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Nuclear Magnetic Resonance Studies of Methyllithium - Lithium Halide Exchange Reactions
(Thesis Report)

David P. Novak June 22, 1971

Introduction

Alkyllithium reagents are of great synthetic utility in organic, inorganic, and polymer chemistry. However, their nature in solution is still not thoroughly understood. These reagents are frequently synthesized from their corresponding alkylhalides and lithium metal in donor solvents(diethyl ether, tetrahydrofuran, etc). The products of this reaction(the alkyllithium reagent and lithium halide) are usually both soluble in these donor solvents. The question remains as to the effect of lithium halide on the reactivity of the alkyllithium reagent in subsequent reactions.

Both proton and ^{7}Li nuclear magnetic resonance spectroscopy have been applied to the study of mixtures of methyllithium and lithium halide(lithium bromide and lithium iodide) in diethyl ether. This system was chosen since it involves the simplist organolithium compound (methyllithium) in a common donor solvent(diethyl ether).

General Background

Methyllithium has been shown to exist predominately as a tetramer in diethyl ether.[1,2] We found lithium bromide also to be essentially tetrameric(degree of association 3.9±.1) in diethyl ether by using an isothermal distillation technique.[3] Because of the obvious similarity between lithium bromide and lithium iodide, as well as their similar ^{7}Li nmr spectra both by themselves and in mixtures with methyllithium, we believe that lithium iodide is also tetrameric ether.

Since methyllithium and lithium bromide(and lithium iodide) are tetrameric in ether it is reasonable to postulate that mixtures of the reagents could contain five possible mixed or cross associated tetramers of the form $Li_4Me_nX_{4-n}$ (n = 0,1,2,3,4) where individual tetrameric units would contain both methyl and halide bridging groups. This cross association phenomenon has previously been studied in other mixtures of oligomeric alkyllithium compounds[1,4,5]

Dr. William Wells[6] initially examined the low temperature ^{7}Li and protons nmr of mixtures of methyllithium and lithium halides(lithium bromide and lithium iodide) in diethyl ether. However, because of the relatively poor quality spectra available from the Varian DP-60 he was able only to deduce that some form of mixed species were being formed in these systems.

Waack, and coworkers[7] found evidence for a 1:1 methyllithium-lithium halide(LiBr and LiI) complex in the low temperature ^{7}Li nmr spectra of

methyllithium-lithium halide tetrahydrofuran solutions. Telalaeva[8], et al, have also isolated methyllithium-lithium halide etherate complexes of varying composition from diethyl ether solutions.

Results and Conclusions

The following results were obtained from a careful examination of the low temperature ^{7}Li nmr spectra(obtained on a Varian HA-100 nmr spectrometer) of etheral methyllithium-lithium bromide mixtures:

1. Mixed tetrameric species are present in a non-statistical distribution at low temperatures.
2. Mixed tetrameric aggregates rich in bromide groups exchange faster than those rich in methyl groups.
3. Intra-and inter-molecular exchange occur at approximately the same rate.
4. The "local environment" model[1] applies in this case.
5. Lowering the temperature shifts the equilibrium towards the pure tetrameric species.

The following results were obtained from the low temperature ^{7}Li nmr spectra of mixtures of methyllithium and lithium iodide in diethyl ether:

1. Only one mixed tetrameric species of the form Li_4Me_3I is present at low temperatures.
2. Exchange is slower in these systems than in those containing lithium bromide.
3. The "local environment" model begins to breakdown.
4. Lowering the temperature shifts the equilibrium towards the pure tetrameric species.

General Observations

These studies indicate that mixtures of methyllithium and lithium halide do not just exist as pure components in donor solvents, but they exist in rapidly exchanging mixed tetramers. Presumably, other alkyllithium reagents present with lithium halides in donor solvents would also form mixed oligomeric species. Knowing what we do now, we can better understand the reactions of organolithium reagents with various substrates, and the effect of lithium halide on these reactions.

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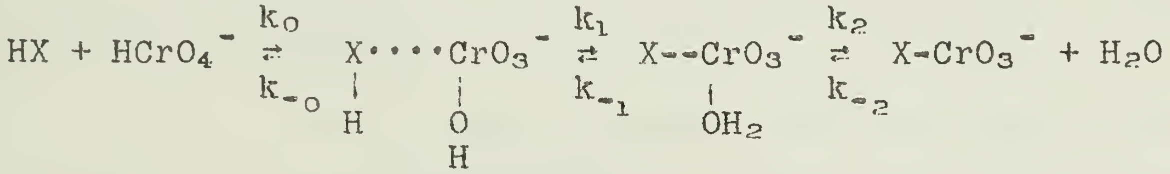
STUDIES OF THE CHROMIUM(VI)-THIOSULFATE SYSTEM
(Thesis Report)

Kathy Muirhead June 29, 1971

Introduction

Rate-determining proton transfer has been observed in the formation of complexes between $HCrO_4^-$ and species such as $H_2PO_4^-$[1] and $H_2PO_3^-$[2] as well as in the formation of dichromate ion by condensation of $HCrO_4^-$ with itself.[3] A mechanism proposed to account for these observations involves formation of a weak five-coordinate chromium(VI) intermediate in an equilibrium step followed by proton transfer and loss of a water molecule from the chromium(VI).[4]



$$HX + HCrO_4^- \underset{k_{-0}}{\overset{k_0}{\rightleftarrows}} \underset{\substack{|\\ H}}{X}\cdots\underset{\substack{|\\ O\\ H}}{CrO_3^-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X{-}{-}\underset{\substack{|\\ OH_2}}{CrO_3^-} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} X{-}CrO_3^- + H_2O \qquad (1)$$

According to the Principle of Microscopic Reversibility, this requires that proton transfer also occur in the activated complex for the hydrolysis of dichromate ion, a requirement that has been confirmed by the recent observation of general acid catalysis for this reaction.[3] This is in contrast with another proposed mechanism which ascribes catalysis of dichromate hydrolysis to nucleophilic attack of a base on dichromate with displacement of a chromate ion followed by rapid hydrolysis of the intermediate formed.[5]

$$B^- + O_3CrOCrO_3^= \underset{k_{-N}}{\overset{k_N}{\rightleftarrows}} CrO_3B^- + CrO_4^= \qquad (2a)$$

$$CrO_3B^- + H_2O \underset{k_F}{\overset{k_H}{\rightleftarrows}} HCrO_4^- + B^- + H^+ \qquad (2b)$$

Several authors have recently reported the formation of a complex between thiosulfate and hydrogen chromate with a formation constant 100 to 1000 times larger than the formation constants known for other complexes of chromium(VI).[6,7] The present study was undertaken to determine the kinetic parameters for the formation of this complex, to determine whether mechanism 1 is applicable to a more polarizable base such as $S_2O_3^=$ (which has been suggested to act as a nucleophilic catalyst in the hydrolysis of dichromate), and to look for direct evidence for mechanism 2.

Results and Discussion

All the kinetics experiments were done on a stopped flow spectrophotometer under conditions where complex formation was much faster than the subsequent redox reaction. With a pseudo-first order excess of $S_2O_3^{=}$, the rate law is found to be $\frac{d[CrS_2O_6^{=}]}{dt} = [k_F[HS_2O_3^-] + kr][HCrO_4^-]$, with $k_f = (2.01 \pm .08) \times 10^4 M^{-1} sec^{-1}$ and $k_r = 2.05 \pm .15 \ sec^{-1}$. There was no evidence for H^+ catalysis in the acid concentration range studied. The formation constant and extinction coefficients for the complex were determined kinetically and spectrophotometrically[8,9] from infinite-time absorbances at two different wavelengths. Values found were $K_{eq} = (1.1 \pm .4) \times 10^4$,

$$\varepsilon = 1130 \ M^{-1}cm^{-1} \text{ at } 420 \ m\mu \text{ and } 770 \pm 90 M^{-1}cm^{-1} \text{ at } 350 \ nm,$$

in good agreement with previously determined values. The exceptionally large formation constant and red shift of the charge transfer band are interpreted in terms of Cr-S bonding in this complex.

The kinetic parameters determined for $CrS_2O_6^{=}$ give strong support to mechanism (1) for formation of chromium complexes by condensation with $HCrO_4^-$. There is a good correlation between K_a for $H_2SO_3^-$ and k_f as would be expected for rate determining proton transfer.

Studies of dichromate hydrolysis using a modified stopped-flow setup with higher $[S_2O_3^{=}]$ and lower $[H^+]$ give qualitative evidence for formation of $CrS_2O_6^{-2}$ and hence for the nucleophilic catalysis mechanism. An intermediate is observed directly at 443 nm and $CrO_4^{=}$ inhibition of hydrolysis is also observed as predicted. Quantitative determination of the rate constants k_N and K_{-N} cannot be made at present because complete kinetic curves are not available.

Summary

Results of the present studies further support a proposed mechanism of chromium(VI) complex formation involving rate determining proton transfer. They also provide the first direct experimental evidence available for the nucleophilic catalysis mechanism of dichromate hydrolysis. Hence, the possibility that two distinct mechanisms may exist for dichromate hydrolysis[3] seems even more likely.

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CONFORMATIONAL STUDIES OF TRIS(PROPYLENEDIAMINE) AND TRIS(ETHYLENEDIAMINE)RUTHENIUM(II) AND PLATINUM(IV) COMPLEXES
(Thesis Report)

Lucille H. Novak August 9, 1971

Introduction

In recent years, extensive analyses by means of nuclear magnetic resonance have been made of the configurations and conformations of tris-propylenediamine and tris-ethylenediamine complexes in solution. Since an individual coordinated diamine ligand can assume a staggered form in metal complexes, conformational isomerism of the individual ligands is possible. The two non-planar conformational forms have been designated as δ and λ conformers.[1] Because of steric interactions, in propylenediamine complexes, all of the ligands exist in the conformation with the methyl group in an equatorial position. In ethylenediamine complexes, the individual ligands have no conformational preference since the δ and λ conformers are enantiomers and therefore have equal energies. However, nonbonded interactions cause a preference for the δ conformer in the Λ absolute configuration.

