from what they have elsewhere), the only valency of iron other than 2 or 3 which we find in isolable compounds of iron is 6 and that in the ferrates. (18) (19).

The stabilities of $[XO_4]^{-2}$ ion decrease with the increase in atomic number in Cr - Mn - Fe series. However solubilities of manganates (VI), chromates and ferrates are comparable. Ferrates range from violet-red to dark red, (compare with permanganate color) and are insoluble in alcohol. The solubility of ferrates closely parallels that of sulphates and chromates as evidenced by the decrease in solubility of the ferrates in Ca - Sr - Ba series. Degree of hydration of some ferrates are: Ca, Sr, Ba - 2; Cu^{+2} - 1; Ag, Pb, Zn, Co, Ni - 0. (18) (7). Ferrates of Zn, Mg, Ca and alkali metals are soluble in water and those of other alkaline earth metals insoluble.

While the parent ferric acid H_2FeO_4 and its anhydride FeO_3 are not known either in the free state or in solution, several metal ferrate salts are fairly well characterized (2) (7) (8) (9) (18). The tendency for anionic aggregation in increasingly high acidic media apparently decreases in the series Cr - Mn - Fe.

The Structure of the Ferrate Ion must resemble that of sulphate, the four oxygen atoms being tetrahedrally coordinated to the iron which is hexa valent like the sulphur in the sulphate ion. Obviously this identity of the structure of the ferrate ion is responsible for the isomorphism of K_2FeO_4 with K_2XO_4 where x = S, Se, Cr, Mo but not Te. Perhaps with Te the size factor intervenes. (18). The effective magnetic moment of 3.96 + 0.02 Bohr magnetrons, as compared with the theoretical value of 2.83 indicates the presence of two unpaired 3d electrons in the FeO_4^{-2} ion. (11)

The recent interest in the metal ferrates stems from the suggested use of potassium ferrate as an analytical oxidizing agent particularly in acidic solutions. Though presently the preparation of K_2FeO_4 of 100 per cent purity and stability is not known, the possibility of such a preparation coupled with the cheapness and high oxidizing potential of the compound is promising. The aqueous solution of a ferrate is a stronger oxidizing agent than $KMnO_4$ and it will oxidize NH_3 to N_2 in the cold. If the solution is acidified, oxygen is at once evolved and iron passes from (VI) to (III) state. (18)

$$4\ FeO_4^{-2} + 20H^+ \rightleftharpoons 4\ Fe^{+3} + 3\ O_2 + 10\ H_2O$$

In alkaline solutions K_2FeO_4 is more stable. Even in this medium it acts as a powerful oxidizing agent. A comparison of the oxidation potentials of K_2FeO_4, $KMnO_4$, $K_2Cr_2O_7$ is revealing:

Medium:	Couple	Equation	E° 298 volts
Acidic:	FeIII - FeVI	$Fe^{+3} + 4H_2O \rightleftharpoons FeO_4^{-2} + 8H^+ + 3e^-$	≤ 1.9
Alkaline:	FeIII - FeVI	$Fe(OH)_3 + 5OH^- \rightleftharpoons FeO_4^- + 4H_2O + 3e^-$	≤ 0.9
Acidic:	MnII - MnVII	$Mn^{+2} + 4H_2O \rightleftharpoons MnO_4^- + 8H^+ + 5e^-$	$- 1.52$
Alkaline:	MnIV - MnVII	$MnO_2 + 4OH^- \rightleftharpoons MnO_4^- + 2H_2O + 3e^-$	$= 0.57$
Acidic:	CrIII -CrVI	$2Cr^{+3} + 7H_2O \rightleftharpoons Cr_2O_7^{-2} + 14H^+ + 6e^-$	$- 1.36$
Alkaline:	CrIII -CrVI	$Cr(OH)_3 + 5OH^- \rightleftharpoons CrO_4^{-2} + 4H_2O + 3e^-$	$+ 0.12$

2. Preparation of Potassium Ferrate:

a. When iron filings are fused with potassium nitrate and the melt is extracted with water, a reddish violet solution containing K_2FeO_4 is formed (7) (13) (18).

b. When solid potassium hydroxide is added to $FeCl_3$ solution containing bromine, the resulting red colored solution is said to contain K_2FeO_4 (16).

c. Electrolytic oxidation of iron in KOH solution results in the formation of K_2FeO_4 (14). Also electrolytic oxidation of a freshly precipitated suspension of ferric hydroxide in a concentrated alkaline solution has been found to give potassium ferrate (18).

d. i. Oxidation of hydrous ferric oxide suspended in 8 M. KOH solution by bubbling chlorine through the solution maintained at 50-55° gives low yields of K_2FeO_4 (10). Later, Scott et al (II) obtained 96.9% pure sample by employing NaOCl as the oxidant.

ii. A convenient procedure for preparation of the potassium salt involves oxidation of iron (III) hydroxide (from ferric nitrate) with sodium hypochlorite in concentrated sodium hydroxide solution at 25-30°, followed by removal of insoluble sodium chloride and ultimate precipitation with KOH. (10) (11) (17).

$$2Fe(OH)_3 + 3ClO^- + 4OH^- \rightarrow 2FeO_4^{-2} + 3Cl^- + 5H_2O$$

The salt is successively washed with C_6H_6, Et.OH and ether and dried in vacuum. Yields of 44 to 76% and purities up to 99% are claimed.

e. The use of ozone as the oxidant to oxidize $Fe(OH)_3$ in alkaline medium to obtain K_2FeO_4 requires further investigation (9).

3. Properties of K_2FeO_4: It is a dark reddish black iridescent powder; the dry substance is stable below 198°, very soluble in water giving blood red solution. (17). When heated at 250°, it forms $KFeO_2$ and liberates oxygen with some ozone (3). Water solutions of the salt decompose to give hydrous iron (III) oxide and oxygen (18).

The stability of aqueous potassium ferrate solution increases with dilution and has maximum stability at pH 8 rather than pH 7 and at 0.5°C. While light has no measurable effect on stability, temperature and alkalinity are major factors affecting the stability of the solutions. (6)

4. Barium Ferrate: A useful procedure for the preparation of the salt involves the addition of pure potassium ferrate (VI) to barium chloride solution in the minimum quantity of water at 0°C. Absence of CO_2, use of the minimum amount of CO_2 free water at 0° and rapid filtration result in a sample of 86.5% purity (12); the chief impurities are $Fe(OH)_3$ and barium carbonate.

It is insoluble in water. It has the same crystal form and degree of solubility as barium chromate. Its suspensions in water may be boiled without decomposition. It is practically unaffected by dil. Sulphuric acid but CO_2, diluted HCl or HNO_3 decomposes it at once (15). The stability of barium salt is explained by its low solubility.

Barium ferrate oxidizes chromite ion in alkaline solution to chromate which is estimated using mohr salt and sodium diphenylamine sulphonate as indicator. This method of analysis of purity of barium ferrate has been employed by Gump and his coworkers (12) (6).

$$Cr(OH)_4^- + FeO_4^{-2} + 3H_2O \rightarrow Fe(OH)_3\cdot(H_2O)_3 + CrO_4^{-2} + OH^-$$

Ferrates of metals like Ca, Sr, Co, Cu^{+2}, Zn, Ni etc. are also known. (2) (7) (8) (9) (18).

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THE HYDRATES OF CHROMIUM (III) CHLORIDE

Bennie A. Ferrone March 8, 1955

Theoretically, chromium (III) chloride 6-hydrate should be capable of existing in six isomeric forms:

I. $[Cr(H_2O)_6]Cl_3$, II. $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, III. $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (cis and trans), and IV. $[Cr(H_2O)_3Cl_3] \cdot 3H_2O$ (cis and trans).

Isomers I and III were first prepared by Recoura (1) in 1887 as grey and dark green complexes, respectively. II, a pale green compound, was reported by Bjerrum (2) in 1907. Recoura (3), in 1932, claimed to have obtained IV (brown in color). The possible cis-trans isomerism for III and IV does not appear to have been investigated.

The ionic chloride content of these complexes was used as the basis for the determination of the structures of I and III by Werner and Gubser (4) and of II by Bjerrum (2). Recoura (3) gave no real proof for the structure of the brown compound. The compound designated as IV was found to be soluble in ether, and this fact was apparently used as evidence for its non-electrolyte nature.

Pamfilov and Gumenyuk (5) have recently re-investigated the chromium (III) chloride hydrates. Attempts to prepare IV yielded a brown, ether soluble product. However, the substance was dismissed as one in which ether had partially replaced water. No evidence was cited for this belief, and the compound was not investigated further. Attempts to prepare II by the method of Bjerrum yielded a dark green compound which resembled III.

Thermograms were obtained for compounds I, II, and III (see Fig. 1). In each case the first break corresponds to the melting point, and the second break to the complete removal of water. Since thermograms II and III were almost identical it was felt that Bjerrum might have been in error in claiming the existence of II. According to these authors (5) X ray powder patterns for II, III, and the anhydrous $CrCl_3$ are the same, whereas that for I is slightly different! (This would seem highly improbable--B.A.F.).

Law (6), in 1936, investigated the chromium (III) chloride hydrates by means of conductometric titrations. Initial titrations were carried out on solutions of I, II, and III that were 0.005M in chromium. The solutions were unbuffered (initial pH = 4.75) and were titrated at a temperature of 1.5°C. Fig. 2 shows the curves obtained. The break in the curve for compound II at 2.1 equivalents is a good indication that Bjerrum did obtain a pentaquo complex. The curve for III appears to be anomolous since a break occurs at 1.54 equivalents. This was

interpreted to be the result of attack, probably hydrolytic, on the coordination sphere. When solutions of III were buffered at pH = 2.3-3.0, end points were obtained that correspond to theory.

Discussion

On the basis of their data, Pamfilov and Gumenyuk conclude that only I and III can be said to exist with certainty. However, prior work offers good proof for the existence of II also. The existence of IV is, as yet, unsettled.

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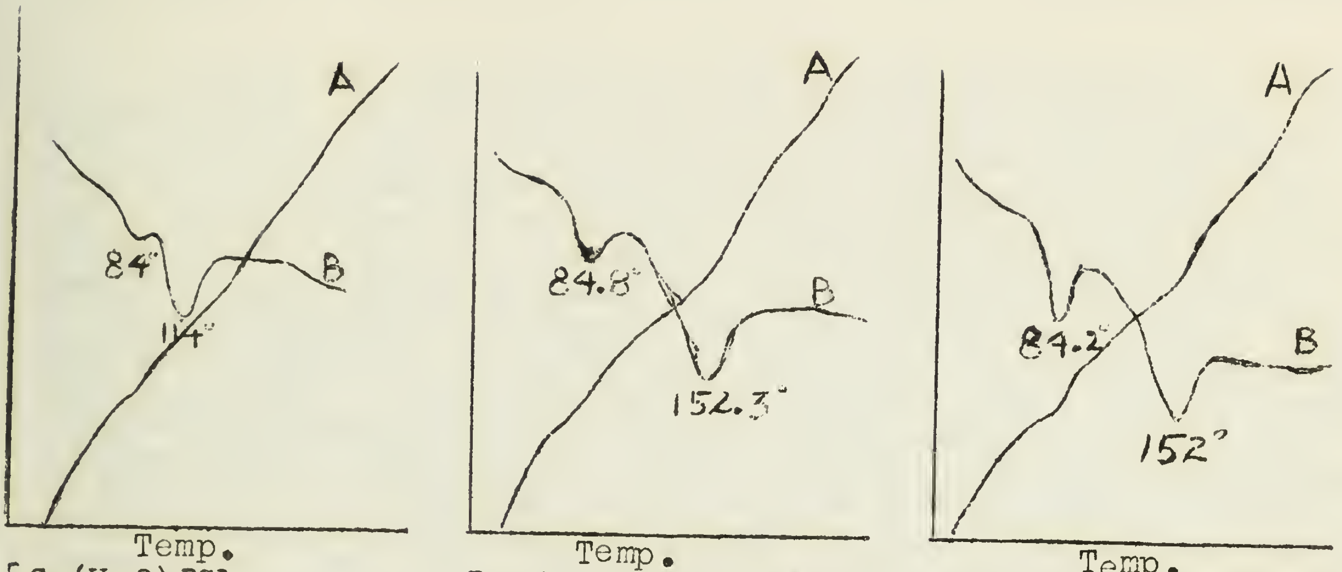
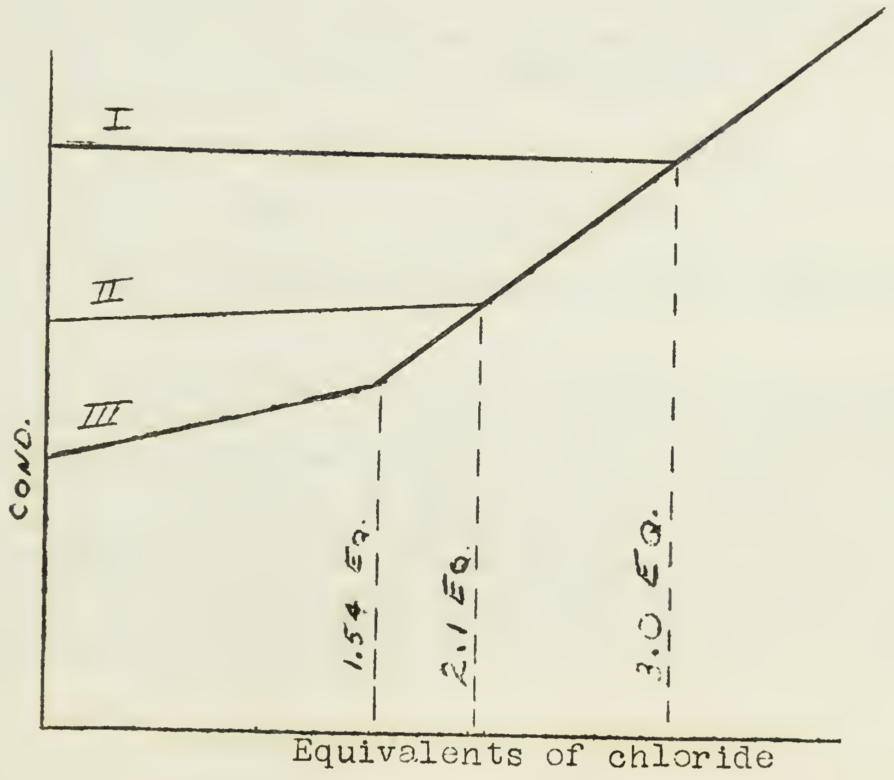
Figure 1



