least six methylene units. Chelates having shorter links tend to form dimers; however, the shorter the link, the less readily are volatile products formed. Phenylene and/or ether linkages can be substituted for some of the methylene groups. The cyclic structure was confirmed by the volatility of the products, elemental analysis, infrared spectra and molecular weight determinations.

Polymer degradation to macrocyclic products was studied using the bis-β-diketone system (II and III R = $+CH_2+_n$), which, unlike the ester and amide derivatives, could be polymerized and depolymerized quantitatively at 200°. (The ester and amide chelates became highly cross-linked upon prolonged heating, preventing very good recovery of cyclic monomer.) At a constant surface area, pressure and temperature, the rate of macrocycle formation was approximately constant. In the series studied, this rate decreased in the order n = 12, n = 10, 10 mg./hr.; n = 8, 9 mg./hr.; n = 7, 4.5 mg./hr.; $n = 6 <$ mg./hr. (205°, 0.05 mm.). This order is that expected by the increasing strain incorporated in the macrocycles with decreasing chain length and roughly parallels literature data on the thermal degradation of polyesters, poly-anhydrides and polylactones.[10] Further qualitative data on the amount of strain incorporated in these macrocycles was evidenced by their rate of polymerization in the melt. The compound IIa (R = $+CH_2+_6$) polymerized instantly upon melting at about 110°, no low viscosity stage being discernible; whereas IIa R = $+CH_2+_{10}$ could be recovered partially even after heating one minute in the melt at 140°.

Under conditions of macrocycle formation the polymer and the macrocycles are in equilibrium. Removal of the volatile components results in an increase in molecular weight of the residual polymer suggesting that the more volatile components of the polymer include chain stopping end groups. Because of the re-equilibration of polymer and macrocycles during degradation, it is difficult to determine whether cycle formation proceeds by unzippering with concurrent repolymerization of monomers or involves random chain cleavage as well. However, attempts to stabilize the polymer against unzippering by mixing 10% of the hexamethylene monomer IIa (R = $+CH_2)_6$— with octamethylene monomer IIa R = $+CH_2)_8$— to produce what is believed to be a copolymer gave polymer which degraded at essentially the same rate as the pure octamethylene polymer III (R = $+CH_2)_8$)—. Likewise, partial crosslinking of the octamethylene polymer by irradiation failed to decrease the rate of macrocycle formation appreciably. These results suggest that, although unzippering may be the principal mode of cycle formation, random chain cleavage and re-equilibration of chains must also be important.

The rate of polymerization in the melt of cyclic chelates derived from a diester (*e.g.*, IIa R = —O$(CH_2)_6$O—) was qualitatively observed to be much faster than for the corresponding diketone chelate containing an equal number of links in the macrocycle (*e.g.*, IIa R = $+CH_2)_8$—). This is contrary to the expected behavior based on strain if only such factors as hydrogen crowding were involved. This suggests that the oxygen atoms prefer to orient coplanar to the ring and participate in resonance stabilization.[11] The geometry of the ring prohibits this except at the expense of additional strain. Thus, the energy content of the monomer relative to the polymer is raised and accounts for the faster polymerization rate. This postulate is in agreement with the observation that both IIa and IIb (R = —$(CH_2)_6$—) can be isolated whereas only the dimer IIb (R = O$(CH_2)_4$O) can be isolated. This postulates also further correlates with the glass transition temperatures of the resulting polymers, a measure of the rigidity of the components of a polymer. The glass transition temperature of the polymer III R = —O$(CH_2)_6$O— (approximately 55°) corresponds to that of III R = —$(CH_2)_6$— rather than III R = —$(CH_2)_8$— (35°), again suggesting that the oxygens adjacent to the chelate ring do not rotate freely as do adjacent methylene groups.