Corey and Bailar[2] have estimated that the inversion of each ligand in tris-ethylenediamine complexes from its stable conformation leads to an increase in inter-ligand repulsions of approximately 0.6 kcal mol^{-1} ligand^{-1}, resulting in the following order for the relative enthalpies of the Λ configuration of a tris-ethylenediamine complex: $\Lambda(\delta\delta\delta) \ll \Lambda(\delta\delta\lambda) < \Lambda(\delta\lambda\lambda) \ll \Lambda(\lambda\lambda\lambda)$. These calculations have been supported by crystal structure studies[3] and studies on the relative stabilities of cobalt amine complexes in solution.[4]

Several attempts have been made to study the conformational energy differences in tris-ethylenediamine complexes by nmr spectroscopy. The nmr spectra have been obtained for Pt(IV),[5] Co(III),[6] Rh(III),[7] Ir(III),[7] and Ru(II)[5] spin-paired d^6 complexes. These spectra vary enormously from a single narrow line for Pt(IV) (with satellite peaks due to proton-^{195}Pt coupling) to a well resolved AA'BB' spectrum of 24 lines for Ru(II). A recent model[8] that was postulated that is consistent with all of the observed $M(en)_3$ spectra proposes that all of the $M(en)_3$ complexes undergo rapid ligand ring inversion and the observed nmr spectra are those of the equilibrium population of the conformers. The observed spectra would be dependent upon two factors: 1) the intrinsic chemical shift difference between the axial and the equatorial methylene protons and 2) the mole-fraction of ligands in each conformer. Unfortunately, neither of these two factors can be determined directly from the $M(en)_3$ spectra without a knowledge of the other. However, an experimental estimate of the intrinsic

chemical shift difference in ethylenediamine complexes can be determined indirectly by analysis of the chemical shift difference between an axial and an equatorial proton in the corresponding propylenediamine complexes.

In this study the nmr spectra of $Pt(pn)_3^{4+}$ and $Ru(pn)_3^{2+}$ were analyzed using the NMRIT computer program. to determine a value for the intrinsic chemical shift difference and to investigate the effect of changing the metal ion and its oxidation state on the chemical shifts of the ligands. The spectrum of $Pt(en)_3^{4+}$ was also analyzed using NMRIT and CALCOMP computer programs. The values for the effective chemical shift difference calculated for $Pt(en)_3^{4+}$ and found previously for $Ru(en)_3^{2+}$[5] were used together with the intrinsic chemical shift differences estimated from the propylenediamine complexes to calculate the amount of conformational averaging which occurs in these complexes.

Results and Discussion

Comparison of the chemical shifts of the ligand protons in $Ru(pn)_3^{2+}$ and $Pt(pn)_3^{4+}$ showed that the proton resonances in the Ru(II) complex were consistently upfield from the corresponding resonances in the Pt(IV) complex. This is presumably the result of increased shielding of the metal d-electrons in the Ru(II) complex because of the greater radial extension of the t_{2g} orbitals in the lower oxidation state Ru(II) complex. It was also found that the axial protons were greatly influenced by changes in the metal ion while the equatorial protons were not. This results in a decrease in the intrinsic chemical shift difference between the axial and equatorial protons from 0.87 ppm for the $Ru(pn)_3^{2+}$ complex to 0.13 ppm for the $Pt(pn)_3^{4+}$ complex.

Using the above intrinsic chemical shift value as an estimate of the intrinsic chemical shift difference in an ethylenediamine complex together with the averaged or effective chemical shift difference obtained from the analysis of the trisethylenediamine spectra, the populational differences in the $Pt(en)_3^{4+}$ and $Ru(en)_3^{2+}$ complexes were calculated. In the Pt(IV) complex, 65% of the ligands were calculated to be in the δ conformation and 35% to be in the λ conformation. In the Ru(II) complex, 63% and 37% of the ligands were calculated to be in the δ and λ conformations, respectively.

In the $Pt(en)_3^{4+}$ complex, the presence of populational differences and unequal coupling constants for the platinum-axial and platinum-equatorial proton coupling leads to unequal line widths for the satellite peaks. Once the mole-fraction of ligands in each conformation is known, values of the platinum-proton coupling constant can be calculated. The values calculated were 40 Hz and 15 Hz for coupling to an equatorial and an axial proton, respectively.

Summary

The extent of conformational averaging found for the tris-ethylenediamine complexes of Rh(III)[9] and Ni(II)[10] is comparable to that found for the Ru(II) and Pt(IV) complexes in this study. This suggests that the charge on the complex does not substantially alter the relative conformational energies and substantiates the theory[8] that the differences in the observed $M(en)_3$ spectra are the result of differences in the intrinsic chemical shift difference between the axial and the equatorial protons. This latter effect is probably a consequence of changes in the oxidation state of the metal ion.

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HETEROGENEOUS CATALYSIS OF THE HYDROGENATION OF OLEFINS BY POLYMERIC PALLADIUM AND PLATINUM COMPLEXES

(THESIS REPORT)

Harold Bruner, Jr. August 31, 1971

Introduction

Heterogeneous catalysis by partially-poisoned metal surfaces and homogeneous catalysis by various transition metal compounds have been investigated in an effort to find a selective catalyst for the partial hydrogenation of the polyolefinic components of soybean oil without producing unhealthful saturated fats.[1] Although many homogeneous catalysts have been prepared with a selectivity greater than the best heterogeneous systems, heterogeneous catalysis is used almost exclusively in commercial processes. The greater ease of recovery of heterogeneous catalysts far outweighs any other factors in industrial reactions.

A polymeric analog of the existing selective, homogeneous catalysts, $Pt(PPh_3)_2Cl_2$ and $Pd(PPh_3)_2Cl_2$,[2,3] was prepared in the hope that this compound would have the limited solubility of a polymer and yet retain the chemical behavior of the monomeric complexes. The polymers were synthesized by the reaction of dichlorodibenzonitrile complexes of palladium(II) and platinum(II) with an organic polymer containing diphenylbenzylphosphine functional groups. A similar rhodium(I) complex has been employed for hydrogenation[4] and carbonylation reactions.[5]

Results and Discussion

The catalytic activity of the palladium(II) polymer is extremely sensitive to changes in the solvent in which the olefin substrate is dissolved. In alcohols, the catalyst is sufficiently active to permit the reductions to be run at room temperature and one atmosphere pressure of hydrogen. Deuterium labeling studies were run employing either methanol-d or deuterium gas as an isotope source. When the olefin substrate is dissolved in nonprotic solvents, higher pressures of hydrogen are required. Less polar solvents maximized the rate of reductions. Activation of catalysts with methanol solvents have been reported previously.[6]

The platinum(II) polymer required much higher temperatures and the addition of a stannous chloride cocatalyst before it would catalyze the hydrogenation reaction.

Both catalysts could be recovered by filtration and reused several times. There was some loss in activity after the first reaction, but subsequent reductions caused no further decrease.

With both catalysts, conjugated dienes were reduced more rapidly than nonconjugated. Only the platinum(II) polymer catalyzed the isomerization of dienes.

Although the palladium(II) polymer did not catalyze the reduction of monoenes when sufficient diene was available, pure monoene substrates did isomerize and reduce readily. The rate of reaction decreased as the steric hindrance to coordination in the monoene increased.

Dichlorobis-(diphenylbenzylphosphine) complexes of palladium(II) and platinum(II) were prepared and compared to their supposed polymeric analogs.

Mull infrared spectra were utilized to elucidate the structures of the polymeric metal complexes.

A detailed mechanism is proposed for the reduction catalyzed by the palladium(II) polymer.

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A DIRECT DETERMINATION OF THE VALENCE ELECTRON DISTRIBUTION IN TETRACYANOETHYLENEOXIDE BY DIFFRACTION METHODS

(Thesis Report)

David A. Matthews September 3, 1971

Introduction

The scattering of X-rays is a process associated exclusively with electrons. In principle, the diffraction of X-rays by crystals is capable of providing detailed information concerning time averaged electron distributions. However, it has been shown by us and others that the spherical atom scattering factor formalism which is used in the conventional X-ray experiment introduces a bias into the least squares refinement procedure which results in systematic error in the derived parameters.[1-5] While these errors are of minimal consequence as far as routine crystal structure analysis is concerned, they tend to almost completely obscure aspherical valence density features in, for example, Fourier difference maps. The standard X-ray diffraction approach is therefore inadequate for obtaining accurate charge densities.

The simultaneous use of accurate X-ray and neutron diffraction data is employed as a means of circumventing the conventional spherical atom scattering factor formalism and providing valuable information concerning the time averaged and static charge distribution in tetracyanoethyleneoxide(TCNO). The electronic structure of this and other three-member ring molecules is of considerable interest due to the apparent breakdown of the concept of directed valence.

Methods and Results

Considerable effort was expended in correcting the experimental data for certain systematic errors which are usually ignored in routine diffraction experiments. We briefly discuss the secondary extinction correction and show how, especially for neutron scattering experiments, neglect of this effect can result in serious errors in the derived thermal smearing function.

Difference Fourier series were constructed according to

$$\rho_{X-N}(x,y,z) = \frac{1}{V}\sum_{hkl}\left(F_X - F_N\right)\exp\left[-2\pi i\left(hx+ky+lz\right)\right]$$

where F_X is the observed X-ray structure factor with the phase of F_N and F_N is the structure factor whose phase and amplitude are calculated from neutron thermal and positional parameters and spherical atom scattering factors. The resultant function, ρ_{X-N}, represents the redistribution of charge density in going from the isolated atoms to the molecule. The experimental X-N difference density in the plane of the ethyleneoxide ring is discussed in terms of semiempirical and SCF-LCAO-MO calculations which have been made on similar strained-ring molecules. The maximum for the

difference density in the endocyclic C-C bonding region is "bent" 12° from the internuclear axis while the density in the C-O bond region is obscured by the tails from a substantial accumulation of density in the center of the ring. Difference Fourier sections through a number of chemically interesting parts of the molecule are discussed. Discrepancies between the X-ray and neutron thermal and positional parameters are interpreted in terms of the bias introduced in the X-ray refinement by the spherical atom scattering factor formalism.