$[Cr(H_2O)_6]Cl_3$ $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

A - Heating curves; B - Differential curves (do not correspond to ordinates used)

Figure 2



ABSORPTION SPECTRA OF METALS IN SOLUTIONS

G.W. Cullen March 15, 1955

A clear cut explanation of the phenomena observed in alkali metal-ammonia solutions is yet to be presented, even though a great deal of work has been done in the field. Investigators have examined and re-examined one another's findings, so that even today there is much disagreement among proponents of the various contemporary theories. As early as 1864 Weyl observed that sodium and potassium dissolve in liquid ammonia; the existence of "metal ammonium" compounds, MNH_3 was postulated. Seely, in 1871, presented evidence to support his conclusion that compound formation does not occur in these solutions. Joannis again took up Weyl's original proposal in 1891, but his vapor pressure and optical studies must be considered invalid. About 1906 Ruff and Geisel (1) in Germany and Kraus (2) in the United States began a series of investigations in this area, employing more modern and exacting techniques. They were able to explain the observations which led the former workers to insist on compound formation, and to prove that true solutions of the metals in ammonia actually exist (3).

Many of the contemporary theories show much merit, but none explain adequately all the observed phenomena. Conductivity, optical and magnetic susceptibility measurements in particular, lead to theories which are not in good agreement.

Kraus' theory (4) has served as a basis for subsequent inquiries. Many of the more recent investigators define their results in terms of agreement or disagreement with his work. Primarily on the basis of conductivity and E.M.F. measurements, Kraus proposed the existence of the equilibria:

$$Na \rightleftharpoons Na^+ + e^- \quad \text{and}$$

$$e^- + nNH_3 \rightleftharpoons (NH_3)_n \cdot e^-$$

the position of the equilibria depending on the concentrations involved.

Optical data, generally obtained in dilute solutions, support the existence of solvated electrons. However, it is difficult to explain conductivity data in dilute solution solely on the existence of such particles. Magnetic susceptibility measurements reveal diamagnetic character at concentrations corresponding to a minimum in conductivity (5). This finding is not at all in agreement with Kraus' equilibria which require that electrons at medium and low concentrations of the alkali metal be bound in some manner to ammonia molecules.

It is possible that the electrons are bound in an orbital of the ammonia molecule, or trapped in a cage formed of ammonia molecules. Blades and Hodgins (6), citing absorption data as evidence, support the latter possibility.

It has been shown previously that there is a single absorption maximum in ammonia solutions whose position is independent of the metal in solution. This maximum which does not appear in the spectra of either pure sodium or ammonia, occurs at 6000 cm^{-1}. A corresponding band is found in sodium-methylamine solutions at about 15,000 cm^{-1}. If the expansion exhibited on dissolving a metal in ammonia is due to the formation of holes in the liquid which represent energy barriers for the escape of the electrons, it was reasoned by Blades and Hodgins that for solvent mixtures absorption bands might appear intermediate between those of the single solvents, or that an intermediate band alone might appear. In investigating this proposal Blades and Hodgins developed the necessary techniques and measured the absorption spectra of solutions of lithium, sodium, potassium and calcium in ammonia and methylamine; lithium and potassium in ethylamine; sodium and potassium in mixed ammonia-methylamine; and sodium in mixed ammonia-ethylamine.

More complex results than predicted complicated the conclusions, but the observed phenomena could be explained by the "hole" theory.

Potassium shows two maxima in methylamine. All other metal solutions exhibit a single maximum which may fall at one of two points — 15,300 cm^{-1} or 7680 cm^{-1} (at -60°C) depending on the metal.

Lithium and potassium solutions in ethylamine show single bands in different positions.

Sodium in a mixed solvent of ammonia-methylamine shows two absorption bands, one of which is difficult to locate because of a large temperature coefficient. The other low frequency band is essentially that observed for pure ammonia. Potassium in the same mixture exhibits but one maximum, identified with the low frequency band of sodium in the mixed solvent.

Sodium dissolved in the ammonia-ethylamine mixture did not appear to yield significant results.

Although these observations are not in agreement with the original hypothesis, they are in accord with a theory presented by Lipscomb (7). Lipscomb proposed that holes, approximately 3A in radius, are present in liquid ammonia solutions. The

hydrogens directed inward form a region of low potential in which the electron may be trapped. The absorption characteristics of this type of structure may be explained by analogy with "F centers" (8). As the ammonia molecules are symmetrical, the transitional level for each hole is identical, and only one absorption maximum is observed in this solvent. But the methylamine molecule may form an ammonia type trap, or the methyl groups may appear in the trap lining. Thus these two possibilities or a mixture of the two lead to a more complex absorption spectrum. Obviously the possibilities for the types of traps present in a medium increase when the solvents are mixed with one another.

Recent investigators have thus presented evidence to show that electrons are bound by traps existing in the structure of the liquid rather than in a molecular orbital about a given molecule. As with the former theories, this proposal is in accordance with some of the over-all observed phenomena, but is in contradiction to others. A conclusive picture of the electron in these solvents is still to be developed.

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CHLORYL FLUORIDE AND ITS DERIVATIVES

Joel Selbin March 22, 1955

Chloryl fluoride, ClO_2F, was first prepared in an all ~~glass~~ quartz apparatus by Schmitz and Schumacher (1) in 1942. Chlorine dioxide (ca. 25 mm) and fluorine (ca. 50 mm) were allowed to react in the presence of nitrogen (total pressure, 1 atm.) at 0°C (Equation 1)

$$(1)\quad 2ClO_2 + F_2 \rightarrow 2ClO_2F$$

The resulting product was described as a colorless gas at ordinary temperatures, condensing to a colorless liquid below -6°C, and solidifying to a white crystalline mass at about -115°C.

Schmeisser and Ehenhöch (2) have studied this same reaction more recently (1954). These investigators first attempted to introduce a solution containing F_2 and ClO_2 into liquid BF_3 at -130 to -110°C, in order to bring about the reaction represented by Equation 2 .

$$(2)\quad 2ClO_2 + F_2 + 2BF_3 \rightarrow 2ClO_2F{\cdot}BF_3$$

It was hoped that ClO_2F could then be obtained subsequently by reaction with a fluoride (Equation 3).

$$(3)\quad ClO_2F{\cdot}BF_3 + NaF \rightarrow NaBF_4 + ClO_2F$$

This preparative method proved unsatisfactory because of the high volatility of $ClO_2F{\cdot}BF_3$. The desired product was obtained by introducing fluorine into a solution of ClO_2 in the inert neutral solvent, trichlorofluoromethane.

Alkali halogenates react with BrF_3 to form tetrafluorobromites (3). Oxygen is liberated quantitatively when bromates and iodates are used; only 1/3 of the oxygen is evolved when chlorates are employed (4). It was suggested that the rest of the oxygen is expelled as either ClO_2 or ClO_2F.

The gaseous product liberated in the $KClO_3$-BrF_3 reaction has now been examined by Woolf (5), who found it too reactive to be handled in a vacuum system since it attacks both greases and mercury. It could be examined in a borosilicate glass apparatus provided that the gas was not kept in contact with the glass too long at room temperatures. The gas was identified chemically after hydrolysis with an excess of alkali, the solution containing practically all of the chlorine in the chlorate form. The total chlorine, determined after reduction with H_2SO_3, was equivalent to that in the $KClO_3$ used to liberate the gas. The Cl:F ratio was very near unity. A molecular weight of 87.8 was found from the

weight ratio of gas to $KClO_3$ (Calcd. for ClO_2F, 86.5). Approximately two equivalents of alkali (2.05 in one experiment) were required for each mole of gas. Thus the formation and hydrolysis of the product are represented by Equations 4 and 5.

$$(4)\quad 12KClO_3 + 20BrF_3 \rightarrow 12KBrF_4 + 4Br_2 + 6O_2 + 12ClO_2F$$

$$(5)\quad ClO_2F + 2NaOH \rightarrow NaClO_3 + NaF + H_2O$$

The liquified gas was pale red at -95°C. The author believes that the impurities were ClO_2 (formed by: $4ClO_2F + SiO_2 \rightarrow SiF_4 + O_2 + 4ClO_2$) which itself forms a red liquid, SiF_4, and possibly some Br_2. The color was intensified after further exposure to glass at room temperatures.

Complete details including a diagram of the apparatus used for the preparation of chloryl fluoride are given by Woolf (5).

The preparation of complex chloryl fluorides has been attempted by methods analogous to those used for the production of nitronium and nitrosonium complexes. The preparation of a red solid, $Cl_2O_5 \cdot 3SO_3$, by Lehmann and Krüger (6) in 1953, provides positive evidence for the existence of the chloryl ion in salts. This compound may be similar in type to $N_2O_5 \cdot 3SO_3$, the structure of which has been recently established (7) as $(NO_2^+)_2(S_3O_{10}^=)$. Therefore, the direct reaction of chloryl fluorides with acceptor fluorides has been attempted and led to the characterization of chloryl complex fluorides. This work has been reported almost simultaneously by two independent groups (2, 5). A summary of chloryl compounds is given in Table I.

In view of the tendency of SbF_5 and BF_3 to form complex anions with fluorides, it seems highly probable that the compounds formed between these fluorides and ClO_2F are chloronium salts: $ClO_2^+\ SbF_6^-$ and $ClO_2^+\ BF_4^-$.

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TABLE I - CHLORYL COMPOUNDS

COMPOUND	STATE	PHYSICAL CONSTANT	METHOD OF PREPARATION	REFERENCE
ClO_2F	Colorless gas	boils at -6°C	$ClO_2 + F_2$ in CCl_3F or $KClO_3 + BrF_3$	2 5
$(ClO_2)_2(S_3O_{10})$	large red needle-like crystals	melts at 75.5°C, becomes amorphous first at 73.5°C	$2KClO_3 + 3SO_3$	6
$ClO_2(BF_4)$	white solid	volatilizes in high vacuum at -78°C	$ClO_2F + BF_3$ in CCl_3F or $ClO_2F_{(l)} + BF_3$ (g)	2 5
ClO_2 (PF_6)	white solid	volatilizes at -35°C	$ClO_2F + PF_5$ in CCl_3F or $ClO_2F_{(l)} + PF_{5(g)}$	2 5
$ClO_2(AsF_6)$	white solid	volatilizes at +50°C	$ClO_2F + AsF_5$ in CCl_3F	2
$ClO_2(SbF_6)$	white solid	melts at +78°C	excess $ClO_2F + SbF_5$	2, 5
$ClO_2(SO_3F)$	red liquid		$ClO_2F + SO_3$	2, 5
$(ClO_2)_2(SiF_6)$			$ClO_2F + SiF_4$	2

PARACYANOGEN

A. T. Tweedie March 29, 1955

Paracyanogen, which probably is a polymerized form of cyanogen, was first described by Guy - Lussac in 1816. Methods of preparation have been summarized by Bircumshaw, Taylor, and Whiffen (1) and include the following procedures:

a) heating of silver or mercuric cyanides, cyanogen, or other cyanide compounds.

b) polymerization of cyanogen by U. V. and by α particles.

c) electrolysis of potassium cyanide solutions and

d) treatment of cyanogen in an electrical discharge tube.[2]

All investigators have found great difficulty in analyzing the resulting products.

