Contribution from the John Harrison Laboratory of Chemistry
and the Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania 19104

Contact Shift Studies of Some Paramagnetic Hexaaquo Metal Ion Complexes

By BRADFORD B. WAYLAND and WILLIAM L. RICE

Received August 3, 1965

The contact shifts of protons in complexed water for the hexaaquo metal perchlorate complexes of Cu^{+2}, Ni^{+2}, Co^{+2}, Fe^{+2}, Mn^{+2}, and Fe^{+3} have been determined. The electron-nuclear coupling constants are all positive. The mechanisms of electron delocalization are discussed in terms of the donor molecular orbitals of water. The contact shift is dominated by a π delocalization mechanism for metal complexes that have unpaired t_{2g} d electrons. The metal–water bond in the Fe^{+3} complex is found to involve significantly greater covalency than the isoelectronic Mn^{+2} complex.

Introduction

Several recent publications have reviewed the status and theory of contact shift measurements.[1-4] When a donor molecule bonds with a paramagnetic metal ion, a net unpaired electron density is induced in the donor orbitals. The unpaired electron density is distributed over the molecule in accord with the various atomic contributions to the donor molecular orbital. The n.m.r. contact shift arises from the coupling of the unpaired electron with the ligand magnetic nuclei *via* the Fermi contact term.[5,6] The presence of unpaired electron density at the nucleus changes the magnetic field sensed by the nucleus. Thus, the position of resonance is shifted. The magnitude of the contact shift is related to the electron spin–nuclear spin coupling constant by eq. 2. The direction of the contact shift is also of great importance, for it can be used to determine directly the sign of the coupling constant from eq. 2. This technique was used to determine experimentally that the sign of the coupling between a pπ electron of sp^2 carbon with a directly bonded proton is negative and that the coupling constant with protons of a directly bonded methyl group is positive.[7] The sign of the coupling constant can be used in determining the mechanism of electron spin density delocalization. Contact shifts have been used to detect electron delocalization into both the π and σ ligand orbitals of paramagnetic complexes.[1-4,8,9]

Paramagnetic metal ions in aqueous solution are known to broaden and shift the proton n.m.r.[10,11] The change in the O^{17} and H^1 relaxation times of water due to the presence of paramagnetic metals ions has been extensively studied.[11-14] These investigations have yielded valuable information about the rate of exchange of coordinated water with the bulk solvent water molecules. The shift in the position of the water proton resonance due to paramagnetic complex formation has not been extensively investigated. The proton shift for water complexed to Co^{+2} was determined to aid in the study of the Co^{+2}–histidine complex in aqueous solution.[15] The water proton contact shifts are reported here for the hexaaquo complexes of Cu^{+2}, Ni^{+2}, Co^{+2}, Fe^{+2}, Mn^{+2}, and Fe^{+3}. The results are used to discuss electron delocalization mechanisms and the relative ability of isoelectronic Mn^{+2} and Fe^{+3} to form covalent bonds.

Experimental Section

Complexes.—The hexaaquo perchlorate salts of Cu^{+2}, Ni^{+2}, Co^{+2}, Fe^{+2}, Mn^{+2}, and Fe^{+3} were obtained from the G. F. Smith Chemical Co. The hydrogen analysis was found to agree satisfactorily with that calculated for hexaaquo complexes.

Representative Analysis.—*Anal.* Calcd. for $Mn(H_2O)_6(ClO_4)_2$: H, 3.32. Found: H, 3.41.

Solutions.—Stock solutions of the internal n.m.r. standard $(CH_3)_3Si(CH_2)_3SO_3Na$ were prepared by dissolving a weighed quantity of standard in a weighed amount of water. These solutions were approximately 2% $(CH_3)_3Si(CH_2)_3SO_3Na$ by weight. The metal ion solutions were prepared by weighing the metal hydrate salt into a 1.0- or 2.0-ml. volumetric flask and then reweighing after filling the volumetric flask with stock solution of standard. By using this procedure both the mole fraction and molarity of the components are known for these solutions.

Apparatus.—The spectra were determined on a Varian H.R. 60 n.m.r. spectrometer. The temperature of the probe was held constant at 40 ± 1°.