---

(10) E. W. Spanagel and W. H. Carothers, THIS JOURNAL, **57**, 929 (1935); M. Stoll and A. Rouve, *Helv. Chim. Acta*, **18**, 1087 (1935), K. Ziegler and H. Holl, *Ann.*, **528**, 143 (1937).

(11) R. J. B. Marsdon and L. E. Sutton, *J. Chem. Soc.*, 1383 (1936); M. Calvin and K. W. Wilson, THIS JOURNAL, **67**, 2003 (1945).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN]

Unusual Proton Affinities of Some Mixed Ligand Iron(II) Complexes

BY ALFRED A. SCHILT

RECEIVED MARCH 15, 1960

The neutral dicyano-bis-(1,10-phenanthroline)-iron(II) and dicyano-bis-(2,2'-bipyridine)-iron(II) complexes have been found to react reversibly with acid and to exhibit appreciable dibasic character. Properties of the complexes and their protonated species have been investigated and are interpreted to rationalize how and where protonation takes place.

Evidence was reported in a previous paper[1] concerning the existence of stable protonated species of the neutral mixed ligand complexes: dicyano-bis-(1,10-phenanthroline)-iron(II) and dicyano-bis-(2,2'-bipyridine)-iron(II). That these complexes react reversibly with protons is most surprising. Certainly it seems unreasonable to expect a ligand as weakly basic as the aromatic diimines in question to retain any significant proton affinity following metal ion coördination. The more strongly basic cyanide ligands might more conceivably have some residual proton affinity; however the coördination properties of hydrogen

---

(1) A. A. Schilt, THIS JOURNAL, **82**, 3000 (1960).

cyanide are quite weak (*cf.* water or amines), and it is reasonable to expect that reaction with acid would be irreversible so that cyanide would be displaced from coördination.

Such considerations led to the present work which was performed to provide more conclusive evidence for the existence and identities of the protonated species and perhaps to provide a basis for a better understanding of their properties.

Experimental

Materials.—The dicyano-bis-(1,10-phenanthroline)-iron(II) dihydrate and the dicyano-bis-(2,2′-bipyridine)-iron(II) trihydrate were available from previous work; details concerning their preparation and purification and the results of their analyses have been reported earlier.[1] A.C.S. reagent grade solvents were employed without further treatment. The glacial acetic acid was found to contain 0.004% water by titration with Karl Fischer reagent; no acidic or basic impurities were detected by potentiometric titrations. Thiourea, C.P. grade, was recrystallized from ethanol and dried *in vacuo* prior to use. Eastman Kodak Co. *o*-chloroaniline (purified grade) was used without further attempts at purification; assay by potentiometric titration in chloroform with standard perchloric acid in glacial acetic acid indicated a purity of 99.9 ± 0.3%. Perchloric acid solutions in acetic acid were prepared according to Fritz[2] and standardized against potassium acid phthalate.

Potentiometric Titrations.—A Beckman Model G *p*H meter and glass and silver–silver chloride electrodes were used. The latter electrode was constructed from a coiled silver wire, electrolytically coated with silver chloride and immersed directly within the solutions titrated. For titrations carried out in acetic anhydride solutions it proved more satisfactory to employ a calomel electrode of the capillary or fiber type in place of the silver–silver chloride reference electrode.

Solutions titrated were in a concentration range of 10^{-4} to 10^{-3} *M;* use of higher concentrations was precluded by the restrictive solubility of the complexes. Standard perchloric acid (10^{-3} *M*) was measured from a 10 ml. buret.

Complications included precipitation of protonated species, slow apparent dissociation of the complex and lack of adequate buffering. To minimize the effects of these, readings were completed as rapidly as possible.

Magnetic stirring was used except during actual measurements. Erratic galvanometer behavior, apparently from the inductive effect of the rotating magnetic field, seems to be a rather common phenomenon when low dielectric solvents are employed in such procedures.