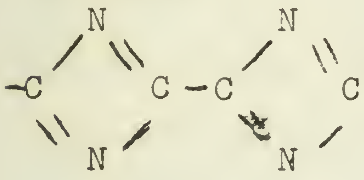
Paracyanogen has been used as a catalyst in the production of ammonia[3,4].

Bircumshaw, et. al found that paracyanogen is obtained in 30 - 40% yields when solid oxamide is heated in a sealed glass tube at 250 - 300°. The product was obtained as a dark brown porous solid. Normal micro-analytical procedures were found to be unsatisfactory. The analytical method finally used involved the treatment of the product in a sealed tube at 400° for 6 hours with potassium sulfate, copper sulfate, and sulfuric acid and then a Kjeldahl type determination of the nitrogen.

Paracyanogen is insoluble in water and most organic liquids and is highly resistant to chemical attack. It is soluble in fused potassium hydroxide to give a brown solution which gradually becomes orange-red and then colorless. The solution contains cyanide, cyanate, and carbonate. Ammonia is liberated. Paracyanogen is soluble in concentrated sulfuric acid from which it is precipitated by water. It is also soluble in syrupy phosphoric, 60% perchloric, and concentrated nitric acids. All these solutions, unlike the solid, exhibit a blue flourescence in ultra-violet light.

Infra red absorption spectra show that paracyanogen has only one broad band at 1570 cm^{-1}. This probably indicates a completely conjugated double bond system in which all the C - N bonds are equivalent. No ultra-violet absorption data are available as yet.

Oxamide has a planar structure with weak interplanar bonding, but strong intermolecular bonding within the plane[5]. Paracyanogen may have a similar planar structure, since in a solid phase reaction those changes which involve the least amount of disturbance of the lattice would be expected to occur most easily. Proceeding on this basis Bircumshaw et.al present three possible structures for paracyanogen.



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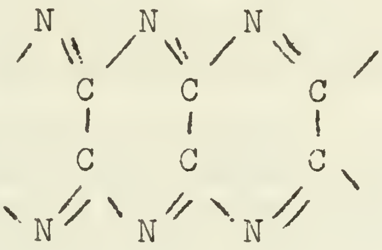

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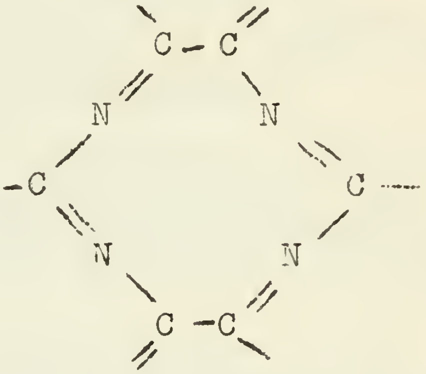

III

Models of each of these show that only structure II can be set up without excessive strain

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OXIDATION OF HYDROGEN ADSORBED ON PALLADIUM

A. R. Pitochelli April 5, 1955

Lewis and Ubbelohde (1) have suggested that oxidation of metals by atmospheric oxygen in the presence of moisture could involve initially the oxidation of hydrogen atoms adsorbed on the metal. The hydrogen atoms are formed by discharge of hydrogen ions from solution. It was proposed that the mechanism of removal of hydrogen from Pd-H may be related to a number of key processes in the physical chemistry of corrosion.

Conflicting statements appear in the literature concerning the stability of Pd-H when exposed to gaseous oxygen (2) (3). From their experiments, Lewis and Ubbelohde concluded that water must always be present before reaction with atmospheric oxygen can proceed at an appreciable rate.

The effects of three different oxidizing systems on the Pd-H alloy were investigated (1). The solutions used were iodine in potassium iodide, potassium permanganate, and ceric ammonium sulfate (all 0.1 or 0.01 M).

The reaction of Pd-H with atmospheric oxygen was also investigated. It was shown by pressure-time measurements in a closed system that the adsorbed hydrogen combines with the oxygen after a variable, but short induction period. It was observed that a definite lengthening of the induction period resulted when the samples were carefully dried. When P_2O_5 was introduced into the reaction vessel very great lengthening of the induction period to an indefinite period was observed in almost all cases.

A number of mechanisms for the removal of H from Pd have been proposed (1). The action of ceric ion was likened to the mechanism for the anodic oxidation described previously by Moore (4), and Nähring (5).

$$\mathrm{Ce^{++++}} + \underset{\mathrm{Pd}}{\overset{\mathrm{H}}{\wedge}} \rightarrow \mathrm{Ce^{+++}} + \mathrm{H^{+}} + \overset{\wedge}{\mathrm{Pd}}$$

Three mechanisms involving attack by oxygen are postulated.

1. Free Radical Formation.

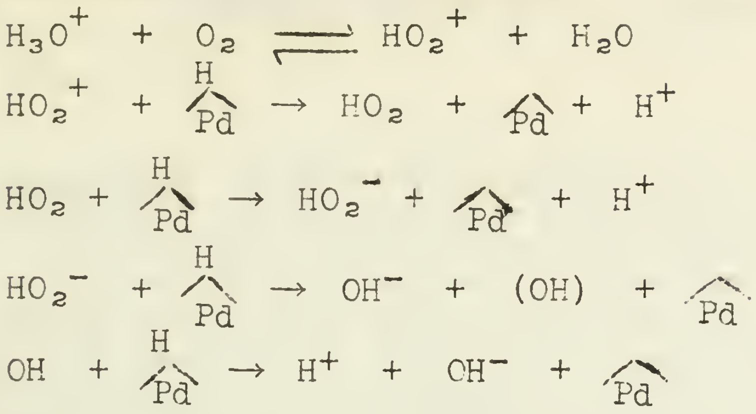
$$\underset{\mathrm{Pd}}{\overset{\mathrm{H}}{\wedge}}{}^{*} + \mathrm{O_2} \rightleftharpoons \mathrm{Pd} + \mathrm{HO_2}$$

$$\mathrm{HO_2} + \mathrm{H_2O} \longrightarrow \mathrm{H_2O_2} + \mathrm{OH}$$

$$\underset{\mathrm{Pd}}{\overset{\mathrm{H}}{\wedge}} + \mathrm{OH} \rightarrow \mathrm{Pd} + \mathrm{H_2O}$$

* The symbol $\underset{\mathrm{Pd}}{\overset{\mathrm{H}}{\wedge}}$ represents a hydrogen atom adsorbed on the surface of the palladium metal.

2. Reaction in Acidic Solution.



$$H_3O^+ + O_2 \rightleftharpoons HO_2^+ + H_2O$$

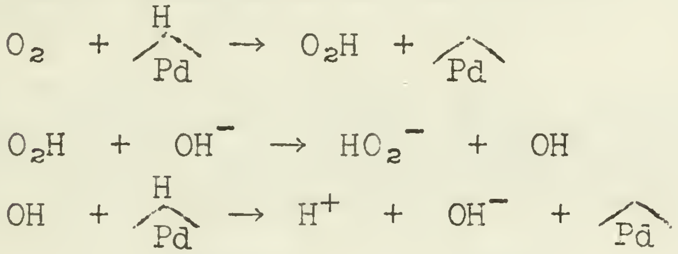
$$HO_2^+ + \overset{H}{\widehat{\mathrm{Pd}}} \rightarrow HO_2 + \widehat{\mathrm{Pd}} + H^+$$

$$HO_2 + \overset{H}{\widehat{\mathrm{Pd}}} \rightarrow HO_2^- + \widehat{\mathrm{Pd}} + H^+$$

$$HO_2^- + \overset{H}{\widehat{\mathrm{Pd}}} \rightarrow OH^- + (OH) + \widehat{\mathrm{Pd}}$$

$$OH + \overset{H}{\widehat{\mathrm{Pd}}} \rightarrow H^+ + OH^- + \widehat{\mathrm{Pd}}$$

3. Behavior in Alkaline Solution.



$$O_2 + \overset{H}{\widehat{\mathrm{Pd}}} \rightarrow O_2H + \widehat{\mathrm{Pd}}$$

$$O_2H + OH^- \rightarrow HO_2^- + OH$$

$$OH + \overset{H}{\widehat{\mathrm{Pd}}} \rightarrow H^+ + OH^- + \widehat{\mathrm{Pd}}$$

The reaction of atmospheric oxygen with hydrogen adsorbed on palladium has been interpreted on the basis of these tentative equations.

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ARSENIC TRICHLORIDE AS A SOLVENT

Chui Fan Liu April 19, 1955

Introduction: Arsenic trichloride as a non-aqueous ionizing solvent was first investigated by Walden (1) some fifty years ago. Recently, after Woolf and Greenwood (2) investigated liquid arsenic trifluoride as an ionizing solvent, interest in arsenic trichloride as a solvent was revived and investigation was undertaken anew. V. Gutmann (3) discovered that arsenic trichloride had a number of desirable properties including a convenient liquid range and a reasonably high dielectric constant. The feasibility of arsenic trichloride as a solvent was further demonstrated by the fact that a large number inorganic salts dissolve easily to form solutions which conduct the electric current.

Pure arsenic trichloride has a specific conductance at 0°C of 1.4 - 1.6 x 10^{-7} ohm^{-1} cm^{-1}. This is of the same order of magnitude as that of water. This small conductance was explained by Walden as due to the self-dissociation of arsenic trichloride.

$$2AsCl_3 \qquad AsCl_2^+ + AsCl_4^-$$

This proposed self-ionization mechanism was subsequently verified by Gutmann experimentally. Accordingly, any substance which can accept chloride ions is capable of behaving as an acid in arsenic trichloride whereas substances which can donate chloride ions are bases (4).

Bases in Arsenic Trichloride: $(CH_3)_4NCl$ is very soluble in arsenic trichloride. A 0.1 M solution of this compound in arsenic trichloride raises the specific conductance of the solvent by four powers of 10. The specific conductance increases with the increase of concentration of $(CH_3)_4NCl$. Fig. 1 shows the relation between the specific conductance and concentration.

By evaporating the excess solvent a white solid is obtained which has the composition $(CH_3)_4NAsCl_4$. This compound is stable in high vacuum at 150°C. and is soluble in water without visible decomposition. Potassium chloride reacts the same way; the other alkali chlorides are also bases in arsenic trichloride.

Acids in Arsenic Trichloride: Chlorides which are capable of forming chloro-complexes are acids in arsenic trichloride. For example, $TeCl_4$ dissolves easily in arsenic trichloride to form a conducting solution (5). A plot of specific conductance against concentration of $TeCl_4$ is reproduced in Fig. 2. However, when the excess solvent is evaporated pure $TeCl_4$ is recovered instead of the expected $(AsCl_2)_2TeCl_6$. In case of $SbCl_5$ a compound of the composition $AsCl_2SbCl_6$ can be isolated. Other compounds which act as acids in arsenic trichloride are $TiCl_4$, $SnCl_4$, and VCl_4.

Metathetical Reactions in Arsenic Trichloride: Typical neutralization reactions like the following may be carried out in arsenic trichloride.

$$(CH_3)_4NAsCl_4 + (AsCl_2)_2TeCl_6 \rightleftharpoons [(CH_3)_4N][AsCl_2][TeCl_6] + 2AsCl_3$$

$$(CH_3)_4NAsCl_4 + [(CH_3)_4N][AsCl_2][TeCl_6] \rightleftharpoons [(CH_3)_4N]_2[TeCl_6] + 2AsCl_3$$

The course of the reaction can be followed conductimetrically. A plot of conductance against the molar ratio of $(CH_3)_4NCl$ to $TeCl_4$ shows two distinct breaks at the ratios 1:1 and 2:1 (Fig.3). Further proof of the correctness of the above proposed reactions is advanced by the isolation of the intermediate and the final products $[(CH_3)_4N][AsCl_2][TeCl_6]$ and $[(CH_3)_4N][TeCl_6]$.

Similar reactions occur with $SnCl_4$, $TiCl_4$, $SbCl_5$, and VCl_4.