An electron valence shell population analysis is carried out in reciprocal space using various models and basis functions for the atomic scattering factors. The most sophisticated treatment enables us to obtain a fit by least squares of the X-ray structure amplitudes (using neutron positional and thermal parameters) to selected orbital products of the first order density matrix. The one electron density function employed here (whose Fourier transform can be thought of as a "generalized" X-ray scattering factor) is defined as

$$\rho = 2 \sum_{\lambda} \sum_{\mu} \sum_{\nu} c_{\lambda\mu} c_{\lambda\nu} \phi_{\mu} \phi_{\nu} \equiv \sum_{\mu} \sum_{\nu} P_{\mu\nu} \phi_{\mu} \phi_{\nu}$$

where the ϕ's are Hartree-Fock(HF) or Slater Type Orbital(STO) atomic basis functions and the $P_{\mu\nu}$'s are variable coefficients of the orbital products. These results are used to facilitate a more convenient comparison with theoretical calculations.

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STEREOCHEMICAL REARRANGEMENTS OF METAL BETA-DIKETONATES

Michael T. Mocella September 21, 1971

Introduction

One of the most interesting unsolved problems of inorganic stereochemistry involves the mechanism of the racemization and isomerization of various tris-chelate metal complexes. Several mechanisms have been proposed involving both bond rupture[1-2] and twisting processes,[3-6] but until recently, inorganic chemists lacked the experimental tools to distinguish clearly among the proposed mechanisms. The suitability of nuclear magnetic resonance spectroscopy as a probe into the stereochemical rearrangements of metal beta-diketonates was first demonstrated in the early 1960's, and since then this class of compounds has been extensively studied in a number of laboratories. This seminar will summarize the results of these studies.

Early Studies

In the pioneering work of Piper and Fay, complexes of the form $M(bzac)_3$ (bzac = anion of 1-phenyl-1,3-butanedione) and $M(tfac)_3$ (tfac = anion of 1,1,1 trifluoro-2,4-pentanedione) were synthesized, separated into geometrical isomers when possible, and examined by several spectroscopic methods.[7-8] Based on the coalescence of n.m.r. signals as determined by variable temperature work, polarimetry on the partially resolved complexes, and point charge ionic model calculations, they favored a bond rupture process to account for the observed stereochemical rearrangements.[9] Similar conclusions were reached for mixed ligand complexes of the form $M(tfac)_n(acac)_{3-n}$, n = 1,2 (acac = anion of 2,4-pentanedione).[10]

Subsequently, Sievers examined the various twisting processes that had been proposed and noted the generality of the trigonal twist as a mechanism for simultaneous racemization and geometrical isomerization of metal complexes. In addition, a new twisting mechanism was proposed.[11] Brady's later work showed that a single twisting process is actually responsible for what had previously been considered different twisting mechanisms.[12] Sievers also presented a discussion of the potential use of n.m.r. in determining rates of optical inversion of racemic mixtures of certain metal tris-chelates.[13]

In an attempt to decide more clearly between bond rupture and twisting processes, Pinnavaia carried out a series of investigations involving beta-diketonate complexes of aluminum and gallium.[14-15] While the activation parameters do not allow a clear choice between mechanisms, arguments based on the magnitudes of frequency factors appear to favor a bond rupture process.

Recent Studies

Fay has studied rates of isomerization and racemization of $Co(bzac)_3$ and has performed a detailed kinetic analysis of the possible rearrangement processes. The data favors a bond rupture mechanism, and the activation parameters suggest a common pathway for the racemization and geometrical isomerization processes.[16]

The most ambitious studies of these rearrangement processes has been carried out by Holm. Racemization and isomerization studies of $Co(mhd)_3$ (mhd = anion of 5-methylhexane-2,4-dione) were reported and a detailed treatment of the kinetics was presented,[17] based in part on a topological representation of the rearrangement processes presented earlier by Muetterties.[18] The related complexes $Al(pmhd)_3$ and $Ga(pmhd)_3$ (pmhd = anion of 1-phenyl-5-methylhexane-2,4-dione) were also studied using the diastereotopic groups on the ligand as a probe into the racemization process. It was concluded on the basis of a kinetic analysis combined with computer-simulated n.m.r. spectra that the most likely rearrangement mechanisms are certain bond rupture processes or twisting processes in various ratios. However, as with all previous studies, no unambiguous choice of a single mechanism was possible.[19]

Conclusions

Geometrical isomerization and racemization of metal beta-diketonates occur by a common intramolecular path. A bond rupture process to give a 5-coordinate intermediate seems the most likely path based on a variety of indirect evidence. However, the need for a strong inference experiment to distinguish between bond rupture and twisting pathways is to be emphasized.

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BONDING AND STEREOCHEMICAL STUDIES OF UNSATURATED ORGANOLITHIUM COMPOUNDS

Joseph J. Brooks September 27, 1971

Introduction

Over the past few years the general area of main group organometallic chemistry has experienced a rapid expansion in scope and interest. This expansion has largely been due to the great variety and usefulness of the reactions of main group organometallic compounds. They find extensive use in polymerization, oligomerization, hydrogenation, and isomerization of unsaturated organic compounds.

Organolithium compounds comprise an important part of main group organometallic chemistry.[1] The current important status of homogeneous reactions of olefins and 1,3-diolefins is largely due to the development of allylic and benzylic organometallic catalysts.[2,3,4,5,6] The polymerization of styrene[7] and isoprene[2] are examples of such reactions which involve organolithium compounds. This type of reaction is thought to proceed via σ- or π-allylic or benzylic organometallic intermediates. Various mechanisms have been proposed for such polymerization reactions,[2] but attempts to firmly establish the true mechanism have been impeded by a lack of stereochemical information concerning the nature of the organometallic intermediates involved. In particular, the degree of solvation expected for organolithium reagents and the nature of the interaction of the metal atom with unsaturated organic groups have been undetermined.

Prior to 1970 the only detailed structural studies of organolithium compounds which had been done were of the unsolvated species CH_3Li,[8] C_2H_5Li,[9] and $LiAl(C_2H_5)_4$.[10] These could generally be described as polynuclear species exhibiting structural properties which suggest electron difficient bonding. The first structural study to address itself to the question of solvated unsaturated organolithium compounds was that of benzyllithium triethylenediamine.[11] The structure is described as solvated intimate ion pairs consisting of a benzyl carbanion and two amine groups coordinated to a lithium cation. The lithium atom is proposed to be sp^2 hybridized if one considers that the benzyl group occupies only one coordination site. The most interesting results to come from this study are: (1) the sp^2 hybridization and coordination number of three for the lithium atom, and (2) the π-benzylic geometry of the lithium atom with respect to the organic group.

The initial findings of Patterman _et al_.[11] raise three questions:

(1) Is the coordination sphere of two solvent sites and one organic site per lithium atom the usual pattern?

(2) Is the π-benzylic geometry assumed by the lithium atom the result of specific intramolecular bonding interactions, or is it simply a solid state packing effect that causes the lithium atom to assume this configuration?

(3) Is it possible to generalize the sterochemistries of solvated Group I organometallic complexes? For example, can one predict the stereochemistries of the alkali metal complexes formed with π organic groups from the ground state properties of the organic species?

With the hope of finding answers to these questions, a structural investigation of a series of unsaturated organolithium compounds was undertaken.

Summary of Findings

Detailed single-crystal X-ray structural studies of $C_{13}H_9Li(NC_7H_{13})_2$, $(C_6H_5)_3CLi[(CH_3)_2N(CH_2)_2N(CH_3)_2]$, and $C_{10}H_8\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2$ have yielded the following results: (1) the coordination sphere of lithium in amine solvated unsaturated organolithium compounds has been firmly established to consist of two amine groups and one organic group per lithium atom, (2) the most suitable area for the coordination of the lithium atom can be predicted on the basis of gross atomic charges from CNDO molecular orbital calculations, (3) the π-benzylic geometry of the lithium-carbanion species is attributed to covalent contributions to the bonding and can be rationalized on the basis of orbital symmetry arguments, and (4) a correlation between lithium-nitrogen bond lengths and carbanion stabilities has been established.

In addition the structural information obtained from these studies should be valuable in establishing mechanisms for reactions which involve species of this type as intermediates. The groundwork laid by these studies forms a base for further research on systems specifically selected to test the conclusions we have drawn which should lead to a more quantitative basis for predicting lithium-organic group interactions.

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KINETICS AND MECHANISMS OF OXIDATION-REDUCTION REACTIONS INVOLVING AQUATED CU(I) AND METAL ION COMPLEXES

Michael Broccardo October 19, 1971

Introduction

Within the last 20 years rapid progress has been made in understanding the mechanisms of oxidation-reduction reactions involving metal ion complexes.[1] Until recently, efforts to study reactions of aquated cuprous ion, $Cu(H_2O)_x$ (X=2 or 4), have been prevented by its instability towards disproportionation in non-complexing aqueous media.

$$2Cu(aq)^+ = Cu(aq)^{2+} + Cu^o(s)$$

Keq = 1.8×10^6 M^{-1} at T = 25.0° C and $\mu = 1.13$ <u>M</u> $NaClO_4$.[2]

For example, cupurous-oxo anion salts, such as Cu_2SO_4, are <u>rapidly</u> decomposed by water to copper and the cupric salt. In fact, the only cupurous compounds which are stable towards water are the highly insoluble ones like CuCl, CuCN, and Cu_2S.[3] On the other hand, copper(I) as a solvated ion is stable in a number of non-aqueous solvents, e.g., nitromethane and acetonitrile.[4] In aqueous solution, the +1 oxidation state may be stabilized by the addition of complexing agents which exhibit a strong affinity for Cu(I) as compared to Cu(II), such as CN^-, I^-, Br^-, Cl^-, nitriles (RCN) thioethers (R_2S), and other sulfur containing ligands. Whereas, "hard" ligands such as F^-, H_2O, carboxylates, and other ligands involving only oxygen (except O^{2-}) do not form complexes at all with Cu(I) or demonstrate their greater affinity for Cu(II) by causing disproportionation.

The earliest attempt to study the rates and mechanisms of redox reactions of hydrated cupurous ion in non-complexing aqueous solution was made by Endicott and Taube.[5] They reported approximate rate constants for the reduction of four Co(III) complexes in perchlorate solution. These studies were based on the use of very small concentrations of Cu^+ in equilibrium with copper metal and high concentrations of Cu^{2+}.