N.m.r. Spectra.—All proton n.m.r. spectra for the hexaaquo complexes in aqueous solution consisted of a single averaged resonance peak. Relaxation studies have revealed that there is fast proton or water exchange from the complex to the bulk water.[11-14] For the case of fast exchange, eq. 1 may be used to calculate the contact shift of just the complexed water.

$$\Delta\nu_{com} f_{com} = \Delta\nu_{obsd} \qquad (1)$$

In eq. 1, $\Delta\nu_{com}$ and $\Delta\nu_{obsd}$ are the proton n.m.r. shifts relative to the resonance position of uncomplexed water, respectively, for the complexed water, and observed $\Delta\nu$ for the solution of complex and bulk solvent. The quantity f_{com} is the fraction of the total water present that is complexed and was determined by assuming the metal ion is six-coordinate in solution. The

---

(1) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 2372 (1965).

(2) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

(3) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Discussions Faraday Soc.*, **34**, 77 (1962).

(4) W. D. Horrocks, Jr., R. C. Taylor, and G. N. LaMar, *J. Am. Chem. Soc.*, **86**, 3031 (1964).

(5) S. I. Weissman, *J. Chem. Phys.*, **25**, 890 (1956).

(6) A. J. Freeman and R. E. Watson, *Phys. Rev. Letters*, **6**, 343 (1961).

(7) A. Forman, J. N. Murrell, and L. E. Orgel, *J. Chem. Phys.*, **31**, 1129 (1959).

(8) J. A. Happe and R. L. Ward, *ibid.*, **39**, 1211 (1963).

(9) R. S. Milner and L. Pratt, *Discussions Faraday Soc.*, **34**, 88 (1962).

(10) N. Bloembergen, *J. Chem. Phys.*, **27**, 595 (1957).

(11) R. A. Bernheim, T. H. Brown, H. S. Gutowsky, and D. E. Woessner, *ibid.*, **30**, 950 (1959).

(12) T. J. Swift and R. E. Connick, *ibid.*, **37**, 307 (1962).

(13) N. Bloembergen and L. O. Morgan, *ibid.*, **34**, 842 (1961).

(14) L. O. Morgan and A. W. Nolle, *ibid.*, **31**, 365 (1959).

(15) C. C. McDonald and W. D. Phillips, *J. Am. Chem. Soc.*, **85**, 3736 (1963).

TABLE I

PROTON CONTACT SHIFTS FOR HEXAAQUO METAL PERCHLORATES

$M(H_2O)_6$-$(ClO_4)_x$, g.	Uncomplexed H_2O, g.[a]	$f_{com} \times 10^2$[b]	$-\Delta\nu_{obsd}$, c.p.s.[c,d]	$-\Delta\nu_{com} \times 10^{-3}$ c.p.s.[e]
$Cu(ClO_4)_2$				
0.1249	1.9260	1.855	4.5	0.24
0.1529	1.8992	2.316	5.5	0.24
0.1611	1.8956	2.416	6.5	0.27
0.2976	1.8158	4.559	12.0	0.26
0.3694	1.7957	5.656	15.0	0.27
$Ni(ClO_4)_2$				
0.1573	0.9259	4.776	24.4	0.51
0.2201	0.8949	6.769	37.0	0.55
0.2646	0.8686	8.251	42.0	0.51
0.2757	1.8380	4.241	22.0	0.52
0.4367	1.7460	6.876	35.7	0.52
$Co(ClO_4)_2$				
0.1332	1.8681	2.061	86.2	4.18
0.1537	1.8802	2.356	98.0	4.16
0.1812	1.8728	2.776	113.1	4.07
0.2045	1.8749	3.119	130.0	4.17
0.2468	1.8201	3.848	155.6	4.04
$Fe(ClO_4)_2$				
0.1467	0.9252	4.506	308	6.84
0.1546	0.9272	4.728	316	6.68
0.2205	0.9003	6.794	447	6.58
0.2427	1.8563	3.745	252	6.73
0.2722	1.8260	4.248	283	6.66
0.4101	0.8000	13.236	876	6.62
$Mn(ClO_4)_2$				
0.0068	1.9386	0.1046	11	10.5
0.0118	1.9682	0.1785	19	10.6
0.0221	1.9455	0.3378	33	9.8
0.0239	1.9546	0.3635	34	9.4
0.0263	1.9592	0.3989	42	10.5
$Fe(ClO_4)_3$				
0.0212	1.9544	0.253	33	13.0
0.0906	1.9192	1.092	141	12.9
0.0982	1.9153	1.183	156	13.2
0.1189	1.9080	1.436	197	13.7
0.1208	1.9020	1.463	186	12.7
0.1745	1.8904	2.113	270	12.8