By carrying out the reactions in arsenic trichloride inorganic derivatives of arsenic pentachloride of the type $AsCl_5 \cdot SbCl_5$ may be prepared. The latter compound is believed by Gutmann (6) to have the structure $(AsCl_4)(SbCl_6)$. This, then, involves a neutralization reaction between the base $AsCl_5$ and the acid $SbCl_5$. A similar compound can be obtained from PCl_5 and $AsCl_5$.

Existence of Crystalline Solvates (7): By careful manipulation a compound of the composition $(CH_3)_4AsCl_4 \cdot 2AsCl_3$ is obtained. This compound loses two molecules of arsenic trichloride when heated in vacuum to 100°C. The third molecule of $AsCl_3$, however, is held very tightly.

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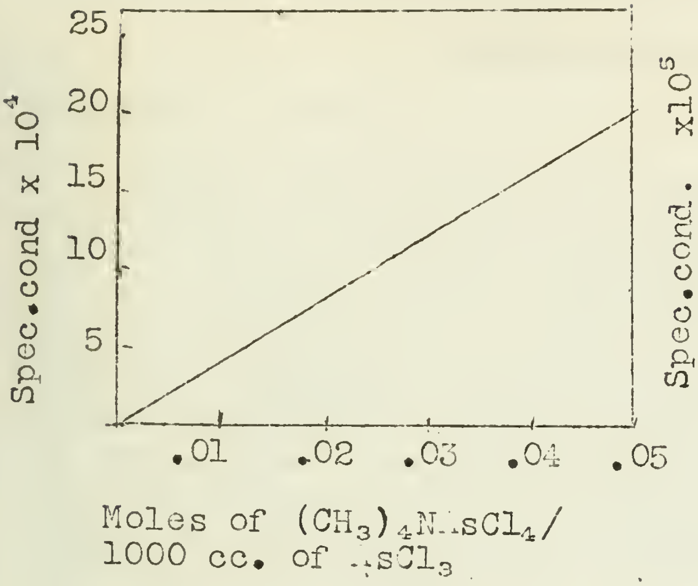

Fig. 1: Spec.cond.of soln. of $(CH_3)_4NAsCl_4$ in $AsCl_3$ at 20°C.

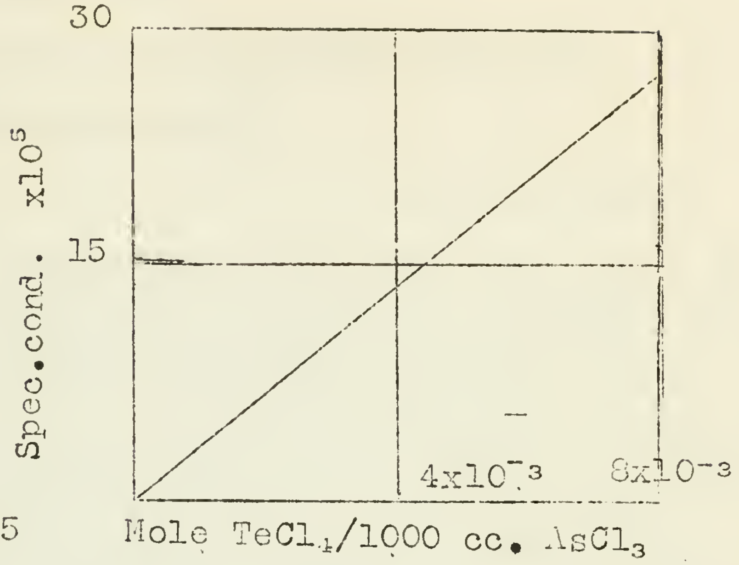

Fig. 2: Spec.cond. of soln. of $TeCl_4$ in $AsCl_3$ at 24°C.

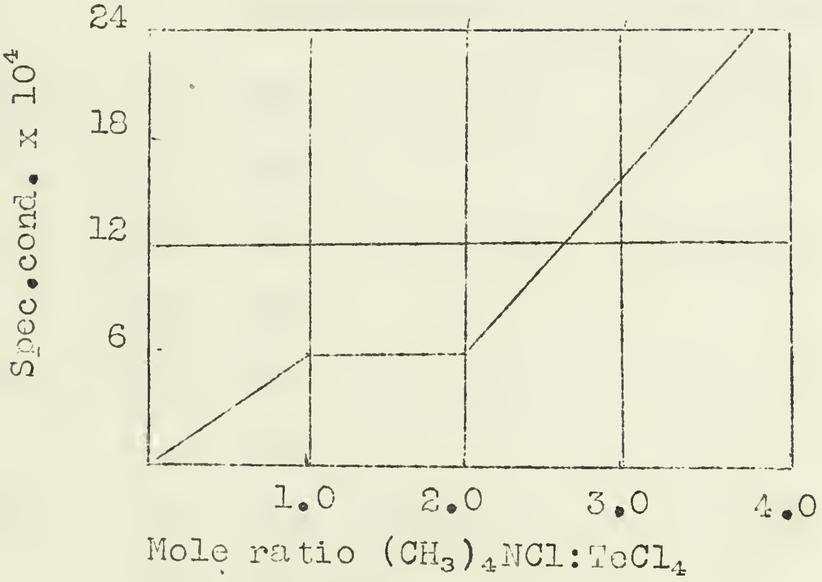

Fig. 3: Conductivetric titration of a soln. of $TeCl_4$ in $AsCl_3$ with $(CH_3)_4NCl$ at 20°C.

THESIS REPORT

DIFFERENTIAL THERMAL ANALYSIS OF SOME HETEROPOLY ACIDS OF MOLYBDENUM AND TUNGSTEN

Sherwood F. West — March 29, 1955

Before the structure of the hydrated, 12-heteropoly acids of molybdenum and tungsten was definitely established[1], Scroggie and Clark[2] found that 12-silicotungstic acid, air dried, dried at 100°, and dried at 220° gave powder diffraction patterns having the same d-spacings. When dried at 100°, the acid contained 8 H_2O, six molecules of which can be removed by dehydration without breaking down the polyacid, giving a product, $H_4SiW_{12}O_{40}$ which is regarded as the anhydrous acid. Since there is very little other data in the literature relating to the dehydration of the polyacids, the thermal behavior of some 12-heteropoly molybdic and tungstic acids has been studied by the method of differential thermal analysis (D.T.A.) in order to define such structural changes with more certainty.

Experimental: Ten gram samples were heated at the rate of 8-10° per minute employing a D.T.A. apparatus previously described[3]. The heating curves revealed the peaks shown in Table 1. The phosphomolybdic acid was prepared according to Linz[4], while the other acids were prepared as directed by North[5].

THERMAL BEHAVIOR OF SOME HETEROPOLY ACIDS

		Drying temperature	Endothermic*	Exothermic*
Phosphotungstic	(a)	25°, vac-H_2SO_4	175-296°	580-595°
	(b)	300°		573-592°
Silicotungstic	(a)	25°, vac-H_2SO_4	140-278°	470-500°
	(b)	300°		487-508°
Phosphomolybdic	(a)	25°, vac-H_2SO_4	63-159°	390-408°
	(b)	200°		397-412°
Silicomolybdic	(a)	25°, vac-H_2SO_4	64-130°	336-355°
	(b)	200°		340-362°

* The recorded temperatures are considered accurate to ± 5°.

As the thermograms revealed a single broad, low temperature endotherm in each of the hydrated samples, repeat runs were made on dehydrated specimens in order to better establish the decomposition temperatures. It is to be noted that the hetero-tungstic acids are more stable thermally than the hetero-molybdic acid. In each case, compounds containing a central phosphorus atom are more stable than those containing silicon.

In the case of the hetero-tungstic acids, the structure of the free acid was maintained up to the exothermic decomposition point, as was shown by x-ray powder diffraction patterns of specimens heated to constant weight at successive, intermediate temperatures. The same samples heated above the decomposition temperature yielded powder patterns characteristic of tungstic oxide, WO_3. The hetero-tungstic acids showed little visible evidence of reduction on heating, as the white color persisted in the undecomposed samples. The hetero-molybdic acids, on the other hand, were far less stable than the corresponding tungstic acids and changed color on progressive heating from yellow, to green, to pale blue, indicating extensive reduction. When heated above the decomposition point, the hetero-molybdic acids yielded identical powder diffraction patterns, characteristic of molybdenum trioxide. Specimens heated below this point yielded diffraction patterns characterized by high background indicating the presence of an amorphous phase, although there is a definite structure in this range. Nickel filtered copper K α radiation and a powder camera of 7 cm. radius were used throughout this work.

Interpretation of Data: An examination of the heating curves reveals the same pattern type in all four examples. The gradual, low temperature endotherm may be ascribed to the removal of water from the lattice. Such water may be described as zeolitic in nature, since its removal does not alter the crystal lattice. The vigorous, high temperature exotherm recorded in each case is readily explained on the basis of x-ray evidence. The decomposition point apparently marks the destruction of the immense cage-like structure of the heteropoly compound giving a more compact crystalline product.

The technique of differential thermal analysis has recently been used to good advantage in the investigation of the thermal behavior of certain catalyst powders[6] giving some insight into the complex mechanism of heterogeneous catalysis. The heteropoly acids have been evaluated in the past as catalysts for various reactions at elevated temperatures since the oxides of molybdenum, tungsten, and vanadium are active catalysts and the cage-like structure of the heteropoly compounds proposed by Keggin should offer a large internal surface. However, these materials are usually ignited at several hundred degrees prior to use, thereby precluding in many instances, according to our data, the existence of the heteropoly acids as such. Past work has served to emphasize the desirability of a large surface area in a highly active catalyst. This condition may best be approached in the heteropoly acids by recognizing their structural dependance on heat treatment.

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NUCLEAR MAGNETIC RESONANCE AND CHEMICAL APPLICATIONS

C.E. Wymore April 26, 1955

Theoretical: Many atomic nuclei, including the neutron, spin like a top and have a magnetic moment. Each nucleus with a spin has a spin quantum number, I, which can have any value which is a multiple of one-half. A nucleus that has a spin other than zero also has a magnetic moment, $\mu = gI \mu_m$, where μ_m is the nuclear magneton, a unit of magnetic strength and g is the gyromagnetic ratio. ^{1}H, ^{7}Li, ^{11}B, ^{19}F, and ^{31}P have strong magnetic moments.

A nucleus with spin I has 2I + 1 possible nuclear energy states or Zeeman levels. Thus the proton with spin one-half has two energy levels. The energy difference when in a magnetic field is given by $\Delta E = 2\mu_p H_o$ in which μ_p is the magnetic moment of the proton, and H_o is the strength of magnetic field in gauss. By equating this with the Bohr relation $\Delta E = hv$, one obtains $H_o = 1/2\ hv/\mu_p$, or in general terms $H_o = Ihv/\mu$. This is the fundamental equation for nuclear magnetic resonance (NMR). It is equivalent to saying that v is the frequency with which the nuclear magnet precesses in the magnetic field H_o.

Detection: In one method the sample is put into a large steady field H_o represented by the permanent magnet in figure 1. At right angles to this an oscillating magnetic field is set up by the transmitter coil. When this field oscillates at the same frequency as the nucleus precesses in the steady field, nuclear magnetic resonance occurs. This causes a change in the magnetic flux of the sample which induces a voltage in the receiver coil and shows up as a peak on a cathode ray tube. In practice the radio transmitter is kept constant and the main field slowly increased with a pair of sweep coils not shown. Figure 2 (1) shows a curve for protons in water. In a field of 10,000 gauss the proton resonance occurs at 41 megacycles per second. Details are given in several excellent reviews (1, 2, 3, 4, 5).

Relaxation: In order for NMR to occur the nuclear energy levels must be unequally populated. This relaxing to lower levels is brought about by interaction of the nuclear magnets with surrounding fields. Spin-lattice relaxation involves interaction of the precessing nucleus with oscillatory magnetic fields produced by other nuclei with magnetic moments through molecular or Brownian movement. Thus magnetic energy is converted into thermal energy. The spin-spin mechanism is direct interaction of two different nuclei with magnetic moments, no energy being lost from the spin system. The second moment is a measure of line broadening which is related to relaxation time. In general liquids have sharp narrow lines and solids broad diffuse lines.

Line shape: With certain rigid lattices (usually acquired by low temperature) in which the magnetic nuclei are isolated, line shape is important. The following systems refer to nuclei with spin one-half.

The two-spin system, as the protons in molecules like H_2O, has a double maximum such as that shown for powdered $CaSO_4 \cdot 2H_2O$ in Figure 5 (1). The three-spin group has a triple-peaked curve shown in Figure 3 (6). The CH_3 group in simple organic molecules, NH_3 and H_3O^+ are common three-spin groups. The four-spin group gives a broad flat topped curve as shown in Figure 4 for NH_4Cl (7).