Preparation of Perchlorate Solutions of $Cu(aq)^+$

In 1967, Espenson, Parker, and Shaw reported that metastable solutions of $Cu(aq)^+$ could be prepared by reduction of an excess of $Cu(H_2O)^{2+}$ with the one-electron reducing agents, $Cr(H_2O)_6{}^{2+}$ and $V(H_2O)_6{}^{2+}$, in dilute perchloric acid.[6]

$$Cu^{2+} + Cr^{2+} \rightarrow Cu^+ + Cr^{3+} \qquad [Cu^{2+}]_o > [Cr^{2+}]_o$$

$$Cu^{2+} + V^{2+} \rightarrow Cu^+ + V^{3+} \qquad [Cu^{2+}]_o > [V^{2+}]_o$$

Both reactions are slow, but go virtually to completion. Under these conditions, the product was verified to be Cu^+ by the following means: (1) the decrease in the Cu^{2+} concentration upon completion of the reactions corresponded quite closely to the 1:1 stoichiometry required; (2) the kinetic data on the reaction of Cu^{2+} with Cr^{2+} and with V^{2+} also confirmed the 1:1 stoichiometry; (3) there was no immediate evidence for formation of copper metal.

The UV-Visible spectrum of $Cu(aq)^+$ showed no maxima; only an increasing absorbance with decreasing wavelength was noted below 3500A°, as expected for an aquo ion with a $3d^{10}$ electronic structure.

These solutions are quite stable for several hours under the following conditions:

a) Oxygen and other oxidizing agents are absent
b) the $Cu(aq)^+$ concentration is low ($\leq 10^{-2}\underline{M}$)
c) the solutions are acidic ($[H^+] \geq 10^{-2}\underline{M}$)
d) no metallic surfaces are present

In the presence of excess Cr^{2+} (or V^{2+}), Cu^+ is readily reduced to the metal

$$Cu^+ + Cr^{2+} \text{ (or } V^{2+}) \rightarrow Cu^o(s) + Cr^{3+} \text{ (or } V^{3+})$$

However, this reaction is unimportant when Cu^{2+} is in excess.

Kinetics and Mechanisms

Oxidation-reduction reactions involving metal ions are generally classified as either inner-sphere or outer-sphere. In an inner-sphere reaction, the two metal ions are linked by a common bridging ligand at the time of electron transfer, while in an outer-sphere reaction, both metal ions retain their inner-coordination spheres during the electron transfer process.

Espenson and Parker have studied the kinetics of the oxidation of $Cu(aq)^+$ in perchlorate solution by a number of cobalt(III) complexes of the general formula $Co(NH_3)_5X^{3-n}$, where X = halide, pseudohalide, or aquo ligands.[9] The reactions were shown to follow the 1:1 stoichiometry given below:

$$Co(NH_3)_5X^{3-n} + Cu(aq)^+ + 5H^+ \rightarrow Co(aq)^{2+} + Cu(aq)^{2+} + 5NH_4^+ + X^{n-}$$

The rate expression is first order in each metal ion and independent of proton concentration (except for the aquo complex).

An inner-sphere mechanism is proposed on the basis of: 1) the high reactivity of the hydroxo complex compared to that of the aquo complex; 2) the high reactivity of the azido complex compared to that of the thiocyanato complex; and 3) the large spread in the values of the rate constants.

Catalytic Reactions Involving Cu(1)

Copper(II) has been found to be an effective catalyst for many different reactions, including certain oxidation-reduction reactions between metal ions.[5,10,11,12] Frequently, Cu(I) is postulated as an intermediate in such processes.

One such reaction is the catalysis by $Cu(aq)^{2+}$ of the oxidation of V^{3+} by Fe^{3+}.

$$V^{3+} + Fe^{3+} + H_2O = VO^{2+} + Fe^{2+} + 2H^+$$

Higginson and Sykes proposed the following two step mechanism to account for the catalytic effect of Cu^{2+} [12]

$$V^{3+} + Cu^{2+} + H_2O = VO^{2+} + Cu^+ + 2H^+$$

$$Cu^+ + Fe^{3+} \xrightarrow{\text{fast}} Cu^{2+} + Fe^{2+}$$

With metastable $Cu(aq)^+$ solutions at their disposal, Espenson and co-workers were able to study the kinetics of these reactions in detail. Their findings demonstrate that Higginson and Sykes proposed mechanism is correct.[13,14,15]

Additional Methods of Preparing Aqueous Solutions of Copper(I) Perchlorate

Altermatt and Manahan have published an electrochemical procedure for generating aqueous solutions of copper(I) perchlorate and have also shown that $Cu(aq)^+$ solutions may be prepared by the careful dissolution of the freshly precipitated hydroxide in perchloric acid.[16,17]

Summary:

Dilute solutions of $Cu(aq)^+$ may be prepared via reduction of $Cu(aq)^{2+}$ with an insufficient quantity of strong one-equivalent reducing agents such as Cr^{2+} and V^{2+} or via electrochemical procedures. These solutions are stable for several hours if protected from oxygen and metal surfaces, and exhibit strong reducing properties. The reduction of metal complexes possessing good bridging ligands by $Cu(aq)^+$ most likely proceeds by an inner-sphere mechanism. Finally, copper(I) is probably an active intermediate in many redox reactions catalyzed by copper(II).

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ELECTROCHEMICAL STUDIES OF METAL 1,2-DITHIOLENE COMPLEXES

Kim D. Johnson October 26, 1971

Introduction

Interest in transition metal complexes coordinated through sulfur is by no means a recent development.[1,2] In the mid 1930's attention was given to the analytical uses of dithiols or dithiolates, particularly the reactions of toluene-3,4-dithiol and 1-chlorobenzene-3,4-dithiol with metal halides.[3,4] The great amount of work done in the last ten years on the metal 1,2-dithiolenes seems to be the outgrowth of a paper by G. N. Schrauzer in August 1962[5] in which he prepared $NiS_4C_4Ph_4$ from $Ni(CO)_4$, sulfur, and diphenylacetylene. Since then many $[MS_4C_4R_4]^z$ and $[MS_6C_6R_6]^z$ compounds have been prepared with widely varying metals and R groups.[6] Two of the more unusual characteristics of this class of compounds which have caused great interest are the trigonal prismatic coordination of the tris compounds[7] and the ease at which they undergo one electron transfer reactions. Much attention has been given to the three-membered series of planar complexes

$$[M\text{-}S_4]^0 \leftrightarrow [M\text{-}S_4]^{-1} \leftrightarrow [M\text{-}S_4]^{-2}$$

Although most of these compounds have been studied by esr and their ir, visible, polarographic, and magnetic data are available, the primary question of ground state electronic configuration is still unsolved.[8]

Polarographic and Voltammetric Studies

In 1967, Davison and Holm[9] systematized the existing $E_{1/2}$ values and made certain generalizations about the synthetic and chemical behavior of the planar 1,2-ditiolenes. This study pointed out the powerful oxidizing ability of $[NiS_4C_4(CF_3)_4]^0$ and its analogs. However, when using this oxidizing agent, care must be taken to avoid ligand exchange reactions as described by Davison and McCleverty.[10] Just as electrochemical studies played a major role in the characterization of these ligand exchange reactions, they also helped in the demonstration that there exists discrete dimeric complex ions which could undergo one-electron transfer reactions.[11] The following process has been demonstrated for cobalt and iron:

$$[M\text{-}S_4]_2^0 \leftrightarrow [M\text{-}S_4]_2^{-1} \leftrightarrow [M\text{-}S_4]_2^{-2} \leftrightarrow [M\text{-}S_4]^{-2}$$

Examination of the $E_{1/2}$ values for a series of compounds shows that for the simple 1,2-dithiolenes the decreasing oxidative stability of the dianions was in the order $R=CN>CH_3>Ph>H>Me>Et$. In other words, the dianions are the most stable to oxidation when R is an electron-withdrawing group. In fact, it has been shown that there is a linear relationship between $E_{1/2}$ and Taft's σ^* constant which is an inductive substituent constant.[12]

The tris complexes behave much the same as the bis complexes and, in certain cases, all the members of the five-member electron-transfer series have been detected,

$$[M\text{-}S_6]^{-3} \leftrightarrow [M\text{-}S_6]^{-2} \leftrightarrow [M\text{-}S_6]^{-1} \leftrightarrow [M\text{-}S_6]^{0} \; (\leftrightarrow [M\text{-}S_6]^{+1})$$

Again there is a marked dependence of the $E_{1/2}$ value with the nature of the R group. The fact that the $E_{1/2}$ value depends more on the R group than it does on the particular metal ion has been used as evidence that the electron in question is in an orbital with a large amount of ligand character.

In 1967, McCleverty published an extensive study of the reaction of charged cobalt and iron dimers with a wide variety of Lewis bases.[13] The dimers dissociated and formed the five-coordinate adducts with no evidence for any further coordination. This and other studies[14] show that all complexes of this type undergo electron-transfer reactions and many are obtainable as the monocationic, neutral, and monoanionic species. A small amount of work has been done on the vanadyl, chromyl, and molybdenyl dithiolene systems using electrochemical data to support the existence of certain species in the series.[15]

Compounds of the metal dithiolenes with cyclopentadienyl molecules have been prepared and several have been studied voltammetrically.[16] It is interesting that the reduction of the complexes became more cathodic in the order Fe<Co<Ni and Co>Rh>Ir.

One of the most unusual studies of the metal dithiolenes was that of Schmitt, Wing, and Maki[17] in which they placed $NiS_4C_4(CF_3)_4$ between layers of an aromatic organic π donor system and obtained a semiconductor.

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STRUCTURAL CHEMISTRY OF CESIUM TRANSITION METAL TRIHALIDES
(Thesis Report)

Ting-I Li November 16, 1971

Introduction

Double salts of the type, RMX_3, where R is a large monovalent cation, M a divalent first row transition metal ion, and X a halide ion, have been known for a long time.[1] Crystal structures of several of these compounds have been determined previously[2-11] and have been found to consist of $[MX_6]^{-4}$ octahedra sharing faces. In most of the structures, the octahedra are in parallel infinite linear chains with hexagonal symmetry and the cations are fitted in between the chains. The metal-metal distances between shared-faced octahedra are relatively short. Magnetic coupling has been found to be significant.[12]

Results

In the series of compounds RMX_3, anomalous structures are expected for the $^2E_g(Cu^{+2})$ and $^5E_g(Cr^{+2})$ configurations. The structures of these and other systems not isostructural with $CsMgCl_3$ were investigated.

$CsCrBr_3$ as well as $CsCrCl_3$ was found to crystallize in infinite linear chains of octahedra sharing faces. A slight distortion from the center of the octahedron was found for the chromium ion. This is an unusual structure for a chromium(II) compound. The optical spectrum was also studied.