Spectrophotometric Titrations.—The extent of reaction as a function of the amount of perchloric acid added was followed spectrophotometrically while maintaining the total concentrations of the other reactive components of the system constant. Individual measurements were made on individually and freshly prepared solutions. Although this procedure is more laborious than a conventional titration, it avoids complications due to possible precipitation of the protonated species. Moreover, it does not involve dilution so no corrections for such need be made, and the independent measurements constitute a better statistical average. With regard to precipitation it is pertinent to note that certain of the solutions after standing overnight contained perceptible amounts of colored, amorphous solids which proved to be protonated forms of the metal complexes. Since precipitate formation is quite slow and very fresh solutions were used, no difficulty was experienced in obtaining steady and reproducible absorbance measurements.

A typical measurement in the titration of the metal complexes in acetic acid involved these steps: 5.00 ml. of 4.00 × 10^{-4} *M* metal complex was delivered by pipet into a 10.0 ml. volumetric flask, a measured volume of 1.00 × 10^{-3} *M* $HClO_4$ was added, and after dilution to volume with acetic acid the resulting solution was examined spectrophotometrically.

In a typical measurement of titration data to determine exchange constants, 5.00 ml. of 0.0500 *M* thiourea (or other reference base) and 2.00 ml. of 4.00 × 10^{-4} *M* metal complex were mixed in a 10.0 ml. volumetric flask, a measured volume of 0.1000 *M* $HClO_4$ was added and immediately thereafter the solution was diluted to volume with acetic acid and measured as before.

Absorption curves were recorded using a Cary Model 11 Spectrophotometer; a Beckman Model D.U. instrument was used to measure absorbancies at individual wave lengths of analytical interest.

Exchange Constants.—Potentiometric or direct spectrophotometric measurement of the over-all dissociation constants for the weakly basic metal complexes in acetic acid proved impractical due to restrictive solubilities and experimental limitations. For example, ionization of the basic complexes in pure acetic acid is so slight that absorption spectra are unaffected by addition of stronger bases. Recourse to exchange measurements therefore was made to provide practical estimates of the relative acid-base strengths of the metal complexes and their protonated forms. Thiourea and *o*-chloroaniline were selected as reference bases for the acid exchange measurements, since they were found to compete suitably with the metal complexes for acid.

The exchange reactions of interest may be represented by

$$BHClO_4 + X = XHClO_4 + B$$

where B is the reference base and X is either the metal complex or its undissociated monoprotonated form. For simplicity of notation the role of acetic acid is not represented. Using the symbolism of Kolthoff and Bruckenstein[3] the equilibrium or exchange constant, K_{ex}, of the reaction would be expressed as

$$K_{ex} = C_{XHClO_4}C_B/C_XC_{BHClO_4} = K_f^{XHClO_4}/K_f^{BHClO_4}$$

where the formation constants describe the individual equilibria between each base and perchloric acid, *e.g.*, $X + HClO_4 = XHClO_4$.

The ratio of C_B/C_{BHClO_4} is determined quite simply from the amount of $HClO_4$ added to a known amount of B, provided that a very small concentration of X relative to B is employed so that the amount of $HClO_4$ bound to X is negligible. The ratio C_{XHClO_4}/C_X is determined spectrophotometrically. Since the total concentration of absorbing species of X is known from the initial amount of X added, a minimum of two absorbance measurements at appropriate wave lengths selected from the data of Table I, suffice to calculate the concentration of each of the three species.