The shapes along with second moments have been used to show that the following formulas are correct:

$H_3O^+NO_3^-$, $H_3O^+ClO_4^-$, $H_3O^+HSO_4^-$ (8); $H_2C_2O_4 \cdot 2H_2O$ (8, 9);

$(H_3O^+)_2PtCl_6^=$, $H_3O^+HSeO_4^-$, $(H_3O^+)_2SO_4^=$, $K^+(H_4B_5O_{10}^-) \cdot 2H_2O$ (10);

$N_2H_6^{++}\ SO_4^=$ (11); and $^+NH_3CH_2COO^-$ (12).

In combination with crystal structure second moments can give accurate interproton distances.

Chemical Shifts: The value of the field in the bulk of the sample is not the same as it is at the nucleus due to interactions with the electrons. The amount of shielding varies, and thus the value of the magnetic field at the nucleus and the resonance frequency. The amount of shift depends upon the field strength. Chemical shifts are small so a high field strength and liquid samples are usually used. In the curve (Figure 6) for the protons in ethyl alcohol the peaks are due to the hydrogens on the OH, CH_2, and CH_3 groups which have slightly different shielding. The areas are in the ratio of the number of hydrogen atoms (3).

Further resolution of ethyl alcohol gives fine multiplet structure due to electron coupled spin-spin interaction. Multiplet structure has been used to show the structure of phosphorus and hypophosphorus acid (13). H_3PO_3 has a doublet and H_3PO_2 a triplet showing that one and two hydrogens respectively are attached to the phosphorus.

NMR has been used to measure keto-enol tautomerism (15) and to show that BrF_5 and IF_5 have a tetragonal pyramidal structure because they have one fluorine that is different from the other four (16). Chemical shifts can also be used for structure determination because different groups, particularly in the fluorocarbons, have different shifts (14).

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Figure 1

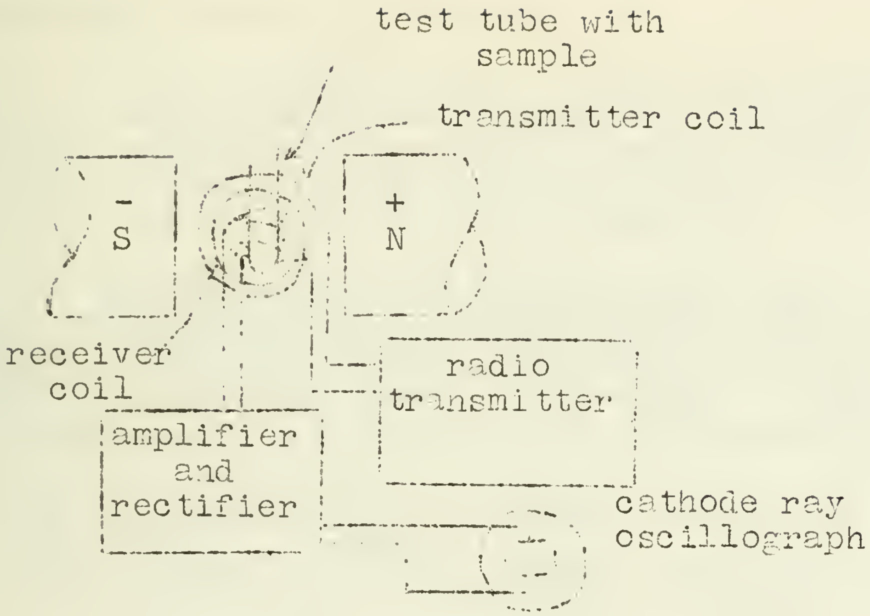
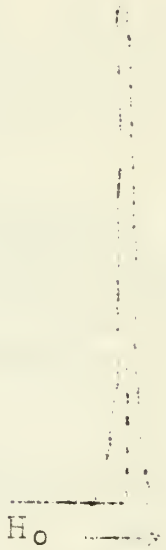
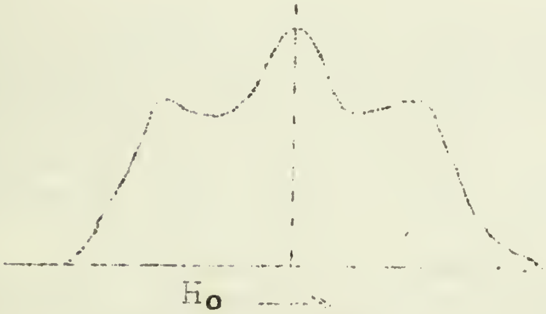


Figure 2



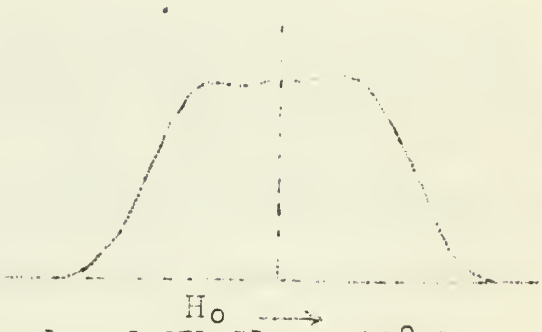
Protons in water

Figure 3



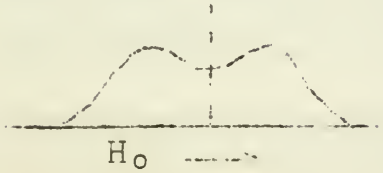
CH_3 group of CH_3CCl_3 at 145°K.

Figure 4



Powdered NH_4Cl at 90° K.

Figure 5



Powdered $CaSO_4 \cdot 2H_2O$ at R.T.

Figure 6

Fine Structure of C_2H_5OH

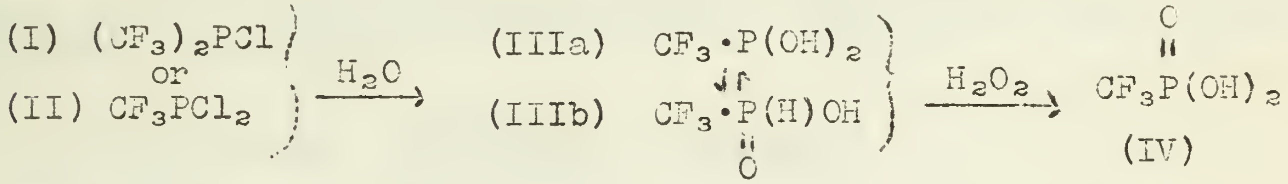
Curves are not to scale

TRIFLUOROMETHYL COMPOUNDS

Bernard Freedman May 3, 1955

Many trifluoromethyl metallic and metallodial compounds have been investigated by Emeleus, Haszeldine and coworkers[1]. Those which have been studied most recently include certain trifluoromethyl phosphorus compounds, trifluoromethanesulfonic acid, and tristrifluoromethylarsine.

The hydrolysis of chlorobistrifluoromethylphosphine (I), or dichlorotrifluoromethylphosphine (II), or the corresponding iodo compounds[2] yields a solution containing trifluoromethylphosphonous acid (III). This acid, by oxidation of its aqueous solution, may be converted to trifluoromethylphosphonic acid (IV).



$$\left.\begin{array}{l}\text{(I) } (CF_3)_2PCl\\ \quad\text{or}\\ \text{(II) } CF_3PCl_2\end{array}\right\} \xrightarrow{H_2O} \left.\begin{array}{ll}\text{(IIIa)} & CF_3\cdot P(OH)_2\\ & \quad\upharpoonleft\!\downharpoonright\\ \text{(IIIb)} & CF_3\cdot \underset{\underset{O}{\|}}{P}(H)OH\end{array}\right\} \xrightarrow{H_2O_2} \begin{array}{c}CF_3\overset{\overset{O}{\|}}{P}(OH)_2\\ \text{(IV)}\end{array}$$

However, IV can be obtained quantitatively by oxidation of trifluoromethylphosphine with 30% nitric acid. This phosphonic acid is one of the strongest known phosphorus acids and is extremely resistant to both acid and basic hydrolysis.

Although III has not been isolated as the free acid, its sodium salt has been isolated as a white solid. The infra red spectrum of this salt has revealed evidence for hydrogen bonding, explicable by the structure IIIa. However, other infra red data, supported by the fact that the acid is strongly monobasic, indicate that IIIb is the predominant species in the equilibrium[3].

Trifluoromethylphosphorus compounds show three types of behavior towards aqueous alkali[4],

(1) Those which yield fluoroform quanitatively.

(2) Those which yield both fluoroform and fluoride ion.

(3) Those which offer marked resistance to hydrolysis.

The first class includes the majority of the compounds studied. The following example may be cited.

$$CF_3\cdot P(OH)O^- \;+\; OH^- \;\rightarrow\; HPO_3^{-2} \;+\; CHF_3$$

Tetrakistrifluoromethyldiphosphine, $(CF_3)_2P-P(CF_3)_2$, was the first metalloid observed to undergo the second type of hydrolysis[2].

A mechanism has been proposed to account for this behavior. The first step is believed to involve hydrolytic fission of the P-P bond as follows:

$$(CF_3)_2P\text{-}P(CF_3)_2 \xrightarrow{H_2O} (CF_3)_2PH + (CF_3)_2POH$$

These products then undergo further decomposition to yield fluoroform and the fluoride ion.

The only compound so far demonstrated to be illustrative of the third type of hydrolysis is trifluoromethylphosphonic acid (IV). Its extreme stability towards hydrolysis is shown by the fact that it fails to react with concentrated sulfuric acid at 140°C or with 10% sodium hydroxide at 100°C.

Trifluoromethanesulfonic acid (VI) has been prepared by the oxidation of bis(trifluoromethylthio) mercury (V) with aqueous hydrogen peroxide[5]:

$$\underset{(V)}{CF_3S\text{-}Hg\text{-}SCF_3} \xrightarrow[\text{ca } 100^\circ C]{35\%\ H_2O_2} \underset{(VI)}{CF_3SO_3H}$$

This acid was isolated as its barium salt which when treated with concentrated sulfuric acid liberates the free acid. Because of the very high electronegative character of the trifluoromethyl group, it was anticipated that VI might be one of the strongest acids known. However, conductivity measurements gave no clear cut results in this regard, although the degree of dissociation, α, was approximated as 0.96.

The kinetics of the pyrolysis of trimethylarsine and tristrifluoromethylarsine have been investigated to compare the reactions of trifluoromethyl radicals to those of methyl radicals[6]. These studies indicate that both arsenic compounds undergo first order pyrolysis. By the use of activation energies, it was determined that the replacement of H by F causes little change in the bond energy of the C-As bond. One major difference, however, was noted in the nature of the decomposition products. Whereas trimethylarsine gave 90% methane, tristrifluoromethylarsine gave 60-90% hexafluoroethane. The methane could be formed by the reaction:

$$CH_3\cdot + AsMe_3 \rightarrow CH_4 + AsMe_2CH_2\cdot$$

and the hexafluoroethane could be formed either by dimerization of trifluoromethyl radicals or by the reaction

$$CF_3\cdot + As(CF_3)_3 \rightarrow C_2F_6 + \cdot As(CF_3)_2$$

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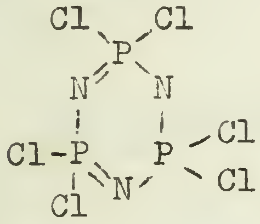
SULFUR TRIOXIDE ADDITION COMPOUNDS

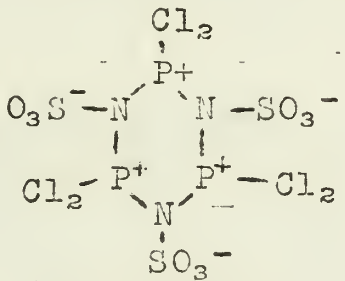
R.L. Pedrotti May 10, 1955

Introduction. In the gas phase and partly in the liquid phase sulfur trioxide is a monomer and has a planar structure. The sulfur atom has an octet deficiency and will therefore accept an electron-pair from a Lewis base. Sulfur trioxide compounds have been formed with pyridine, tertiary amines, dioxane, and other Lewis bases. These compounds have been used as special sulfonating agents. Recently Goehring, Hohenschutz, and Appel have investigated the reaction of sulfur trioxide with purely inorganic ring systems that contain atoms which may serve as Lewis bases.

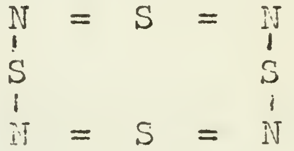
Phosphonitrile Chloride $(PNCl_2)_3$. This compound reacts with gaseous SO_3 to form a syrupy substance containing SO_3(1). After careful evacuation at 40° and vacuum distillation at 25° the colorless compound $(NPCl_2)_3 \cdot 3SO_3$ was obtained. It is hygroscopic and decomposes if heated to 50° at 15 mm. Since sulfonic acid is one of the hydrolysis products, sulfur trioxide is believed to be attached to the nitrogen atoms.