$CsCuCl_3$ has been found previously to possess a lower symmetry.[4] The central copper atom is displaced significantly from the trigonal axis by a Jahn-Teller distortion. $CsCuBr_3$ was found not to be isostructural with $CsCuCl_3$. It crystallizes as facial-shared dimeric octahedra which are polymerized by sharing every corner of each dimer. It was found that this compound is diamagnetic.

The $CsMnCl_3$ structure was found to contain facial-shared trimeric octahedra and is polymerized by sharing two corners of each trimer and is in the rhombohedral $R\bar{3}m$ space group.

A preliminary structural study of $CsTiCl_3$ was also carried out. This compound was found to crystallize in $P6_3/mmc$ with six molecules per unit cell. It is proposed that the structure consists of alternating monomeric and dimeric octahedra linked through two corners of each unit. Preliminary studies of several iodide compounds show that they are isostructural with $CsMgCl_3$.

Correlation of the available data allow one to systematize the crystal structures of the RMX_3 compounds so that predictions of unknown structures of this group of compounds can be made. The types of structures which can be obtained and the factors which determine which structure is obtained will be briefly discussed.

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METAL-METAL INTERACTIONS IN COPPER-CONTAINING PROTEINS

Elvira F. Hasty November 18, 1971

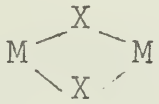
Recently several transition metal elements have been found to form interesting compounds containing two or more metal atoms per molecule. Interactions between these metal atoms have been observed and could be classified as of two types:[1]

1. Direct metal-metal interactions.

M-M

2. Indirect metal-metal interactions.

M-X-M



X = halogens, oxygen, sulfur

Studies on Cu(II) compounds exhibiting metal-metal interactions have been most extensive with Cu(II) acetate and its homologs. The structure for $Cu(OAc)_2$ monohydrate has been determined and a copper-copper interaction has been established.[1]

Copper in biological systems.

In 1890 Bertrand introduced the term "oxidase" on his work on the oxidation of phenol catalyzed by the proteins laccase and tyrosinase. He incorrectly identified the metal as manganese. In the 1930's, it was clearly demonstrated that both enzymes contain copper. Since then, much research has been done on copper-containing proteins.

There appears to be three main forms of copper in copper-containing proteins:[2] two paramagnetic forms distinguished by their spectral properties, and a diamagnetic form.

1. Blue-Cu or type 1 copper(II).
2. Non-blue Cu or type 2 copper(II).
3. ESR-nondetectable copper.

Fungal Laccase.

Fungal laccase is a copper-containing oxidase which catalyzes the oxidation of diphenols and substances of similar nature by molecular oxygen. It contains four copper atoms per molecule; two of these give ESR signals; the other two are diamagnetic. Of the two copper atoms giving ESR signals, one is known to be a type 1 copper(II) absorbing at 610 mμ, and the other, a type 2 copper(II) with no significant absorption in this region.

Anaerobic oxidation-reduction titrations were performed by Malmström and co-workers[3] using several reductants and following the course of the reduction by both optical and ESR measurements. These

gave evidence for the possible existence of a Cu(II)-Cu(II) pair. Further research on fungal laccase by Malmström, Malkin and Vånngård[4] resulted in a spectroscopic differentiation of the electron-accepting sites. A two electron accepting site was related to the Cu(II)-Cu(II) pair with an absorption band at 330 mμ. Similar results have been observed on Rhus Vernicifera laccase.[5,6]

Cytochrome Oxidase.

Cytochrome oxidase is the terminal oxidase in the mitochondrial respiratory chain. Its molecular weight is still unknown. Different units have been proposed, but that of a minimal cytochrome oxidase unit containing two iron atoms and two copper atoms has been accepted. The iron in the heme units is present as Fe(III), one in the low-spin form and the other one in the high-spin form.

Beinert and co-workers[7] studied the state of copper in cytochrome oxidase by ESR spectroscopy. The integrated signal intensity of the copper accounts for about 40% of the total copper present. A few years later, Beinert and Van Gelder[8] studied the heme components of cytochrome oxidase by ESR spectroscopy at different states of oxidation, both in the presence and in the absence of specific ligands. Results obtained from these experiments, together with magnetic susceptibility measurements performed by Ehrenberg and co-workers,[9,10] led to the conclusion that an Fe(III)-Cu(II) interaction is present in the native enzyme. The most probable type of interaction is an antiferromagnetic coupling of electron spins.

Hemocyanin.

Hemocyanin is an oxygen carrying pigment found in the blood of Mollusca and Arthropoda. It has been established that the binding of oxygen by hemocyanin is a reversible process which involves two copper atoms per oxygen molecule. Hemocyanins from various sources have molecular weights from one million to several millions, and undergo reversible association-dissociation processes.

For years, it was assumed that the copper in hemocyanin and in oxyhemocyanin is present as Cu(I). Neither gives an ESR signal and both are diamagnetic. However, the blue color and the absorption spectrum of oxyhemocyanin are very similar to those of Cu(II) complexes. Klotz and Klotz[11] observed that in oxyhemocyanin about half of the copper content of the enzyme had been converted to Cu(II). They concluded that in oxyhemocyanin a Cu(I)-Cu(II) pair with a bridging O_2^- is present. Later, Van Holde[12] observed four components in the optical and circular dichroism spectra of oxyhemocyanin. By comparing the absorption bands and their intensities with those of copper-proteins known to contain Cu(II), he concluded that Cu(II) is present in oxyhemocyanin. Also a band at 347 mμ was related to either a Cu(I)-Cu(II) charge transfer or to a charge transfer between copper and oxygen. Van Holde explained these observations as due to a Cu(II)-Cu(II) interaction having an $O_2^=$ unit as a bridging group.

Ceruloplasmin.

Ceruloplasmin is an intensely blue copper protein isolated from plasma. It has a molecular weight of 160,000 and contains 7 or 8 copper atoms per molecule. It catalyzes the oxidation of Fe(II) and certain diamines and polyphenols with reduction of oxygen to water. Malmström, Vänngård and others have done much work on the state of the copper, its environment, and the electron accepting sites in ceruloplasmin.[13-17] Due mainly to its similarity to laccase in the optical absorption and in ESR measurements, the possibility of a copper-copper interaction has been discussed; however, there is not enough evidence to indicate surely that this interaction is present.

Conclusion.

Experimental observations seem to indicate that metal-metal interactions are present in some copper-containing proteins. Further research in this area is extremely important for a better understanding of the role of copper in biological systems.

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PHYSICAL AND CHEMICAL PROPERTIES OF SOME MACROCYCLIC LIGANDS WITH NITROGEN DONOR ATOMS

Martha S. Okamoto

March 23, 1972

Introduction

Transition metal complexes of macrocyclic ligands are well known in biological systems. They include compounds such as Vitamin B_{12} and heme, containing a corrin ring and a porphyrin ring, respectively. Until recently, however, there were very few synthetic macrocycles available for study. The development of new approaches to the synthesis of these compounds has enabled a great deal of work to be done in this field.

Synthesis

A common feature in the synthesis of macrocyclic ligands is the metal ion template effect, that is, most of the ligands cannot be made in the absence of the metal ion. The mechanisms of these reactions, however, are quite complex, and it is not entirely clear whether this is a kinetic or a thermodynamic effect.

One of the first of these complexes was isolated by N. F. Curtis[1,2] from non-aqueous solutions of $[Ni(en)_3](ClO_4)_2$ and acetone. After some difficulty the product of this reaction was found to be that of the macrocyclic ligand CT (structures are given on the last page). Other ligands formed via condensation of amines and carbonyls include TIM, first made by Baldwin and Rose;[3] Jager's compounds;[4] AT and its trifluoro methyl analogue, made by Cummings and Sievers;[5] CR, made by Curry;[6] and TAAB and TRI made by Busch and coworkers.[7]

Spin-State Equilibria

Because of the strong in-plane ligand field exerted by these ligands, the complexes can approximate either square planar or pseudo-octahedral (tetragonal) symmetry depending on the field strength of the axial ligands. With square planar geometry, the complexes are diamagnetic, and with tetragonal symmetry, they are paramagnetic. It should be possible to find ligands of intermediate strength in which the singlet and triplet states exist in equilibrium. This has been found to be the case with many of the macrocyclic complexes. However, their magnetic behavior in various solvents and in the solid state suggests that there are many complex factors involved.[8,9]

Electrochemistry

It has been found that the macrocyclic ligands are capable of stabilizing unusual oxidation states of metals. Complexes in which the metal ion is formally in the +1, +2, and +3 oxidation states have

been prepared and characterized for Cu,[10,11,12] Ni,[13,14] and Co,[15,16,17] using CT, CTH, CR, CR + 4H (the tetramine derived from CR), and TAAB. Most of these complexes have been isolated and some are quite stable. The ability of the macrocycles to stabilize these states has been attributed partially to the negligible rates of dissociation of the complexes. The relative ease of oxidation and reduction with different ligands has been related to structural parameters such as the degree of unsaturation.

Future Work

It seems clear that in the future the emphasis will lie less on the syntheses of macrocyclic compounds (for by an extension of the syntheses already employed almost any desired macrocycle can be made) and more on the study of their physical properties and redox chemistry. There is still a great deal of work to be done in this area. Much insight into natural systems can then be gained from a fuller understanding of the synthetic macrocycles.