TABLE I

ABSORPTION CHARACTERISTICS IN ACETIC ACID

A. Dicyano-bis-(1,10-phenanthroline)-iron(II)

Species	Molar absorptivity at wave length, mμ 545	467	387
$FePh_2(CN)_2$	7720	6320	805
$FePh_2(CN)_2 \cdot HClO_4$	1210	6320	4040
$FePh_2(CN)_2 \cdot 2HClO_4$	52	1240	5510

B. Dicyano-bis-(2,2′-bipyridine)-iron(II)

	554	491	412
$FeBipy_2(CN)_2$	6010	3940	2780
$FeBipy_2(CN)_2 \cdot HClO_4$	488	3940	2780
$FeBipy_3(CN)_2 \cdot 2HClO_4$	30	520	4250

Results

Solutions of the iron(II) complexes were titrated potentiometrically to determine reaction stoichiometry and to estimate relative basicities. In no case was more than one end-point distinguishable from the titration curves, and although the sharpness of the breaks varied considerably from solvent to solvent, very little difference between the two complexes was evident. Within experimental error, all end-points coincided with the stoichiometric point expected for a monoequivalent base.

Titrations in nitrobenzene failed to give any distinct inflection point for the curves. Weak inflection points were observed in the titration

---

(2) J. S. Fritz, "Acid Base Titrations in Nonaqueous Solvents," G. Frederick Smith Chemical Co., Columbus, Ohio, 1952.

(3) I. M. Kolthoff and S. Bruckenstein, THIS JOURNAL, **78**, 1 (1956).

curves for both iron(II) complexes in glacial acetic acid and in chloroform; precipitation of the neutralization products occurs in these solvents and undoubtedly contributes favorably to improving end-point recognition. A combination of equal volumes of chloroform and acetic acid proved to be a more satisfactory solvent for the titration of the complexes than either solvent individually. The solubilities of the protonated complexes are noticeably less in this mixed solvent system. Acetic anhydride proved to be the most satisfactory solvent; not only were more distinct end-points obtained but also the protonated species remained soluble throughout the titrations. Some difficulty was experienced in obtaining constant potentiometric readings. These gradually decreased in magnitude, due apparently to slow decomposition of the iron(II) complexes and aggravated by the low buffering capacity of the solutions titrated. For this reason the shapes of the titration curves shown in Fig. 1 may be slightly distorted even though the titrations were performed in a relatively short time to minimize this effect. The apparent decomposition of the complexes was not sufficient over a period of an hour to affect the end-point within experimental error.

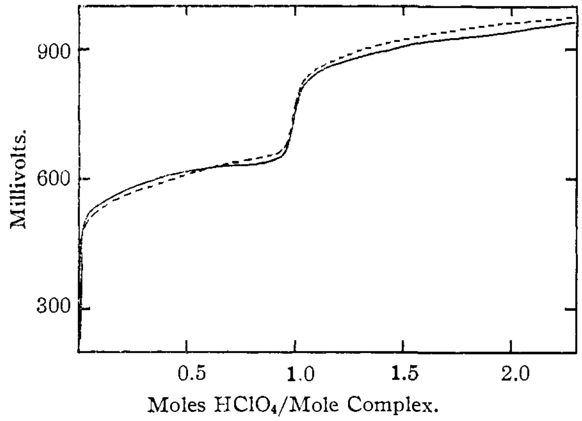

Fig. 1.—Potentiometric titration of dicyano-bis-(1,10-phenanthroline)-iron(II) (solid curve) and of dicyano-bis-(2,2'-bipyridine)-iron(II) (dashed curve) in acetic anhydride with standard perchloric acid in acetic acid.

The spectrophotometric data, presented graphically in Figs. 2 and 3, show conclusively that in the perchloric acid–acetic acid–metal complex systems studied there are three and only three equilibria species of the mixed ligand complexes. Well defined sets of isosbestic points are displayed in the spectral series when the molar ratio of perchloric acid to metal complex is less than unity. Distinctly new sets appear when the same ratio is greater than one. In the immediate neighborhood of a mole ratio of one, all three species are present in relatively significant amounts since the isosbestic character of the spectral series is absent. Treatment of the data in the usual manner to determine the stoichiometry of the reactions indicates that the three species are the neutral metal complex and its mono and diprotonated form.