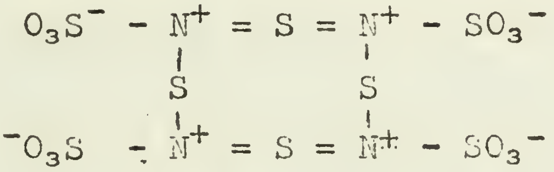
$(PNCl_2)_3$



$(PNCl_2) \cdot 3SO_3$



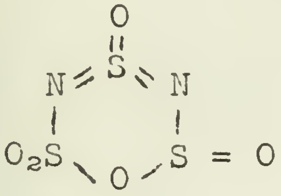
N_4S_4



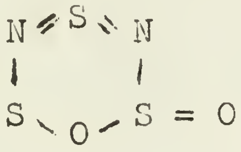
$N_4S_4 \cdot 3SO_3$

Nitrogen Sulfide (N_4S_4) Nitrogen sulfide reacts with limited amounts of SO_3 diluted with nitrogen at 0° to form two addition products (1, 2). If the reaction is stopped after the yellow solution of N_4S_4 changes to a brown color, $N_4S_4 \cdot 2SO_3$ may be isolated but if the reaction is allowed to proceed for a longer time a brick-red colored compound, $N_4S_4 \cdot 4SO_3$, may be isolated. Both compounds are hygroscopic and yield on hydrolysis sulfamic acid in addition to other products.

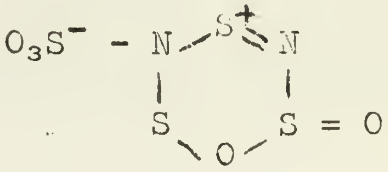
Trisulfur dinitrogen pentoxide, ($S_3N_2O_5$) and trisulfur dinitrogen dioxide ($S_3N_2O_2$). Thermal decomposition of $S_4N_4 \cdot 4SO_3$ at 50° or treatment of N_4S_4 with excess SO_3 at room temperature yields a new compound $S_3N_2O_5$ (2). It is a colorless crystalline compound which is easily sublimed. The structure below was postulated on the basis of results of hydrolysis and labled SO_3 experiments. It does not react with SO_3 to form an addition compound.



$S_3N_2O_5$



$S_3N_2O_2$

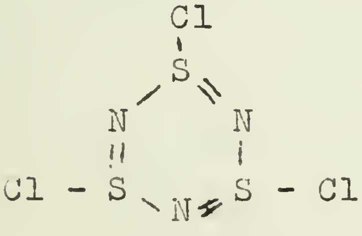


$S_3N_2O_2 \cdot SO_3$

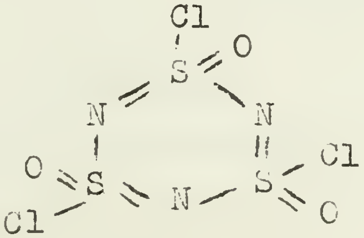
An analogous compound $S_3N_2O_2$ may be prepared by treating thionyl chloride with ammonia or by treating S_4N_4 with SO_2 in a solution of thionyl chloride (3). It melts at 100.7° without decomposition and is stable in a dry atmosphere. Treatment of $S_3N_2O_2$ with gaseous SO_3 at room temperature leads to the formation of a black solid substance $S_3N_2O_2 \cdot SO_3$, which decomposes slowly to form $S_3N_2O_5$ and SO_2.

Thiotrithiazyl chloride (S_4N_3Cl). S_4N_3Cl reacts with gaseous SO_3 diluted with nitrogen at 0° to form a solid light yellow substance of composition $S_4N_3Cl \cdot 2SO_3$ (1). The compound is obtained in a pure form if addition of SO_3 is continued until a yellow syrup is formed; the mixture is then evacuated at 80° for 4 hours. In this case it is not known whether the SO_3 is attached to nitrogen or chlorine atoms.

Trithiazyl trichloride $(NSCl)_3$. This compound takes up SO_3 under the same conditions as S_4N_4. After evacuating at 50-60° a light yellow substance analyzing for $(NSCl)_3 \cdot 3SO_3$ remains as the reaction product (1). It is sensitive to hydrolysis but thermally very stable. In contrast to trithiazyl trichloride, sulfanuric-chloride does not take up SO_3 under the above conditions.



$[NSCl]_3$



$[NSOCl]_3$

$(NSCl)_3$ is prepared by treating N_4S_4 with chlorine in CCl_4 (4, 7). It is a yellow crystalline compound and may be considered a sulfur analog of cyanuric acid chloride.

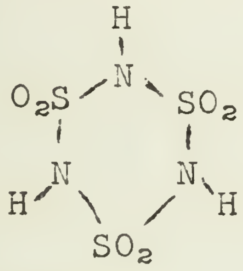
Ammonia. Appel and Goehring (6,8,9) have reported that the reaction of SO_3 with ammonia results in the formation of $(NH_4)_2S_3O_{10}$ and sulfimide ($HNSO_2$). The reaction is carried out by dissolving SO_3 in nitromethane at 0° and treating with dry gaseous ammonia. $(NH_4)_2S_3O_{10}$ crystallizes from solution. Evaporation of the nitromethane leaves a white residue which is transformed into $AgNSO_2$ by addition of $AgNO_3$. Treatment of $AgNSO_2$ with CH_3I in methyl alcohol results in formation of $(CH_3NSO_2)_4$ and $(CH_3NSO_2)_3$. The reaction is believed to proceed as follows:

$$SO_3 + NH_3 \rightarrow HNSO_2 + H_2O$$

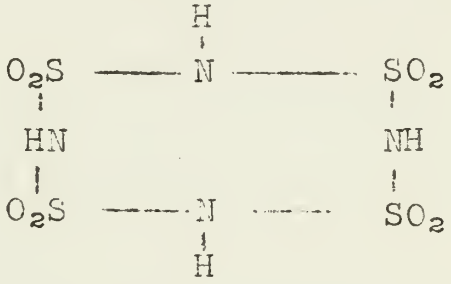
$$3SO_3 + H_2O \rightarrow H_2S_3O_{10} \xrightarrow{2NH_3} (NH_4)_2S_3O_{10}$$

Sulfimide had been isolated previously, as its silver salt, from the SO_2Cl_2 - NH_3 reaction product. In the free state it is believed to exist both as trimer and a tetramer. It resembles cyanic acid (CONH) which is known to exist as a trimer, cyanuric acid.

Sisler and Audrieth (11), had previously obtained ammonium imidodisulfonate ($NH_4N(SO_3NH_4)_2$) as the sole reaction product between liquid NH_3 and SO_3. They also found that SO_3-addition compounds react with liquid NH_3 to form sulfate, sulfamate, and imidodisulfonate. The ratio of the amounts of the latter two compounds has been used as an indication of the strength of the coordinate bond between SO_3 and the Lewis Base.



$[HNSO_2]_3$



$[HNSO_2]_4$

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π-BONDS INVOLVING d-ORBITALS

Gordon L. Johnson May 17, 1955

According to Linus Pauling (1) several questions need to be answered with respect to covalent complexes of the transition elements. 1. Why is the cyanide group so facile in the formation of complexes with the transition elements while the carbon atom in other groups such as the methyl group does not form bonds with them? 2. Why do the transition elements form more stable cyanide complexes then other elements? In the covalent complex $[Fe(CN)_6]^{-4}$, the iron atom has a formal charge of -4 if one assumes that it forms six covalent bonds with the six surrounding groups. 3. How can this latter assumption be rationalized with the tendency of metals to lose electrons and to form positive ions? In order to answer these questions, it was postulated that atoms of the transition elements are not restricted to the formation of single covalent bonds but can form multiple covalent bonds with electron-accepting groups by making use of the electrons and orbitals of the shells within the valence shell.

It has been established that olefins serve as ligands in complex compounds. Work by Chatt (2) indicates that these complexes involve the formation of π bonds. A freezing point curve of the system ethylene-trimethylborine shows definitely that there is no association down to the freezing point of the mixed gases. The fact that platinum can form ethylene compounds whereas boron cannot suggests that filled d-orbitals participate in the formation of a stable bond.

Carbon monoxide coordinates with BH_3 to form an unstable complex. However, Pt(II) carbonyl halides are very stable. This supports the hypothesis that the coordinate link has considerable double-bond character arising from interaction with d-orbitals of the central atom.

The trans- effect which is exhibited by many ligands may be due to π-bonding which involves the use of d-electrons (4). Experiments using phosphorus trifluoride as the ligand were carried out in order to test this idea. If the trans influence is due to the use of one or more filled d-orbitals in the platinum atom to bind the donor atom by π-bonding, then replacement of the alkyl groups in trialkylphosphines by more electronegative groups should increase the drift of electrons in the d-orbitals toward the phosphorus atom and should cause the phosphines to be stronger coordinators as the electronegativity of the element attached to the phosphorus is increased. This was confirmed.

The stability of the cis-isomer relative to the trans-compound was increased by replacing the alkyl groups in trialkylphosphine by fluorine. This also supports the view that d-orbitals in the platinum atom take part in coordination. In the cis-isomer, different orbitals are available to bind each molecule of the phosphine. In the trans-isomer the same d-orbital would have to bind both phosphorus atoms to the platinum atom. This would lead to a weaker bond (4).

Kabesh and Nyholm (6) suggest that the relative strengths of attachment of a series of ligands to a metal is determined by two main factors, a) the electronegativities of the bonded atoms and b) the possibility of double bond formation between the metal and the ligand. Chatt and Wilkins (7) found that these two factors counterbalance each other in the series, $(P\ Et_3)_2Pt\ Cl_2$, $(As\ Et_3)_2Pt\ Cl_2$, and $(Sb\ Et_3)_2Pt\ Cl_2$.

π -bonds involving d-orbitals may prevail in many silicon compounds. (9,10). This may be the answer to the shorter bond distances which have been observed in many of these compounds.

The subject is still debatable. Craig et al (11) have discussed this question in detail and have concluded that dπ - pπ bonding, applicable in most of the above cases, may be a fairly common phenomenon leading to formation of strong bonds.

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AN ELECTROSTATIC APPROACH TO ACID STRENGTH

F. Wassmundt May 24, 1955

Attempts have been made to correlate the strength of an oxygen-containing Brønsted acid with the structural features of the molecule, with the electronegativity of the central atom, and with size-charge considerations.

One useful approximation has been cited by Pauling:[1]

1. the successive acid constants, K_1, K_2, K_3, ... are in the ratios $1:10^{-5}:10^{-10}:$....
2. the value of the first ionization constant is determined by the value of m in the formula XOm(OH)n:

$$\begin{aligned} &\text{if } m = 0, & K_1 &\geqq 10^{-7} \\ &\text{if } m = 1, & K_1 &\cong 10^{-2} \\ &\text{if } m = 2, & K_1 &\cong 10^{+3} \\ &\text{if } m = 3, & K_1 &\cong 10^{+8} \end{aligned}$$

By plotting the pKa value against the difference in electronegativities between the hydrogen atom and the central atom ($X_H - Xx$) of an oxyacid, Gallais[2] obtained two functions describing the first ionization constant for several acids (Fig.1)

$$pKa = 8.3 + 4.2\ (X_H - Xx)$$
$$pKa = 2 + 2.2\ (X_H - Xx)$$

Acids are visualized as hydroxides of non-metals; the difference in electronegativities determines the mode in which a hydroxide may dissociate.

$$XO^- + H^+ \rightleftharpoons XOH \rightleftharpoons X^+ + OH^-$$

For water (hydrogen hydroxide) the value for $XH - Xx$ is zero; water is a neutral substance with respect to aqueous solutions. Hence, the y-coordinate must separate the acidic hydroxides from the basic ones. It is found that all the acids are to the left of the ordinate in Figure 1 and the amphoteric materials are to the right.

Cartledge[3] demonstrated how ionic potential (ϕ) could be employed to predict the character of hydroxides:

if $\sqrt{\phi} < 2.2$, the hydroxide is basic
if $2.2 < \sqrt{\phi} < 3.2$, the hydroxide is amphoteric
if $\sqrt{\phi} > 3.2$, the hydroxide is acidic

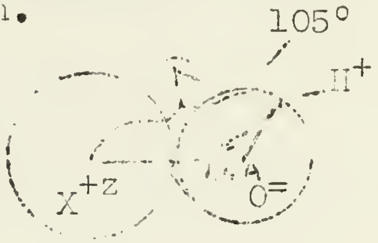
A later article by Sun[4] restates the conditions thus:

if $\phi < 6$, the hydroxide is basic; the smaller the value, the stronger the base.

if $\phi > 6$, the hydroxide is acidic; the larger the value, the stronger the acid.

if $\phi \cong 6$, the hydroxide is amphoteric.