[a] Grams of water added as solvent. [b] f_{com} is the fraction of water that is complexed and is calculated by assuming the metal ions are six-coordinate in solution. [c] The n.m.r. shifts are measured relative to $(CH_3)_3Si(CH_2)_3SO_3Na$ as an internal standard. The shift for pure water at 40° relative to this standard is 280 c.p.s. [d] Δ_{obsd} is the averaged proton n.m.r. shift for the solution of rapidly exchanging complexed and uncomplexed water relative to the proton resonance position for uncomplexed water. [e] $\Delta\nu_{com}$ is the proton shift calculated for the complexed water relative to uncomplexed water assuming the limit of fast exchange.

uncomplexed water proton resonance was found to occur at −280 c.p.s. relative to $(CH_3)_3Si(CH_2)_3SO_3Na$ at 40 ± 1°. All resonance shifts were measured relative to $(CH_3)_3Si(CH_3)_3SO_3Na$ as an internal standard and then referenced to the resonance position for the uncomplexed water protons.

No significant concentration dependence of the proton contact shifts was observed in the concentration range studied (Table I). Thus, the changes in ion pairing and anion–water interactions, in the range of concentrations studied, caused no detectable affects on the n.m.r. shifts.

The electron nuclear coupling constants were calculated by substitution of the contact shift ($\Delta\nu_{com}$) into eq. 2,[10,12] where

$$\frac{\Delta\nu}{\nu} = -A_n\frac{\gamma_e}{\gamma_n}\frac{g\beta S(S+1)}{3kT} \qquad (2)$$

$\Delta\nu$ is the n.m.r. shift, A_n the electron-nuclear coupling constant, ν the resonant frequency (60 Mc.), g the Lande g factor, β the Bohr magneton, S the electron spin, and γ_e/γ_n is the ratio of the magnetogyric ratio for the electron and nucleus.

TABLE II

N.M.R. CONTACT SHIFTS AND ELECTRON SPIN-PROTON SPIN COUPLING CONSTANTS

Metal ion	$-\Delta\nu_{com} \times 10^{-3}$ c.p.s.[a]	S[b]	$A/h \times 10^{-5}$ c.p.s.[c]	St_{2g}	$A\pi/h \times 10^{-5}$ c.p.s.[d]
Cu^{+2}	0.26 ± 0.01	$^1/_2$	1.5 ± 0.1	...	...
Ni^{+2}	0.52 ± 0.01	1	1.1 ± 0.1	...	...
Co^{+2}	4.12 ± 0.07	$^3/_2$	4.2± 0.1	$^1/_2$	18.3 ± 0.4
Fe^{+2}	6.68 ± 0.10	2	5.0 ± 0.1	1	14.0 ± 0.2
Mn^{+2}	10.1 ± 0.5	$^5/_2$	5.9 ± 0.3	$^3/_2$	12.7 ± 0.6
Fe^{+3}	13.0 ± 0.3	$^5/_2$	7.7 ± 0.1	$^3/_2$	16.5 ± 0.4

[a] Average proton contact shift relative to the resonance position of uncomplexed water. [b] Total spin S. [c] Coupling constant A/h calculated from eq. 2 using the total spin S. The g values are estimated from the magnetic moments using the relationship $g = \mu_{eff}/\sqrt{S(S+1)}$. [d] Coupling constant calculated from eq. 2 and the electron spin in the t_{2g} d orbitals (see text for discussion).

Results

The proton contact shift data for hexaaquo metal perchlorate complexes are listed in Table I. Several solutions for each metal ion have been studied. The results indicate the absence of a concentration dependence in the concentration range studied. All of the contact shifts for the water protons in these paramagnetic complexes occur downfield from the resonance position of uncomplexed water. The signs of the coupling constants as seen from inspection of eq. 2 must all be positive.