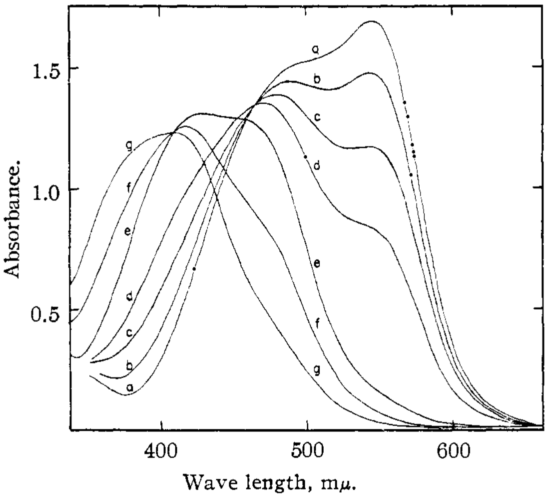

Fig. 2.—Absorption characteristics of dicyano-bis-(1,10-phenanthroline)-iron(II) in glacial acetic acid as a function of moles of $HClO_4$ added per mole of neutral complex. Formal concentration of complex = 2.14×10^{-4} mole per liter; moles of $HClO_4$ per mole of complex: a, none; b, 0.22; c, 0.44; d, 0.66; e, 1.33; f, 2.21; g, 4.42.

Further use of the titration data was made in calculating molar absorptivities of the various species at analytically significant wave lengths. By extrapolation of appropriate data or by simple calculations based on the justifiable assumption that reaction prior to the first equivalence point is essentially complete, it was possible to obtain molar absorptivity values for the monoprotonated complexes indirectly. Spectral constants for the neutral and for the diprotonated complexes (in the presence of a 500 fold excess of $HClO_4$) were measured directly. These results are given in Table I and are reported here since they were employed in exchange constant measurements.

The results of the exchange constant measurements are compiled in Table II. The experimental absorbance and titration data from which the mean values of the constants were obtained are omitted for reason of brevity.

TABLE II

EQUILIBRIUM (EXCHANGE) CONSTANTS[a] FOR: $BHClO_4 + X = XHClO_4 + B$ IN ACETIC ACID

X	B o-Chloroaniline	 Thiourea	 Solvent[b]
$FePh_2(CN)_2$	1.1 ± 0.1	44 ± 5	[c]
$FeBipy_2(CN)_2$	0.9 ± .1	35 ± 3	[c]
$FePh_2(CN)_2 \cdot HClO_4$	.03 ± .01	0.15 ± 0.03	9000
$FeBipy_2(CN)_2 \cdot HClO_4$	.01 ± .01	0.11 ± 0.01	3000

[a] Each value is the mean of four or more independent measurements; all measurements fall within the stated limits. [b] The constants in this column actually refer to the equilibrium in acetic acid: $HClO_4 + X = X \cdot HClO_4$. [c] Value of the constant is too large to estimate by spectrophotometric titration technique.

Discussion

It is a matter of considerable interest, now that the dibasic character of these complexes has been established, to learn how and where protonation occurs. Although conclusive answers must await further experimental verification, certain rationalizations can be made which do not appear altogether unreasonable and from which a tentative