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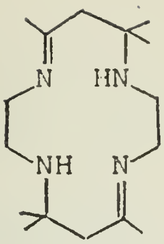

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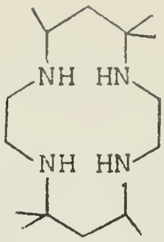

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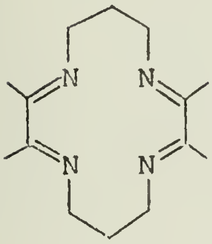
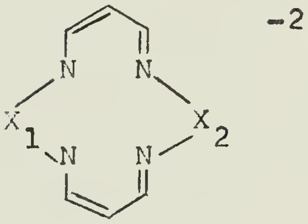
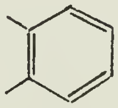


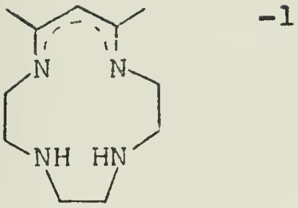
TIM



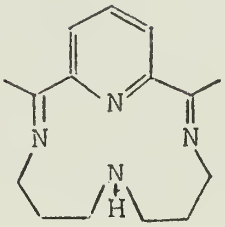
Jager

$X_1, X_2 = (CH_2)_2$

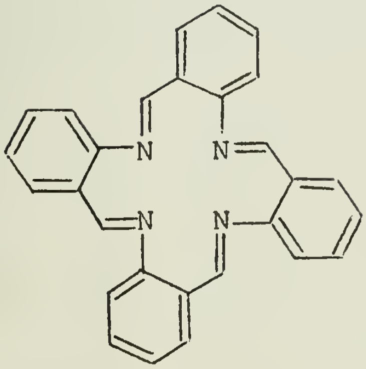




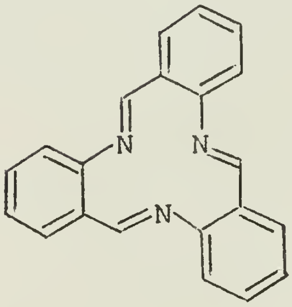
AT



CR



TAAB



TRI

Metal Binding Sites in Nucleic Acid-Mercury(II) Complexes

Blaine H. Byers April 4, 1972

Introduction

Early studies of metal interactions with nucleic acids emphasized the alkali and alkaline-earth metals. In most of these reactions, the metals were electrostatically bonded to the negatively charged oxygen atoms of the phosphate groups. More recently, some metals have been found to interact also with the purine and pyrimidine bases.[2] Silver(1), mercury(II), and platinum(IV) appear to react almost exclusively with the heterocyclic bases. Both silver(I) and mercury(II) are unique in that they bond very strongly, yet reversible with the purines and the pyrimidines. Attempted identification of these base binding sites for mercury(II) complexes has led to some very contradictory results.

Early Studies

In 1952, Katz[3] first discovered the reaction of $HgCl_2$ with DNA. Upon addition of excess chloride or cyanide ion, complete physiochemical reversibility was obtained, and further studies indicated reversibility of biological activity as well.[5-7] Spectrophotometric data[4] suggested metal interaction with the nitrogenous bases in both 1:1 and 2:1 DNA-mercury(II) complexes. Although other authors[1,5,7-12] reported similar 1:1 and 2:1 complexes for DNA and RNA of varying base composition, identification of specific binding sites was only speculative. With simplified systems containing only nucleosides, more information regarding mercury(II) binding sites was obtained. Predictions for polynucleotide complexes were then possible.

Binding Sites

Most of the initial mercury-nucleoside experiments were concerned with the release (or lack of release) of protons during complexation.[1,6,13,14] Since mercury-nitrogen bonds are known to be stronger than mercury-oxygen bonds in most systems, only nitrogen sites were considered by all investigators except Eichhorn.[13] If only nitrogen sites are involved, there are four possible generalized reaction schemes.

(1) $Hg(OH)_2 + NH = NHgOH + H_2O$ no pH dependence

(2) $Hg^{2} + NH = NHg^{+} + H^{+}$ more mercuration as pH increases

(3) $Hg(OH)_2 + N = NHgOH + OH^{-}$ more mercuration as pH decreases

(4) $Hg^{2+} + N = NHg^{2+}$ no pH dependence

NH represents a protonated nitrogen atom and N is an unsaturated ring nitrogen atom. Hg^{2+} is either a solvated ion or an undissociated salt such as $HgCl_2$. Since reactions (1) - (4) show varying pH dependence, numerous experimental studies of the pH dependency of the systems were investigated. In general, these proton release studies concluded that at a particular pH mercury binding

occurred at the same sites as protonation. Thus, amino nitrogens were included as possible binding sites. Using these assumptions, Simpson[15] was able to calculate association constants for most of the nitrogen sites in methylmercury-nucleoside complexes. In general, his values were similar to hydrogen ion association constants for the same nucleoside sites Gruenwedel pursued the methylmercury reaction further and found that methylmercury denatured DNA irreversibly.[14]

Raman spectra of the mercury-cytidine complex confirmed bonding to unsaturated ring nitrogens and suggested that at a pH of 5-6 no amino nitrogens were involved in mercury(II) bonding.[16] In addition, no evidence for a $HgCl_2$-cytidine complex was observed. On addition of excess chloride ion, resonances attributable to the species $HgCl_3^-$ and $HgCl_4^{2-}$ appeared. Further support for unsaturated ring nitrogen bonding was obtained in an NMR study conducted in DMSO.[17] Again the mercury-cytidine complex was studied. The amino proton resonance was shifted downfield and split into a broad doublet, indicating hindered rotation about the carbon-nitrogen bond. This supported strong metal interaction at the #3 nitrogen atom. (see structures below)

A recent crystal structure of the 2:1 uracil-mercuric chloride complex raises some new questions with respect to earlier experimental results. Each mercury atom is bonded to four chloride ions and the #4 carbonyl oxygen of two different uracil bases. The binding of oxygen to the metal is consistent, however, with the conclusions drawn by Eichhorn[13] in mercury-uridine and mercury-quanosine complexes. Since the complex is with uracil and not uridine, comparison with earlier results may not be valid.

Summary

Metal interactions with bases, nucleosides, and polynucleotides are not necessarily identical. Generalized assumptions coupled with intersystem comparisons may results in erroneous conclusions. Due to the apparent large pH dependency, systems studied at different acidities may yield completely different results. Before any final conclusions can be obtained regarding nucleic acid-mercury(II) binding sites, these systems must be studied in a more systematic manner.

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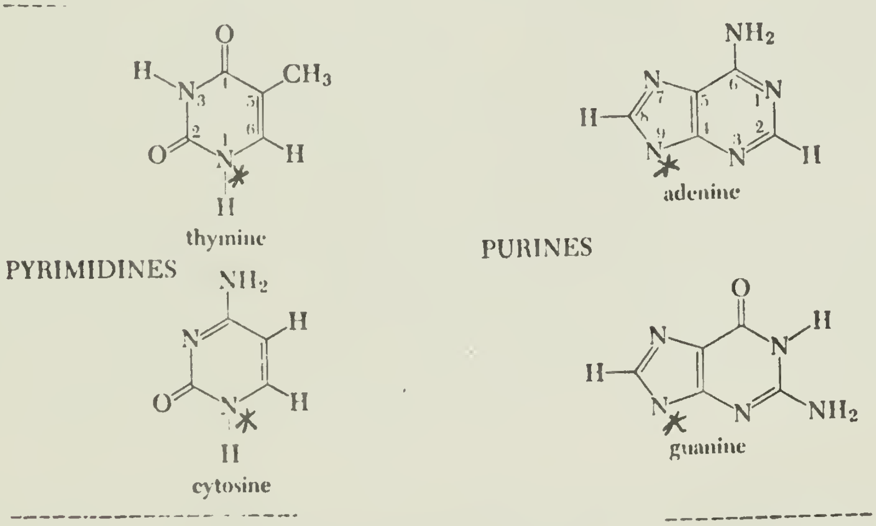

* Site of Bonding to Sugar

PHOTOISOMERIZATION REACTIONS OF PLATINUM(II) COMPLEXES

R. Martin Guidry

April 11, 1972

Introduction

During the past decade, the seemingly forgotten area of the photoisomerization chemistry of platinum(II) complexes has had a reawakening. The geometrical photoisomerization of the Pt(ethylthioglycolato)$_2$ system, reported by Ramberg in 1910, was the first light-induced isomerization reaction of a divalent platinum complex. Lifschitz and Froentjes[4,5,6] investigated the photoisomerization chemistry of nearly a dozen other platinum(II) complexes. Despite this groundwork, chemists ignored this truly exciting and relatively unknown area of chemistry for the next thirty years. Then, during the early 1960's, the Italians and Americans replaced the pioneer Germans in the investigation of the photoisomerization reactions of divalent platinum.

Discussion

In 1965, Balzani and coworkers[7] reported the cis to trans photoisomerization reaction of the bis(glycinato)platinum(II) complex. They noted that, although the thermal isomerization reaction requires free glycine to occur, the photochemical isomerization reaction proceeds whether free glycine is present or not. Furthermore, if free labeled glycine is introduced into the system, it is found that the photoisomerization reaction, unlike the thermal reaction, produces no products containing labeled glycine. From this data, Balzani and his coworkers concluded that the light-induced isomerization reaction must proceed through an intramolecular mechanism without bond rupture. They postulated that this mechanism involved a twisting mode in which the complex went through a triplet tetrahedral excited state. After noting that the trans to cis photoisomerization reaction did not occur, they further postulated that the excited state must actually be distorted tetrahedral.[7,8,9] A theoretical study of this particular system by Shillady and coworkers[10] supported the work of Balzani's group. Using an extended Hückel method, Shillady was able to show that the excited state equilibrium geometry was indeed a triplet distorted tetrahedron favoring the trans isomer.

Working independently of each other, Mastin and Haake[11] and Martin[12] both observed the cis to trans photoisomerization reaction of Pt(pyridine)$_2$Cl$_2$ in chloroform solution. Martin[12] was able to show that much higher quantum yields could be obtained in solutions which were not deoxygenated. It was not, however, until Balzani and coworkers[13] thoroughly investigated this system that any genuine attempt was made to elucidate the mechanism by which this reaction proceeds. Through preliminary experimentation, Balzani and his coworkers were able to determine that, both in the presence and in the absence of free pyridine, the cis and trans isomers of this compound in chloroform solution are thermally inert. Furthermore, by very

carefully controlling the conditions of the irradiation and by varying the length of time by which the secondary thermal reaction was allowed to proceed during the postirradiation period, they were able to show that this reaction actually proceeds by two different mechanisms. During the period of irradiation, an intramolecular pathway is followed in the transformation of the cis isomer to the trans isomer. It is not certain, however, whether or not this mechanism involves bond rupture. One likely possibility involving bond rupture is the photodissociation of a Cl^- with the subsequent formation of the ion pair $Pt(py)_2Cl^+ \cdot Cl^-$. There is then a recombination within the ion pair to form either the cis or trans isomer. The second mechanism, which occurs primarily in the postirradiation period, is an intermolecular mechanism. It is believed that at the end of the irradiation period, the complex $Pt(py)Cl_2S$ exists in a cis:trans ratio of 2:1. During the postirradiation period, the researchers suggest that a free pyridine molecule replaces the solvent molecule in the coordination sphere leading to both cis-$Pt(py)_2Cl_2$ and trans-$Pt(py)_2Cl_2$. The formation of the solvent coordinated complex is believed to proceed through the tricoordinate intermediate $Pt(py)Cl_2$.