The electron-nuclear coupling constants (A) calculated from the total spin S are listed in Table II. The utility of the A values for the metal complexes of Co^{+2}, Fe^{+2}, Mn^{+2}, and Fe^{+3} is very limited, for the coupling constant contains contributions from both π and σ bonding effects. Single crystal e.s.r. and n.m.r. studies have been partially successful in resolving the π and σ contributions in metal fluorides.[16–20] Assuming that the contact shift due to the two unpaired σ e_g d electrons for all these metal ions is about the same as that for the Ni^{+2} complex, the σ contribution to the shift may be subtracted out. The approximate coupling constants (A_π) due to unpaired π electron density may then be calculated. The approximate A_π values are listed in Table II. The fact that the π effect dominates the contact shift gives credence to this means of approximating A_π. The A_π values increase regularly from Mn^{+2} to Fe^{+2} to Co^{+2}. The coupling constant due to unpaired s electron density (A_s) for the corresponding metal fluorides has been found to increase in the same order.[16,17]

Discussion

The sign of the coupling constant can be useful in suggesting possible electron delocalization mechanisms.

---

(16) T. P. P. Hall, W. Hayes, R. W. H. Stevenson, and J. Wilkens, *J. Chem. Phys.*, **38**, 1977 (1963).
(17) T. P. P. Hall, W. Hayes, R. W. H. Stevenson, and J. Wilkens, *ibid.*, **39**, 35 (1963).
(18) R. G. Shulman and V. Jaccarino, *Phys. Rev.*, **103**, 1126 (1956).
(19) R. E. Watson and A. J. Freeman, *Phys. Rev. Letters*, **6**, 277 (1961).
(20) R. G. Shulman and K. Knox, *ibid.*, **4**, 603 (1960).

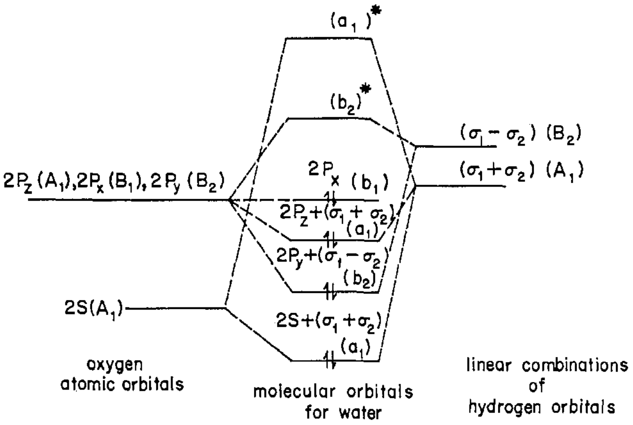


Figure 1.—Molecular orbital diagram for water.

The coupling constants can yield information concerning the properties of orbitals that contain unpaired electron density.[2,8,19] The metal ions Ni^{+2} and Cu^{+2} in an octahedral ligand field have filled π-type t_{2g} d orbitals and partially filled σ-type e_g d orbitals. The unpaired electrons in octahedral complexes of Ni^{+2} and Cu^{+2} are to a good approximation confined to σ-type orbitals. Unpaired electron density is placed directly in the σ molecular orbitals of water by complex formation with these metal ions. The σ molecular orbitals of water contain some hydrogen 1s character (Figure 1). Thus, unpaired density is directly transferred from the metal e_g d orbital to the hydrogen 1s orbital by σ bond formation. This mechanism predicts the observed positive coupling constant which is manifested in a downfield shift for the proton resonance.

The proton contact shifts for water complexed to Co^{+2}, Fe^{+2}, Mn^{+2}, and Fe^{+3} also occur downfield from the resonance position for uncomplexed water (Table I). The electron proton coupling constants are thus positive. Each member of this group of metal ions contains unpaired electrons in both the π-type t_{2g} and the σ-type e_g d oribitals. In complex formation unpaired electron density may thus be transferred to both the σ and π molecular oribitals of water. The large increase in the downfield contact shift when unpaired π electrons are present clearly indicates that the sign of the π electron–proton coupling constant is positive. The coupling constant for an electron in a p orbital of oxygen with a directly bonded proton (O–H) is known to be negative.[21] The coupling constant for a pπ oxygen electron with the proton has also recently been evaluated from the hyperfine splitting in substituted aromatic radical anions.[22] This coupling is completely analogous to the very well-known indirect coupling of unpaired carbon pπ electrons with the in-plane protons of aromatic radicals.[23] The theory of π–σ exchange coupling has been worked out to explain the negative coupling constant.[5,24] The observed π electron–proton coupling constant in these water complexes is, however, positive. The π bonding that dominates the contact shifts in these complexes must involve a π donor molecular orbital of water that contains appreciable hydrogen 1s character. A crude molecular orbital diagram for water is given in Figure 1. The diagram is constructed from the transformation properties of the atomic orbitals under the C_{2v} point group. An approximate molecular orbital diagram for the hexaaquo complexes assuming octahedral symmetry is given in Figure 2. In an octahedral complex the two a_1 water molecular orbitals are σ donors while the b_1 and b_2 orbitals may be used for π donation.