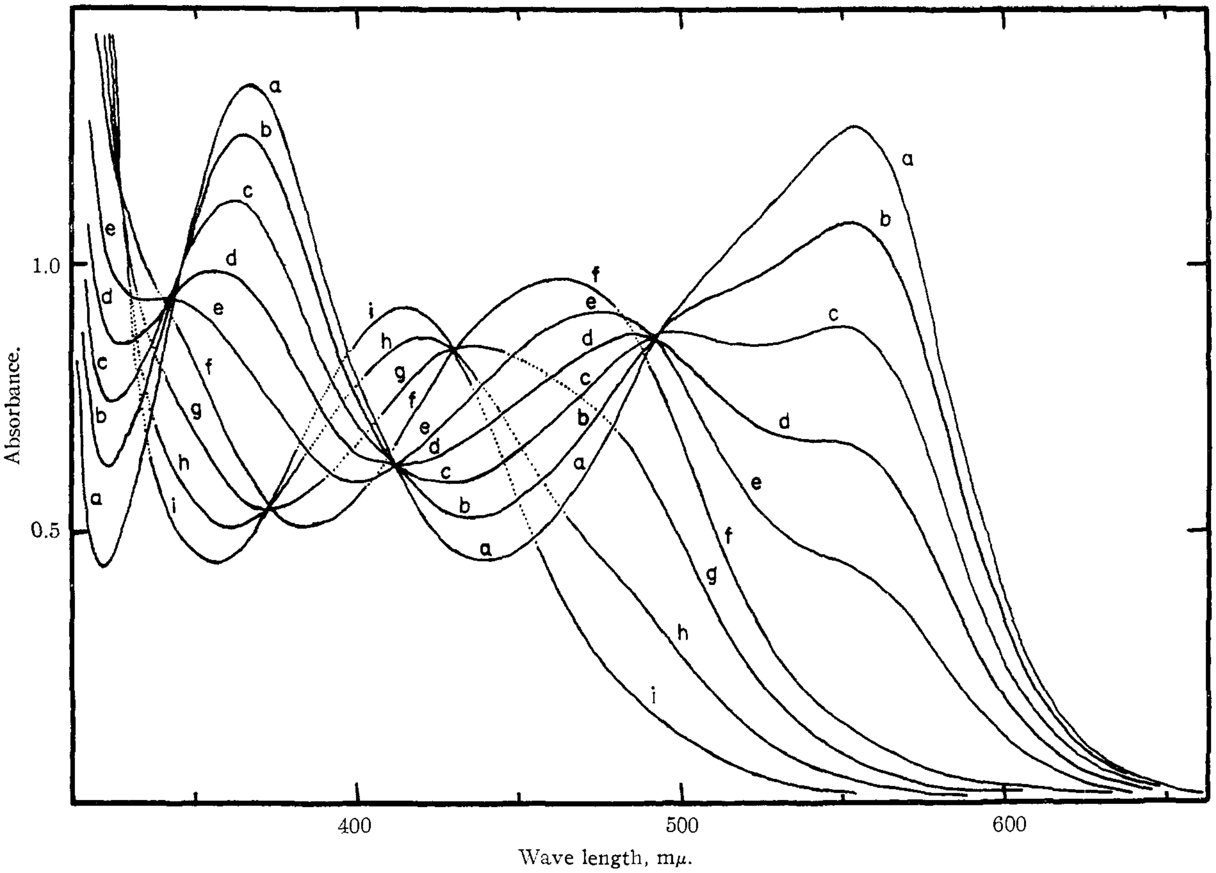

Fig. 3.—Absorption characteristics of dicyano-bis-(2,2′-bipyridine)-iron(II) in glacial acetic acid as a function of moles of $HClO_4$ added per mole of neutral complex. Formal concentration of complex = 2.17×10^{-4} mole per liter; moles of $HClO_4$ per mole of complex: a, none; b, 0.22; c, 0.44; d, 0.66; e, 0.87; f, 1.31; g, 2.18; h, 4.36; i, 21.8.

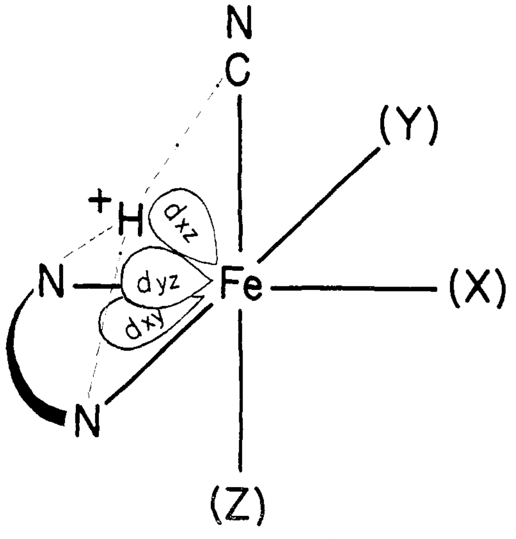

Fig. 4.—Diagrammatic model of the protonated species. Dashed lines between the proton and each of the donor atoms of the ligands are intended to depict orientation, not interaction.