If the statement by Sun is correct, there must exist some linear function relating the proton release of a molecule to some size-charge relationship. It was found that the following concept did not afford an unreasonable approach.



A typical hydroxide is composed of atoms envisaged as point charges. The charges corresponding to the oxidation number of the atom. These point charges are separated by a distance which equals the sum of the ionic radii involved. The X-O-H bond angle is approximated as the same as that for water - namely, 105°. The attractive force between oxygen and hydrogen is assumed to be the same for all such hydroxides. Accordingly, then, the repulsive force between X and H effects the proton release. By Coulomb's law, this force is proportional to the product of the charges on X and H and inversely proportional to the square of the distance (R^2) between them. By plotting the <u>pKa</u> values <u>vs</u>. the calculated values of Z/R^2 for a number of hydroxides, Figure 2 was obtained.

If these calculated values for a few elements are listed, it is seen that these elements may be divided into several catagories, though the division between them are not sharp. Flood and Förland's findings[5] that the acid strengths in potassium carbonate at 1000° for the anions

$$PO_3^- > BO_2^- \cong SiO_3^= > TiO_3^=$$

are in the order indicated are predictable to a degree by reference to this listing. Unfortunately, the listing does not appear to predict the relative strengths in a quantitative fashion.

The calcination of carbonates to oxides may be treated as an acid-base reaction. A plot of the temperature at which the dissociation pressure of carbon dioxide is one atmosphere <u>vs</u>. the values for ZZ'/R^2 gives Figure 3. Apparently, this linear relationship is valid for relatively ionic carbonates only. Sidgwick[6] estimated the decomposition temperature for $BeCO_3$ to be 25°; seemingly, this approximation is not unreasonable. A similar plot for the bicarbonates is not so satisfying (Figure 4).

An interesting relationship may be derived by a plot of the logarithms of the equivalent conductance of some acetates in glacial acetic acid against the ZZ'/R^2 values (Figure 5). Curiously, the alkali acetates do not lie on the line described by the other acetates.

			$\frac{Z}{R^2}$	
bases			less than 0.2.0	alkali metal hydroxides alkaline earth (exc.Be, Mg)hydroxid
		ions amminated	0.20	$Hg(OH)_2$
			0.23	$Fe(OH)_2$, $Zn(OH)_2$
			0.24	$Co(OH)_2$, $Ni(OH)_2$, $Mg(OH)_2$
	chlorides hydrolyze		0.28	$Bi(OH)_3$
ampholytis			0.32	$Be(OH)_2$
			0.35	$Sc(OH)_2$
			0.39	$Cr(OH)_3$
			0.40	$Ga(OH)_3$
			0.41	$Al(OH)_3$
			0.47	$Pb(OH)_4$
			0.527	$Ti(OH)_4$
			0.529	$B(OH)_3$
			0.60	$Ge(OH)_4$
			0.62	$Si(OH)_4$
acids			0.71	$OC(OH)_2$
			0.74	$OAs(OH)_3$
			0.77	$O_2N(OH)_2$
			0.80	$OP(OH)_3$
			(0.94)	O_2NOH
			0.96	$O_2S(OH)_2$
			1.01	$OI(OH)_5$
			1.18	O_3ClOH

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Figure 1

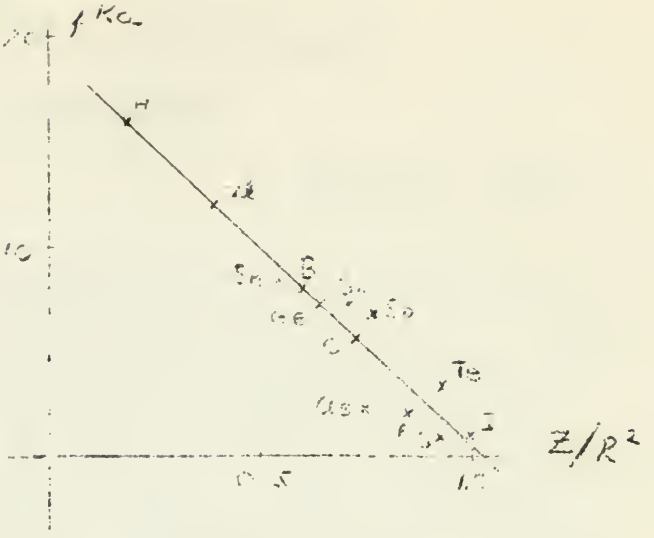

Figure 2

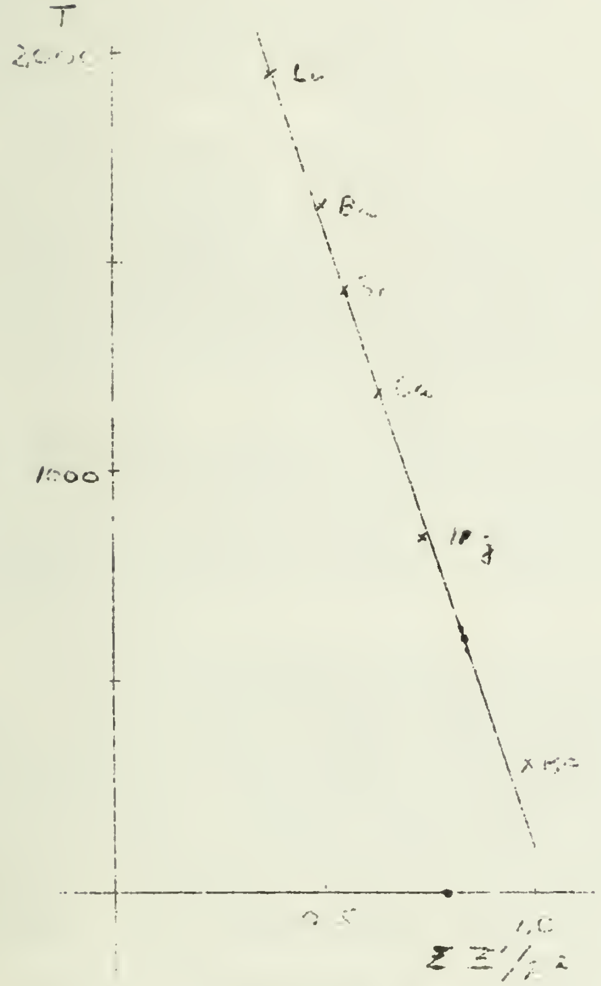

Figure 3

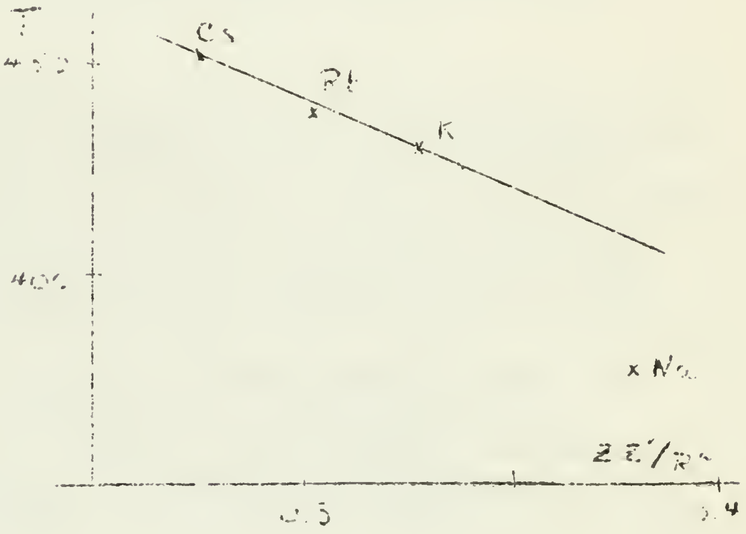

Figure 4

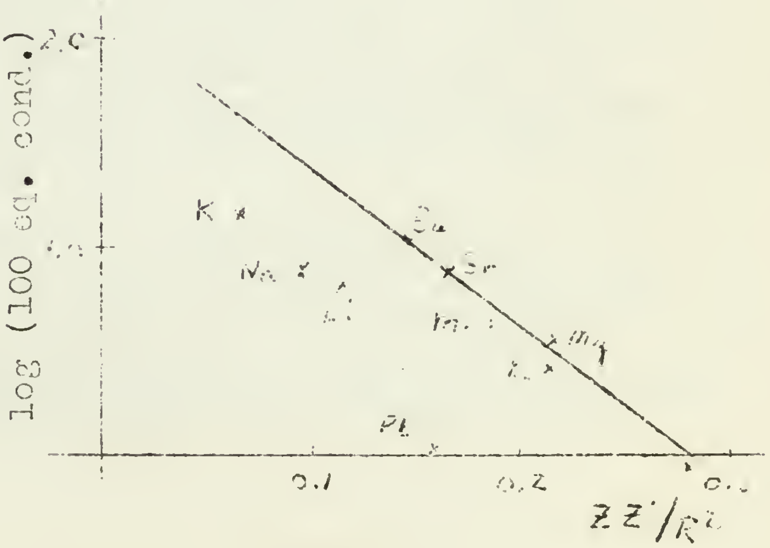

Figure 5

THESIS REPORT

OBSERVATIONS ON THE RARE EARTHS: SOME STUDIES INVOLVING CHELATE COMPOUNDS

Elsie Gulyas May, 24 , 1955

Introduction. Spectrophotometric studies of rare earth metal chelates show that the 4*f* electrons of the inner transition elements are not involved in the formation of the metal-ligand bond (9, 12). Consequently, the bonding in these complexes either involves the higher *d*, *s*, and p orbitals or it must be ionic. Covalent bonding implies stable spatial configurations of the chelates. If the metal-ligand bond in the acetylacetonates, and certain other chelates, of the sexacoordinate metals are covalent, then the chelates should exist in enantiomeric forms. Accordingly, resolution of the metal chelates into their optically active antipodes would be evidence for d^2sp^3 covalent bonding (4, 6). Once resolution has been achieved, the rate of racemization of the enantiomeric forms indicates the stability of the covalent bond (4).

The acetylacetonates of the tervalent sexacoordinate metals are inner complexes. The usual methods of separation of the enantiomeric forms, involving the formation of diastereoisomers with differing physical properties, is inapplicable in the case of these electrically neutral inner complexes. However, resolutions of a number of such compounds have been achieved by the preferential adsorption of one of the enantiomers by an optically active adsorbent (1,2,5,7,10,11).

Marshall (8) attempted resolutions of yttrium acetylacetonate and some other rare earth chelates in order to elucidate the nature of the rare earth metal-ligand bonds. He obtained evidence, though not of a conclusive nature, for the partial resolution of the yttrium chelate by liquid chromatography with lactose hydrate as the absorbent.

The present investigation was a continuation of Marshall's work. Though yttrium resembles closely the metals of the inner transition series, particularly erbium and holmium, it is not strictly, on the basis of its electronic configuration, a member of that series. Hence, gadolinium acetylacetonate was selected for study as representative of the inner transition series proper. For purposes of comparison, the acetylacetonates of scandium, yttrium, gallium, and indium were investigated also.

The chromatographic behavior of the acetylacetonates of chromium(III), iron(III), and cobalt(III) were studied in order to ascertain the general efficacy of the method for the resolution of enantiomeric forms. The optically active forms of these acetylacetonates prepared by Dwyer and Gyarfas provide a convenient measure of the efficiency of the chromatographic separation method. (3)

Experimental and Results.

1. Apparatus and Materials

A Schmidt and Haensch polarimeter, No. 9143, calibrated to 0.001° was used for the polarimetry. The pH was controlled in the preparation of the acetylacetonates with either a Model H or a Model G Beckman pH meter.

The chromatographic column was a glass tube 100 cm. long with an inside diameter of 2 cm. equipped with a vacuum stopcock.

The carbon and hydrogen assays were made by the microanalytical laboratory of the Chemistry Department.

The yttrium, scandium, and indium sesquioxides, hydrated gallium sulfate, and the acetylacetonates of gadolinium, chromium(III), iron(III), and cobalt(III) were obtained from the stocks of the Inorganic Chemistry Division of the Chemistry Department of the University of Illinois.

The chromatographic adsorbents were Merck U.S.P., and Baker and the Adamson reagent grade, lactose hydrate. In two separate instances starch and _d_-quartz were used.