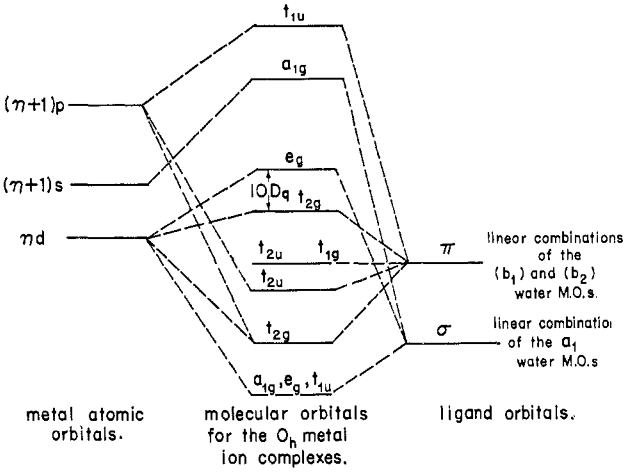


Figure 2.—Molecular orbital diagrams for octahedral complexes.

The two a_1 σ donor molecular orbitals are constructed from oxygen 2s or $2p_z$ with the $(\sigma_1 + \sigma_2)$ combination of two hydrogen 1s orbitals (Figure 1). Covalent σ bonding with the metal e_g d orbitals directly places unpaired electron density in the hydrogen 1s orbital in agreement with the positive coupling constant.

The b_1 π donor orbital is principally an oxygen atomic $2p_x$ orbital (Figure 1). The b_2 orbital is constructed from the oxygen $2p_y$ and the $(\sigma_1 - \sigma_2)$ combination of the two hydrogen 1s orbitals. Covalent π bonding of the b_1 oxygen orbital with the metal t_{2g} d orbitals places unpaired electron density in the oxygen $2p_x$ orbital. This situation is analogous to the O–H radical and a negative coupling constant is anticipated. Covalent π bonding with the b_2 molecular orbital of water, however, directly places a net unpaired electron density in an orbital that has a contribution from the hydrogen 1s. This process predicts the observed positive coupling constant.

The b_1 nonbonding m.o. undoubtedly is responsible for the majority of π donation by water. The b_1 orbital transfers electronic effects to the proton by the relatively inefficient π–σ indirect coupling. The contribution to the contact shift from π bonding is the net effect of the opposing b_1 and b_2 mechanisms. The contact shift is dominated by π bonding with the b_2 m.o. because the b_2 m.o. contains hydrogen 1s character. It is surprising that the b_2 m.o. is so strongly involved in π donation to the metal, for it must be responsible for a large portion of the bonding energy in the H_2O molecule (Figure 1).

---

(21) H. E. Radford, *Phys. Rev.*, **126**, 1035 (1962).

(22) G. P. Rabold, K. H. Bar-Eli, and K. Weiss, *Chem. Commun.* (London), 38 (1965).

(23) A. Carrington, *Quart. Rev.* (London), **17**, 67 (1963).

(24) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

The striking increase in the magnitude of the contact shift in passing from the Ni^{+2} to the Co^{+2} complex is obviously due to the presence of unpaired π electrons. Electron delocalization in water complexes must be strongly influenced by π bonding. These results suggest that the Co^{+2} complex should be stabilized by water π donation relative to the Ni^{+2} complex. The anticipated discontinuity between Co^{+2} and Ni^{+2} is, however, not realized in the thermodynamics of metal ion hydration.[25] This result gives experimental support for the theoretical prediction of Sugano and Shulman that π bonding is important in electron delocalization, but σ bonding dominates the bond energy.[26]

The effect of metal ion charge on the extent of electron delocalization was evaluated for the isoelectronic metal ions Fe^{+3} and Mn^{+2}. The contact shift data indicate that the metal–water bond in the Fe^{+3} complex involves a significantly larger amount of covalency than in the Mn^{+2} complex. This result is consistent with analogous e.s.r. measurements.[16]

Acknowledgment.—The authors wish to thank the Petroleum Research Fund for their support of this research through grant No. 226-G.

[25] P. George and D. S. McClure, *Progr. Inorg. Chem.*, **1**, 281 (1959).