explanation of the facts can be drawn. One such rationalization suggests that all six donor atoms of the combined ligands in the diprotonated complex are affected to essentially the same degree by the bound protons. This can be argued on the basis that if either a cyanide or an aromatic diimine ligand were preferentially protonated, then considerable loss in its coördination ability would result and its subsequent displacement from the iron(II) complex should be facilitated greatly. Strongly acidic solutions of the metal complexes however display remarkable stability over long storage periods[4]; prolonged heating is necessary to effect decomposition. Another rationalization concerns the disposition of the two bound protons with respect to one another and the electrostatic repulsion between them. The most probable arrangement in keeping with a minimum of proton–proton interaction would be for the protons to be bound in a *trans* configuration about the metal complex.

A reasonable, tentative structure for the diprotonated metal complexes is therefore one in which one proton is symmetrically situated with respect to three adjacent donor atoms (two nitrogen atoms of a single aromatic diimine ligand and the donor atom of one of the cyanide ligands) and the other proton is similarly disposed with respect to the other three donor atoms. Such an arrangement requires that the protons be *trans* to one another! Hence a *trans* configuration

---

(4) For example, a dilute solution of $FePh_2(CN)_2$ in 12 *M* H_2SO_4 was observed spectrophotometrically to have undergone only 8% decomposition over five months' storage at ordinary laboratory conditions.

is reasonable not only on the basis of minimum electrostatic repulsion but also is a necessary consequence if each donor atom in the complex is to be affected to essentially the same degree by the bound protons.

A diagrammatic structural model for the protonated metal complexes is given in Fig. 4. Only one-half of the model is depicted in order to make visual presentation and interpretation easier; the undepicted set of ligands and accompanying proton if shown would complete the octahedral-like disposition of donor atoms about iron.

The question as to how the protons are bound remains to be answered. It seems unlikely that any significant bonding occurs between the proton and the donor atoms in the metal complex.[5] One is led therefore to speculate that the protons are attracted and bound to the central metal ion by electron pairs in normally non-bonding orbitals. This seems less speculative than to suggest that two hypothetical metal-ligand π bonds can each be protonated; however the question is a moot one.

The successive shifts in wave lengths of maximum absorption to lower values on successive protonation of the metal complexes, illustrated in Figs. 2 and 3, are consistent with the probable nature of the excitation process[6] and give evidence in support of a model wherein significant interaction occurs between protons and the non-bonding d-orbitals of the central metal ion.[1,7]

With regard to the proton affinity of related complexes it is pertinent to note that hexacyanoferrate(II) behaves as a moderately weak dibasic ion[8] and that some evidence has been found concerning the existence of protonated species of the tris-(2,2-bipyridine)-iron(II) ion and of the 1,10-phenanthroline analog.[9] In the former there is the question of how significant the large negative charge is in determining the proton affinity, hence comparisons are not readily made between it and the neutral mixed ligand complexes of this study. The latter cases remain to be substantiated by more direct evidence.

Finally it may be noted that $HCo(CO)_4$ and $H_2Fe(CO)_4$ resemble in some respects the protonated species of the present study; structures for these have been proposed wherein the hydrogen atom interacts with both the metal ion and adjacent carbonyl ligands.[10]

---

(5) Infrared spectra of the solid protonated species show no sign of significant interaction, *i.e.*, the $C\equiv N$ stretching frequency is unchanged and the over-all character of the spectra differs only very slightly from those of the unprotonated complexes.