Although the above is the only thorough mechanistic work which has been attempted, several other photochemical rearrangements have been observed in divalent platinum complexes. Among these are the geometrical isomerization reactions of the bis(triethylphosphine)-dichloroplatinum(II) complex.[14,15] Haake and Hylton[14] have determined that this reaction is very solvent dependent, i.e., the higher the dielectric constant of the solvent, the higher the cis:trans ratio of the products. Another system which is believed to photoisomerize is the cis isomer of the complex ion $[Pt(NH_3)_2(H_2O)_2]^{2+}$. Perumareddi and Adamson[16] have speculated that, due to a change in the absorption spectrum of the cis isomer upon irradiation, a photoisomerization reaction occurs. There is, however, little experimental evidence to support their conclusions.

A final light-induced isomerization reaction which has recently been found is that of the (dicyanoacetylene)bis(triphenylphosphine)-platinum(II) complex, which on irradiation by sunlight slowly photoisomerizes to the cyano(cyanoacetylido)bis(triphenylphosphine)platinum(II) complex over a period of three to five years.[17] Baddley and coworkers[17] discovered this reaction while remeasuring the infrared spectra of some complexes that they had synthesized several years earlier. They noticed that, for this particular complex, several new bands appeared in the spectrum. Upon further irradiation of the aged sample in acetone solution, it was observed that only the new infrared bands remained. By employing this infrared data and a crystallographic study, the researchers were able to determine that the new complex was the cyano(cyanoacetylido)bis(triphenylphosphine)platinum(II) compound, which contains the novel cyanoacetylido group.

Conclusion

In most cases, it has been observed that, in order for photoisomerization to occur, the ligand field bands of the complex must be irradiated. Furthermore, if unfiltered light is used in the photoreaction, often the primary process becomes the photodecomposition reaction because of the irradiation of the charge transfer bands. It is generally found that, if a particular ligand field band is irradiated, the cis to trans photoisomerization reaction occurs much easier than the corresponding trans to cis photoisomerization process. The quantum yields for the light-induced reaction of divalent platinum complexes have been found to be very dependent on the solvent and the wavelength of irradiation. Although relatively little work has been done on the elucidation of the mechanisms of these photoreactions, it does appear that no one general mechanism will satisfy all platinum(II) photoisomerization reactions. It has been found that the light-induced reaction proceeds through both an intramolecular and intermolecular mechanism--the particular mechanism or mechanisms depending on the compound under study. Because so little work has been done in this area, it presents itself as one of the true frontiers of chemistry.

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TRANSITION METAL CHEMISTRY OF CYCLOPROPANE

Jimmy H. Davis April 25, 1972

Introduction

Cyclopropane is similar, in many ways, to olefins. From the results of spectroscopic measurements and theoretical calculations, it was suggested as early as 1949 that there must be electron delocalization in the cyclopropane ring comparable to that of olefins. It was subsequently found that cyclopropane, like olefins, undergoes an addition reaction with bromine to yield 1,3-dibromopropane[2] and is capable of forming addition polymers in a manner analogous to olefin derivatives in vinyl polymerization.[3] A study[4] comparing the reactivity of cyclopropane with that of olefins was responsible for the birth of the transition metal chemistry of cyclopropane.

Platinum Chemistry

The products of the reaction of cyclopropane and hexachloroplatinic acid was reported by Tipper to be a dimer with the three membered ring intact.[4] Later, it was suggested[5,6] that Tipper's Compound is a polymer and that the ring is opened. The crystal structure[7,8] of the pyridine adduct of Tipper's Compound confirmed the ring opening. However, recent mass spectral and molecular weight data[9] show that Tipper's Compound is tetrameric.

A propylene analog of Zeise's dimer[10] and a cyclobutenium cation[11] have been reported as products from cyclopropane reactions with platinum complexes. It has been found that the reactivity of substituted cyclopropanes increases with increasing electron density in the ring[12] and that the selectivity of ring bond breaking depends upon the donor capacity of the carbon center forming the carbon-platinum bond.[13]

Palladium Chemistry

Cyclopropane is unreactive[14,15] toward $[(C_2H_4)PdCl_2]_2$, but bromocyclopropane yields a pi-allylic palladium complex while phenylcyclopropane isomerizes in the presence of palladium chloride.[16] Pi-allylic complexes are also formed by spiropentane,[14,15,17] dicyclopropyl,[14,15,18] and dicyclopropylmethane.[14,15,18]

Vinylcyclopropane[15,19] reacts with bisbenzonitriledichloropalladium yielding a pi-allylic complex analogous to butadiene. A cyclopropylcarbonyl cation[14,15,19,20] has been suggested as an intermediate in these reactions. Methylenecyclopropanes[15,21] also give pi-allylic complexes.

Rhodium Chemistry

A keto-complex[22] is produced in the reaction of cyclopropane with $[Rh(CO)_2Cl]_2$. Substituted cyclopropanes[23] yield similar complexes.

Conclusion

There is still much that can be done in this area of chemistry: crystal structures are needed in order to characterize the palladium and rhodium systems; the palladium research needs to be repeated for platinum; and more research is needed to fully develop the rhodium area. A possible application of this chemistry is in the transition metal isomerization of cyclopropanes.[24,25] Cyclopropane transition metal chemistry is a relatively young field and the future promises many new discoveries.

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MÖSSBAUER SPECTROSCOPY OF IRON METALLOPROTEINS

William H. Morrison, Jr. May 9, 1972

Introduction

The Mössbauer effect was first discovered in 1957, and its first application to materials of biological interest was in 1961. There are now over 100 papers concerned with the Mössbauer effect in biological application; most of these involve ^{57}Fe studies with various metalloproteins, although some work with iodine has been reported.[1] The present seminar will only be concerned with iron systems, since they can be interpreted in substantially more detail.

Iron proteins are generally classified as heme or non-heme. The non-heme proteins consist mainly of iron-sulfur proteins called ferredoxins. The only non-heme iron containing protein studied by Mössbauer that is not formally a ferredoxin is hemerythrin, which does not contain acid-labile sulfur. There have been several recent reviews on Mössbauer spectroscopy of ^{57}Fe protein systems.[2-4]

Theory

The general theory of the Mössbauer effect and general chemical applications can be found in the standard references[5-7] and the very useful bibliographies.[8,9] We will mention briefly the main interactions which affect line shape and intensity, the energy position, and the number of nuclear transitions.

For ^{57}Fe the source is ^{57}Co, which decays following electron capture chiefly (91%) through the ^{57}Fe $I = {}^3/_2$ to $I = {}^1/_2$ 14.4 eV transition. The recoiless fraction f is a function of both the energy of the transition and the mean square displacement of the nuclei involved. This limits biological studies to frozen solutions or lypholyzed solids. The line shape of a ^{57}Fe Mössbauer absorption is Lorentzian with a line width (full width at half height) of 9.3×10^{-9} eV or 0.19 mm/sec. This is approximately twice the natural line width because both source and absorber are involved. Additional broadening also results from lattice effects. No detailed line shape study has been undertaken in biomolecules, so further consideration of line shape will not be discussed. A small shift in the energy of the absorber relative to the source ($\sim$ -0.02 mm/sec. at 77°K.) occurs as a result of the second-order Doppler shift. Its utility as a source of information about biological materials is small and is chiefly used only as a correction to raw data.

The major sources of information in Mössbauer spectra are the isomer shift, the electric quadrupole interaction, the nuclear hyperfine interaction, and magnetic interactions caused by externally applied fields. The isomer shift is the small change in the center of gravity of the Mössbauer transition of the absorber relative to the source, or to some standard such as iron foil. An increase in electron density at the absorber moves the transition to lower energy for ^{57}Fe.

The excited state of the ^{57}Fe nucleus has an electric quadrupole moment ($I = {}^3/_2$). As a result, it can interact with surrounding charge density and split into two states ($\pm {}^3/_2$, $\pm {}^1/_2$). This results in two transitions in the Mössbauer spectrum instead of one. The center of gravity of the transition does not change. Nuclear hyperfine arises when an unpaired electron couples with the nucleus through either dipole or contact coupling. This is the same type of hyperfine coupling seen in ESR. If an external field is applied, and there are no unpaired spins, the ground and excited states split due to the nuclear Zeeman interaction. There will be six transitions due to this splitting. Combinations of these effects, plus spin-orbit coupling, cause very complicated Mössbauer spectra. These spectra are the largest source of structural information.

Experimental Problems

The main experimental problem is that the Mössbauer effect can only be seen in solids. Thus proteins either have to be freeze-dried (lypholyzed) or frozen into solutions. There is always the question of conformational changes during these processes which result in studying it under unphysiological conditions. The conformation of the protein is known to change upon drying; if a solution is frozen quickly, no drastic changes are expected in general. For a more thorough discussion of this, see references 1-4.

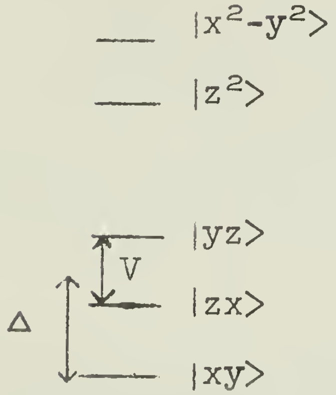
The other major problem is the low concentration of ^{57}Fe in protein systems. On the average, it takes approximately 0.1 mg of ^{57}Fe to obtain reasonable count rates. Large sample sizes are not desirable, because the 122 keV radiation is attenuated very little and the relative amounts of background increases rapidly with thickness. Thus enrichment is usually desirable.[1-4] Finally, it should be mentioned that the small dose of radiation encountered by the protein ($\sim$0.1 Roentgen/cm) is not expected to cause damage to it.