[26] S. Sugano and R. G. Shulman, *Phys. Rev.*, **130**, 517 (1963).

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
UNIVERSITY OF ARIZONA, TUCSON, ARIZONA, AND OREGON STATE UNIVERSITY, CORVALLIS, OREGON

Silver(I) Complexes of Bicyclic Tertiary Amines[1]

BY HAROLD M. HILLIARD[2] AND JOHN T. YOKE III[3]

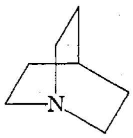
Received July 12, 1965

Triethylamine and N,N,N′,N′-tetramethylethylenediamine have been compared with their bicyclic analogs, quinuclidine and triethylenediamine, as ligands toward $AgNO_3$. Potentiometric titrations in dimethyl sulfoxide, using the cell, Ag, AgCl (satd.) + NaCl(satd.)|$NaNO_3$ (0.10 *M*)|$NaNO_3$ + $AgNO_3$(μ = 0.1) + amine, Ag were carried out at 25.0° under N_2, and the stepwise formation constants were calculated according to Fronaeus. Only 1 mole of triethylamine per Ag(I) was found to coordinate in DMSO; bis(amine) complexes were formed with the other amines. Solid complexes were prepared, containing (per mole of $AgNO_3$) 1.5 moles of triethylenediamine or 2 moles of the other amines. The tetramethylethylenediamine complex was characterized as the bis chelate, $[Ag((CH_3)_2NCH_2CH_2N(CH_3)_2)_2]NO_3$. The complexes of the bicyclic amines with bridgehead nitrogen were more stable thermally with respect to oxidation–reduction than the others; the triethylamine complex decomposed at 0°.

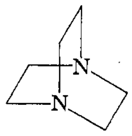
Introduction

Tertiary aliphatic amines do form metal complexes[4]; however, they are relatively weak ligands. Brown and Sujishi[5] showed the importance of steric hindrance in a comparison of triethylamine and its bicyclic analog, quinuclidine, as bases toward the reference acid trimethylborane. No comparable study using metal ion reference acids has been reported. A metal cation might show various coordination numbers toward the amine ligands, and competition between amine, anion, and solvent may be expected. Trimethylborane is limited to the formation of 1:1 adducts.

We have studied the silver nitrate complexes of these two amines, and also of two similarly related diamines, N,N,N′,N′-tetramethylethylenediamine and its bicyclic analog, triethylenediamine or 1,4-diazabicyclo[2.2.2]octane. In addition to differing steric requirements, the latter pair also provide the possible comparison of a chelating and a nonchelating but bidentate diamine.



Quinuclidine



Triethylenediamine

Silver(I) complexes in aqueous or partly aqueous triethylamine–triethylammonium salt systems have been studied previously,[6] and values have been reported for the first and second complex formation constants. There have been no reports of solid silver(I) triethylamine complexes. No metal complexes of quinuclidine have been reported. Formation of the bis(tetramethylethylenediamine)silver(I) complex ion was demonstrated by Streuli during potentiometric titration of silver(I) perchlorate in anhydrous acetone.[7] Neither stability studies nor preparations of solid complexes

---

[1] Abstracted from the Ph.D. Dissertation of H. M. H., University of Arizona, 1965. Presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965. This work was supported by the National Institutes of Health, Public Health Service, through grants GM 11511-01 and 12642-01.

[2] Koppers Co. Summer Fellow, 1962; Research Corporation Fellow, 1962–1963; N.S.F. Summer Fellow, 1963.

[3] To whom inquiries should be addressed at the Department of Chemistry, Oregon State University, Corvallis, Ore. 97331.

[4] W. E. Hatfield and J. T. Yoke, *Inorg. Chem.*, **1**, 463 (1962).

[5] H. C. Brown and S. Sujishi, *J. Am. Chem. Soc.*, **70**, 2878 (1948).

[6] (a) F. G. Pawelka, *Z. Elektrochem.*, **30**, 180 (1924); (b) H. T. S. Britton and W. G. Williams, *J. Chem. Soc.*, 796 (1935); (c) J. Bjerrum and S. Refn, unpublished results, cited by J. Bjerrum, *Chem. Rev.*, **46**, 387 (1950); (d) C. T. Anderson, Dissertation, The Ohio State University, 1955.

[7] C. A. Streuli, "Titrimetric Methods," D. S. Jackson, Ed., Plenum Press, New York, N. Y., 1961, p. 97.