(6) R. J. P. Williams, *J. Chem. Soc.*, 137 (1955).

(7) G. J. Brealey and M. Kasha, THIS JOURNAL, **77**, 4462 (1955).

(8) B. V. Nekrasov and G. V. Zotov, *J. Appl. Chem. (U.S.S.R)*, **14**, 264 (1941); *C. A.*, **36**, 1834 (1942).

(9) (a) T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 2348 (1948); (b) D. W. Margerum, R. I. Bystroff and C. V. Banks, *ibid.*, **78**, 4211 (1956); (c) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952); (d) E. A. Healey and R. K. Murmann, THIS JOURNAL, **79**, 5827 (1957).

(10) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 345–350.

[CONTRIBUTION FROM CHEMISTRY DEPARTMENT, NAGOYA UNIVERSITY, CHIKUSA, NAGOYA, JAPAN]

Covalency of Metal–Ligand Bonds in Potassium Hexahaloplatinates(IV) Studied by the Pure Quadrupole Resonance of Halogens

BY DAIYU NAKAMURA, YUKIO KURITA, KAZUO ITO AND MASAJI KUBO

RECEIVED MARCH 15, 1960

The pure quadrupole resonances of halogens in potassium hexahaloplatinates(IV) were determined at liquid nitrogen, Dry Ice and room temperatures. Potassium hexachloroplatinate(IV) showed only one resonance line, indicating that all chlorine atoms are crystallographically equivalent in agreement with the results of X-ray analysis. The same was true for potassium hexabromoplatinate(IV) above a transition point lying between the liquid nitrogen and Dry Ice temperatures. below which two resonance lines were observed. Three resonance lines observed for potassium hexaiodoplatinate(IV) along with X-ray powder patterns suggested the presence of crystallographically nonequivalent iodine atoms in the crystals. The ionic character of platinum–halogen bonds calculated from the quadrupole coupling constant ranges from 0.30 to 0.53, the net charge on a platinic ion being reduced to a fraction of an electronic charge. The electronegativity of platinum was estimated at 1.9.

Introduction

The nature of metal–ligand bonds in metal complex compounds has been discussed by Pauling[1] on the basis of the atomic orbital theory. In contrast to the crystalline field theory,[2-7] this theory puts too much emphasis on the covalency of metal–ligand bonds in some complexes. Based on the so-called "magnetic criterion for bond types," Pauling classified metal complexes into two groups, namely "essentially covalent" complexes and "essentially ionic" ones. His concept is in harmony with a general feeling among chemists that, for example, $[Ni(H_2O)_6]^{++}$ and $[Co(NH_3)_6]^{+++}$ represent different types of chemical bonding. This simple concept might suggest that no ionic contribution is involved in the bonds of diamagnetic complexes,[8,9] although this contradicts the results of electronegativity considerations that the covalency of metal–ligand bonds amounts to only about 45% even in a

---

(1) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York, 1948.

(2) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

(3) Y. Tanabe and S. Sugano, *ibid.*, **9**, 766 (1954).

(4) Y. Tanabe and S. Sugano, *ibid.*, **11**, 864 (1956).

(5) L. E. Orgel, *J. Chem. Soc.*, 4756 (1952); *Quart. Revs. (London)*, **8**, 422 (1954); *J. Chem. Phys.*, **23**, 1004, 1819, 1958 (1955).

(6) L. E. Orgel, *J. Chem. Phys.*, **23**, 1824 (1955).

(7) C. K. Jørgensen, "Absorption Spectra of Complexes with Unfilled *d*-Shell," Xth Solvay Conference, Brussels, 1956; "Energy Levels of Complexes and Gaseous Ions," Jul. Gjillerups Vorlag, Copenhagen, 1956.

(8) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, New York, N. Y., 1952.

(9) W. C. Fernelius, *Rec. Chem. Progr.*, **2**, 17 (1950).