The solvents were chemically pure chloroform, analyzed reagent grade benzene, low-boiling petroleum ether, and _n_-hexane.

2. Preparation of the Acetylacetonates of Yttrium, Scandium, Gallium, and Indium.

The chelates were prepared by precipitation from aqueous mixtures of the metal salts and acetylacetone in dioxane at the appropriate pH.

3. Chromatography of the Acetylacetonates

Liquid chromatograms of the acetylacetonates were obtained with the use of lactose hydrate or anhydrous lactose as the adsorbent by elution with organic solvents.

a. Chromium(III), Iron(III), and Cobalt(III) Acetylacetones. Both the chromium and cobalt chelates yielded optically active eluates which were stable to racemization for varying periods up to fourteen days. The chromatographic separation achieved with the cobalt complex was in one run 25% efficient, and in another run 50% efficient, provided the optically active forms of Dwyer and Gyarfas, used for comparison of the specific rotations, were pure (3).

The iron(III) chelate was not resolved chromatographically.

b. Gallium, Indium, and Scandium Acetylacetonates. None of these was resolved.

c. Yttrium and Gadolinium Acetylacetonates. These complexes were partially resolved. Evidence was obtained for only one of the enantiomeric forms in the eluate fractions. The optically active solutions were surprisingly stable to racemization in some cases. The solvent, apparently, had a profound effect on the rate of racemization.

The analyses of the residues from certain of the optically active eluate fractions are in good agreement with the analyses of the starting materials.

Conclusion

The successful resolution of the enantiomeric forms of yttrium and gadolinium acetylacetonates and the comparatively high optical stabilities of the active fractions suggest that the metal-ligand bonding in these complexes is of the d^2sp^3 covalent type.

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THESIS REPORT

I. VALENCE STABILIZATION THROUGH LAKE FORMATION
II. STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

Fred McCollough May, 24, 1955

Part 1

Introduction. Lake formation takes place by the coordination of a dye to a metal atom. The presence of two substituents (such as OH, COOH, NH_2) ortho to the azo linkage greatly increases the stability of the lake. With di-o-hydroxy substituted dyes, three secondary valences and two primary valences of a metal are satisfied when a lake is formed. If the metal is bivalent, the resulting lake is an uncharged molecule. In the case of a trivalent metal, the lake formed is a positively charged cation. Cobalt, for example, can be stabilized in either the +2 or the +3 oxidation state. (1)

In the present work, the chromium lakes of several o,o'-dihydroxy-azo dyes were investigated. Assuming an analogy exists between the chromium and cobalt lakes of o,o'-disubstituted dyes, it is reasonable to predict that the chromium might be stabilized in the +2 oxidation state. Since any tendency in this direction would show up as a lower reduction potential of the chromium in the chromium(III) lake, this problem was attacked polarographically.

Experimental and Discussion of Results. Two dyes and their chromium lakes were prepared: 2'-methoxybenzeneazo-β-naphthol-6-sulfonic acid and 2'-methoxybenzeneazo-β-naphthol. The polarographic half-wave potentials for these compounds were determined for the pH range 3 to 10. At all corresponding pH values, the half wave potentials of the unsubstituted lake are more negative than those of the unsubstituted dye, which in turn are more negative than those of the unsubstituted dye, which in turn are more negative than those of the sulfo-dye. These facts indicate that the presence of the negative sulfo-dye. These facts indicate that the presence of the chromium ion stabilizes the dye towards reduction, whereas the presence of the negative sulfo-group makes it easier to reduce. The sulfo-lake was found to be insoluble.

Values of the diffusion coefficients for the unsubstituted dye and its chromium lake, calculated by means of the Ilkovic equation, indicate that the reduction, at the dropping mercury electrode, in both cases uses four electrons per molecule. Coulometric measurements on these same compounds confirm the four electron reduction.

No evidence for the stabilization of the bivalent state of chromium was found, since under the experimental conditions used, the dy molecule was reduced before chromium.

Part 2

Introduction. Certain derivatives of biphenyl, having bulky groups in the 2,2'6,6' positions, are capable of being separated into optically active isomers. The source of this optical activity is the coaxial-non-coplanar configuration of the molecule caused by the restricted rotation of the benzene rings. Anything which prevents the coplanarity of the benzene rings should produce optical activity in the molecule. If, for example, the 2 and 2' positions of a biphenyl derivative are linked in an organic ring of seven or eight members, the benzene rings are held out of coplanarity and the molecule shows optical activity. (2, 3, 4)

If a metal ion is coordinated to substituents in the 2,2' positions of a biphenyl derivative, a seven-membered or larger ring results and by analogy to the above case, the complex should be optically active. In the present investigation, 2,2'-diaminobiphenyl was chosen as the ligand because of the coordinating tendency of the $-NH_2$ group.

Experimental and Discussion of Results.. Bis-ethylenediamine (2,2'-diaminobiphenyl) cobalt(III) chloride was prepared by the method described by Middleton (5). Theoretically, this compound should have four optical isomers since there are two centers of asymmetry - the cobalt atom and the biphenyl. The compound was resolved by recrystallization of the chloro-tartrate and four isomers were isolated. The rotatory dispersion curves were determined for the four isomers and the results show the presence of two mirror image pairs. Bis-ethylenediamine (2,2'-diaminobiphenyl) cobalt(III) bromide was found to be resistant to racemization.

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THESIS REPORT

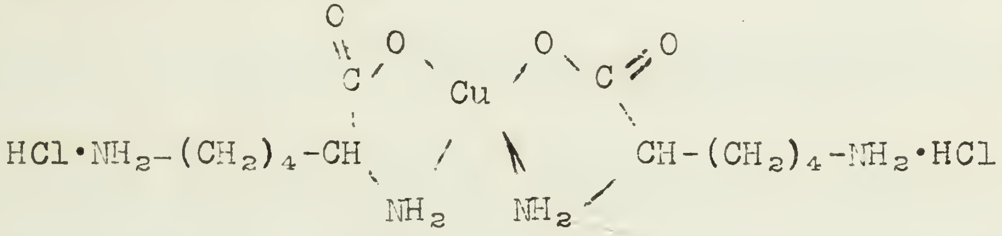
PREPARATION AND STUDY OF HETEROPOLYNUCLEAR INORGANIC COMPLEXES

Robert L. Rau May 24, 1955

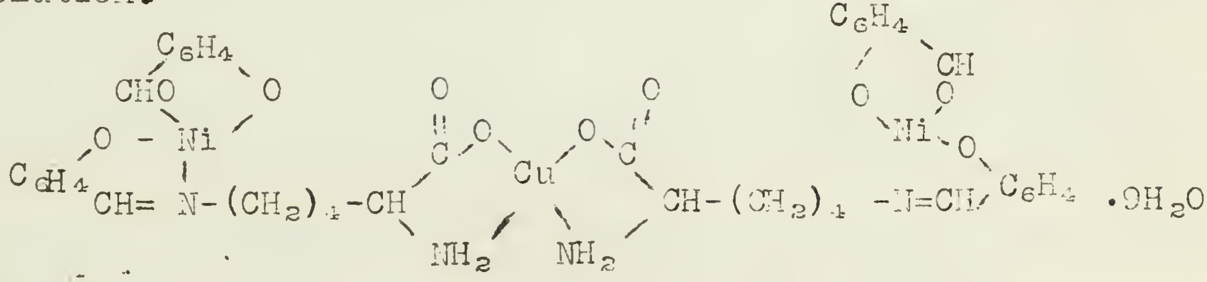
Cuthbertson, Parkinson and Rooksby[1] have recently reported that by electrolyzing an aqueous solution containing $SnCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, NaF and NH_4F they were able to obtain an alloy of tin and nickel in a 1:1 ratio. The composition of this alloy is, within wide limits, independent of the ratio of Sn++ to Ni++ in the electrolyte. The alloy is reported to have properties more desirable than those of chromium and is now being produced on a commercial basis in England.

The method of continuous variations, using refractive index as the measured property, was employed to determine the nature of the species formed in the electrolyte. A study of $SnCl_2 \cdot 2H_2O$ vs. NaF or NH_4F indicates the species, $SnF_4^{=}$, is formed in solution. A similar study of $NiCl_2 \cdot 6H_2O$ vs. NaF or NH_4F indicates that there is no reaction between Ni++ and F^-. Using $SnF_4^{=}$ and Ni++ as the two constituents in another study, evidence was obtained which indicates the formation of $NiSnF_4$. Such a species could have a brdiged structure with fluoride ions briding the tin and nickel. A possible mechanism of alloy deposition could be one of adsorption on the cathode surface prior to reduction.

If one adjusts a solution of lysine monohydrochloride to a pH of 7.1 with potassium hydroxide, adds excess cupric oxide, and refluxes gently for 30 minutes, a product having the following composition can be obtained



If this product is allowed to react with two mols of Ni(salicylaldehyde)$_2$ the following product can be obtained from the reaction solution.



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THESIS REPORT

THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

Mary Joan Sirotek May 24,1955

I. THE USE OF BIOCHEMICAL PROCESSES FOR THE RESOLUTION AND STUDY OF THE CONFIGURATION OF SOME COBALT COMPLEXES

Microorganisms have been used to effect a partial resolution of optically active organic compounds since the time of Pasteur. Kinoshita(1) found that certain molds can utilize the ammonia in some cobalt ammine complexes as a nitrogen source. Hence, a study was undertaken to determine if a mold would attack one isomer of $[Co(en)_3]Cl_3$ preferentially where the complex is the only nitrogen source available. The mold *aspergillus niger* was used.

Early results indicate that when a culture of *A. Niger* is grown on a substrate containing one of the optical isomers the mold then will attack this isomer at a more rapid rate than the other in subsequent experiments. The Warburg technique of oxygen uptake was used to follow the process. The experiments have been complicated by the high endogenous rate of the mold and the sensitivity of the mold filaments to homogenizing. This study may give some insight into the absolute configuration of some stable optically active inorganic complexes since the isomers which are attacked more readily by the microorganism probably will have the same absolute configurations.

II. THE PARTIAL RESOLUTION OF RACEMIC *TRANS*-1,2CYCLOHEXANEDIAMINE THROUGH AN OPTICALLY ACTIVE COBALT INORGANIC COMPOUND

Bailar (2) has reported the resolution of certain optically active organic compounds through preferential coordination of the compounds to complexes containing optically active ligands. It appears that these ligands can determine which configuration of another coordinating agent will enter the complex. *Trans*- 1,2cyclohexanediamine was chosen for this study because it has *two* asymmetric carbons and thus may be more readily resolved. The cyclohexanediamine was prepared from 1,2cyclohexanedionedioxime by a sodium reduction in absolute ethanol according to the method of Jaeger (3). An attempt to prepare the diamine from hexahydro phthalic anhydride was unsuccessful because of the instability of the intermediates.

The reaction of *trans*-1,2cyclohexanediamine with $[Co(l\text{-}pn)_2Cl_2]Cl$ in a molar ratio of *two to* one did not yield the complex $[Co(chxn)(l\text{-}pn)_2]Cl_3$ which was expected. Instead, a mixture of $[Co(chxn)_2(l\text{-}pn)]Cl_3$ and $[Co(chxn)_3]Cl_3$ was obtained. This result is probably due to a solubility relationship. If the precipitate which gradually forms is removed, the last fraction contains $L[Co(d\text{-}chxn)_3]^{+++}$ ($[\alpha]^{25}_D$ =-14.8). This indicated an 18% resolution.

When $[Co(l\text{-}pn)_2Cl_2]Cl$ is allowed to react in absolute ethanol with *trans*-1.2cyclohexanediamine in a molar ratio of one to six, $L[Co(d\text{-}chxn)_3]Cl_3$ ($[\alpha]_D^{25} = -2.84$) is formed. This result shows a 3.5% resolution. This work indicates that levo-propylenediamine and dextro-1,2cyclohexanediamine have the same configuration. These results agree with those of Jaeger(4) who reported that of the eight isomers of $[Co(chxn)_3]Cl_3$ which are theoretically capable of existence only $L[Co(d\text{-}chxn)_3]Cl_3$ and $D[Co(l\text{-}chxn)_3]Cl_3$ have been prepared.

Several other approaches to the problem have been and are being investigated. An attempt was made to resolve the diamine by allowing it to react with $D[Co(en)_3]Cl_3$ in a molar ratio of six to one. The $[Co(chxn)_3]Cl_3$ which precipitates is not optically active. The reaction of $L\text{-}K[Co(enta)]$ with *trans*-1,2cyclohexanediamine is now being studied. Kirschner(5) has reported a resolution of 4% for propylenediamine when this method is used.

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