Heme Proteins

Heme proteins have been studied by Mössbauer spectroscopy for a number of years.[1-4,10-22] Recently, Lang *et al.*[2] have done a systematic study of various heme proteins and their derivatives. Various theoretical treatments have also been done ranging from molecular orbital[23] to crystal field theory.[24-26] An excellent series of theoretical papers on ferrous iron in hemoglobin has been published by Eicher.[27-30]

Probably the most thoroughly studied heme protein are cytochrome c and its derivatives. A theoretical study by Lang[31] on spin-$^1/_2$ iron salts serves as a good model for fitting cytochrome c Mössbauer

spectra.[32-35] He found the following energy scheme appropriate for the d-orbitals



which were taken from a model derived by Griffith.[36] This is indicative of octahedral symmetry with a strong tetragonal and weak rhombic distortion with covalent bonding between the $|yz\rangle$ and $|xz\rangle$ and the porphyrin ring. The Mössbauer spectra are found to be somewhat insensitive to Δ and V due to large spin-orbit effects among these orbitals. The g-values agree closely with ESR measurements ($g = 1.24, 2.25, 3.06$).

Metmyoglobin and myoglobin fluoride have also been investigated in detail by Mössbauer spectroscopy.[37] Their Mössbauer spectra are characteristic of high spin ferric iron, and are similar to hemoglobin fluoride. The Mössbauer spectra indicate the presence of a strong axial field, with $2D = 20 \pm 2\ \text{cm}^{-1}$ for metmyglobin and $12.6 \pm 1\ \text{cm}^{-1}$ for myoglobin fluoride. These agree well with the values found from susceptibility ($20\ \text{cm}^{-1}$ and $14\ \text{cm}^{-1}$).[38]

Non-Heme Systems

A number of ferredoxin systems have been studied by Mössbauer spectroscopy.[39-46] The ferredoxins contain from two to eight iron atoms per molecule and the same amount of acid labile sulfur. The structure of the active site is not known, and all models are only tentative. Putidaredoxin is one of the more extensively studied ferredoxins,[47,48] and a recent paper by Debrunner *et al*. gives Mössbauer data which supports the model of two bridging sulfur atoms connecting two coupled iron III ($S = {}^5/_2$) in the oxidized form, and one iron II ($S = 2$) coupled to one iron III ($S = {}^5/_2$) in the reduced form.

Hemerythrin is an iron containing protein which can be dissociated into 8 subunits each containing two Fe atoms and can bind reversibly one O_2 molecule. There is no acid-labile sulfur in the molecule. The nature of the binding site is unknown, and several Mössbauer measurements[49-52] have been made to elucidate it. The

oxidized derivative exhibits a single quadrupole pair of lines with a large splitting (1.8 mm/sec.) similar to methemyoglobin, and metmyoglobin which indicates a large distortion around the Fe center. Deoxygenated forms also show only a single quadrupole pair (2.8 mm/sec.), but with a large splitting indicative of high-spin Fe II. There is no hyperfine down to 4° K. The oxygenated form consists of two pairs of quadrupole lines indicating two distinct Fe sites. Again, there is no evidence of hyperfine down to 4° K. The absence of any hyperfine indicates a spin paired diamagnetic molecule and thus supports a model in which the two Fe are interacting. The exact nature of the site is still not clear, but further work is in progress.

Summary

Mössbauer spectroscopy has proven very useful in determining the nature of the iron sites in various metalloproteins. In conjunction with other magnetic techniques, the oxidation and spin state along with electronic configuration has been determined for many iron proteins. Its chief advantages over other magnetic techniques are that it can be used to gain detailed structural information in both diamagnetic and fast relaxing systems. Such determinations as mentioned above are germane to understanding the chemical basis of protein function.

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CIRCULAR DICHROISM OF TRANSITION METAL d-d TRANSITIONS: THE NON-EMPIRICAL APPROACH

D. Michael Duggan May 16, 1972

The potential ability of circular dichroism studies to give detailed stereochemical and electronic information about chemical systems is well recognized. At present the great sensitivity of this method is the major deterrent to its more general application, in that we do not now possess the theoretical framework upon which to fully interpret CD data. Here we will mention some of the current trends in non-empirical, i.e., theoretically based, treatment of CD for metal complex systems.

I. Basic Information

In this seminar we will mainly be concerned with circular dichroism, as opposed to its counterpart, optical rotatory dispersion. It is desirable to measure CD spectra because they are comprised of simple positive and negative Gaussian bands in the area of electronic absorptions, whereas ORD spectra are dispersion curves which become experimentally intractable where overlapping is significant.

CD is essentially a phenomenon occurring when a system absorbs one hand of circularly polarized light more than the other. Experimentally, this means that if the incident light is plane polarized, the transmitted light will be elliptically polarized. The ellipticity is proportional to $\epsilon_L - \epsilon_R$ where these are the extinction coefficients for a particular absorption band for left and right circularly polarized light. It was shown by Rosenfeld[1] in 1928 that the <u>rotatory strength</u> (analogous to the dipole strength of an electronic absorption), may be given by:

$$R_j = \mathrm{Im}(\langle a|\vec{\mu}_e|j\rangle \cdot \langle j|\vec{\mu}_m|a\rangle)$$

where Im(a+ib) = b, $\vec{\mu}_e$ is the electronic dipole operator, $\vec{\mu}_m$ is the magnetic dipole operator, and $|a\rangle$ and $|j\rangle$ represent the ground and excited state wavefunctions. The rotatory strength is of major importance in CD studies, for it can be calculated as above from a quantum-mechanical knowledge of the system and it can be determined experimentally from the area under (or over) the CD curve (again analogous to the determination of dipole strengths from absorption experiments). It should also be noted that the above equation can be used to derive symmetry rules for optical activity such as those discussed below.

II. Coordination Compounds as Model Systems

Electronic transitions for a given metal complex are commonly divided into three catagories: 1. d-d transitions, 2. Charge transfer bands, and 3. Transitions localized on the ligands. The CD properties of metal complexes are similarly catagorized and groups 1 and 3 have received by far the most intense theoretical attention. As inorganic chemists interested in using metal spectroscopic properties as indicators of molecular structure, we are naturally attracted to a study of d-d band CD, for the d-d bands in an

unfamiliar complex molecule would bear the most resemblance to familiar systems. We can then use our model systems as zero-order approximations to a description of the compound to be studied. This seminar will be directed toward d-d band treatments for the reason that a generally valid approach in this area will provide the greatest general applicability. A selection of references treating the CD of ligand based transitions is given at the end of this abstract.[2-6]

III. d-d Band Interpretation

The study of d-d band CD effects may proceed from a general symmetry approach or through specific application of a quantitative calculation.

A. Symmetry - Sector Rules

Sector rules have been formulated to explain the CD of a transition in an inherently symmetric chromophore as a function of the dissymmetric distribution of charges around this chromophore.

Originally the Octant Rule was proposed to explain optical activity in n-pi* ketone group transitions for organic systems.[7] This rule is applied by dividing the space around the chromophore into 8 sectors, or octants in this case, bounded by the symmetry planes of the MO's of the C=O group. If each octant is labeled by a sign opposite that of its neighbors and each atom labeled corresponding to the octant where it resides, the sum of the signs over all atoms will indicate the sign of the n-pi* CD band. Of course if the sum is zero, then the transition will be optically inactive.

The great success of the n-pi* octant rule in predicting absolute configurations of organic compounds made it seem desirable for the inorganic chemist to have a sector rule of his own. An octant rule for transition metal complexes was first proposed by C. J. Hawkins in 1965[8], based on the known spectra of a small basis set of well studied complexes. Even though the rule as proposed is not generally practicable, the octant rule has been used extensively in the literature of metal system CD.

Is there a theoretical basis for the application of sector rules to transition metal complexes? This has been a key question since 1965. Schellman[9,10] and Richardson[11-14] have addressed their efforts to this question with perturbation and coupled oscillator approaches in order to determine the symmetry of the molecule required to produce optically active bands. At present there are great hazards inherent in indiscriminate use of sector rules, but theoretical studies have pointed out the origin of some of the major problems and how to avoid them when possible. With caution the simple sector rules may sometimes be useful.

B. Quantitative Applications

Symmetry rules for CD have been proposed for related metal complexes with respect to predicting the relative sign of a particular d-d band or total rotational sign of a group of bands. If we wish to account for the magnitude of the CD bands as well as the sign, we have at first two major problems. First, we must calculate good trial wavefunctions for the molecule under consideration. Second, we must be able to use well understood

experimental data in order to test these wavefunctions. At present we have no completely satisfactory theoretical model from which to generate good wavefunctions, and the extent of our understanding of experimental observation is similarly poor. This latter point is well illustrated using the example of $Coen_3^{+3}$.

More CD studies on metal complexes have been directed toward this compound than any other, although the complex was selected more for historical reasons than as a matter of simplicity. The visible region of the $COen_3^{+3}$ absorption spectrum reveals two bands, a $^1T_{1g} \leftarrow {}^1A_{1g}$ and a $^1T_{2g} \leftarrow {}^1A_{1g}$. The CD spectrum of the first band, which is only magnetically allowed in O_h symmetry, shows both positive and negative components. The $^1T_{1g}$ CD structure has been interpreted in several ways. Historically, the first interpretation was the obvious guess that the two bands arise from trigonal components of E and A_2 symmetry from the $^1T_{1g}$ state. Splittings were measured and correlations with geometric changes were made (see ref. 15 for further references). The second explanation for the splitting was derived from a series of low temperature single crystal studies performed in the late 1960's[16-19]. The conclusion of these studies was that the trigonal splitting is essentially zero, seemingly invalidating all previous work. Various interpretations of the splitting were then advanced, involving vibronic structure and Jahn-Teller distortion[18]. At the moment, possible vibronic contributions to CD are neither proven nor understood. Richardson hopes to investigate solutions to this problem within the next few months.

It is interesting to note that as late as 1967 some workers believed[17,20] the CD splitting to be due to the equilibrium concentrations of "ob" and "lel"[21] forms of $Coen_3^{+3}$ in solution. This has been strongly refuted, but the hypothesis points out the great confusion in the interpretation of CD for some systems.

IV. Conclusions

Symmetry rules have constituted the bulk of this survey because at present the details of CD spectra are not completely understood, so only qualitative arguments can have any chance of success. The symmetry calculations are becoming more and more useful as they consider more types of interactions; so we may perhaps look forward to the eventual emergence of a generally useful theory.

However, it is clear that due to the second order nature of optical rotational properties, CD arguments will always be difficult to apply with certainty; this spectroscopic technique will probably be the last to be well understood.

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See also Refs. 6 and 15.

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