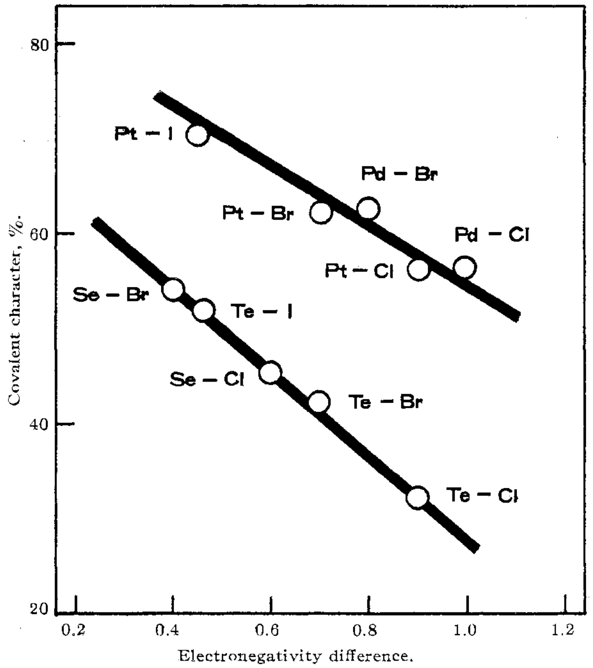

Fig. 2.—Dependence of the covalent character of metal–ligand bonds in hexahalo complexes on the difference between the electronegativities of ligands and the central atom.

0.12 for hexachloro complexes and 0.11 for hexabromo complexes. The close agreement of the two values with each other suggests that the covalent character of bonds between the central atom M and ligands X is in linear relation to the electronegativity difference $\Delta\chi = \chi_X - \chi_M$. The relation between the covalent character and $\Delta\chi$ is shown in Fig. 2. It will be seen that hexahaloselenates(IV) and hexahalotellurates(IV), having the same outer electronic configuration of the central atoms, yield a single straight line, while the data for hexahaloplatinates(IV) and hexahalopalladates(IV) lie approximately on another straight line. This simple rule of linearity is useful, because it permits one to estimate the extent of covalent character of M–X bonds whenever necessary data are available for complexes of analogous structure.

The net charge on a selenium atom in these complexes is close to a unit charge rather than to zero, as might be expected from Pauling's electroneutrality principle.[17] We already have pointed out that tellurium(IV), having an outer electronic configuration $4d^{10}5s^2$, can avail itself of only three 5p orbitals for forming bonds with halogen in a $[TeX_6]^{2-}$ ion, because 5d and 6s orbitals are less stable than 5p orbitals and accordingly no significant resonance structures carrying no formal charge on the central atom are conceivable. The same reasoning applies to hexahaloselenates(IV) provided that all principal quantum numbers are reduced by one. The observed net charge on a selenium atom ranging over 0.8–1.3*e* is consistent with this theoretical conclusion.

(17) L. Pauling, *J. Chem. Soc.*, 1461 (1948); "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 172.

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# The Chelate Effect Studied by Calorimetry, Potentiometry, and Electron Spin Resonance

By G. Atkinson and J. E. Bauman, Jr.[1]

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The thermodynamics of chelation of complexes of 2,2′-bipyridine and pyridine with Mn(II), Ni(II), Cu(II), and Zn(II) were studied by calorimetry and potentiometry. The chelate stabilization for pyridine is of the same order as that for ethylenediamine complexes. The enthalpy and entropy contributions to the chelate effect are analyzed, the former being significant for the Cu(II) and Ni(II) ions. The chelate effect is further divided into cratic and unitary portions. Possibilities of using electron spin resonance as a tool in studying complex stabilities are illustrated. Good agreement is obtained between e.s.r. and traditional measurements.

## Introduction

The pyridine and bipyridine systems of transition metal complexes provide an excellent pair for studying the bonding of chelates. Previous work on the thermodynamics of bipyridine complexes[2] has developed methods for the systematic investigation of a variety of ligands with transition metal ions employing both calorimetry and potentiometry. The chelate effect was defined by Schwarzenbach[3] as the added stability conferred upon a complex containing bidentate or higher order ligands as compared with that from unidentate ligands. The effect can be studied if a suitable coördinating ligand and its corresponding dimer can be found. Spike and Parry[4] studied the chelate effect with primary amines and discussed enthalpy effects with Cu(II). Schwarzenbach[2] studied ethylenedi-

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(1) Department of Chemistry, University of Missouri, Columbia, Mo. Abstracted in part from Ph.D. Thesis of J. E. Bauman, University of Michigan, 1961. This work was supported by the National Institutes of Health (CF-12,177).

(2) G. Atkinson and J. E. Bauman, Jr., *Inorg. Chem.*, **1**, 900 (1962).

(3) G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 2344 (1952).

(4) C. G. Spike and R. W. Parry, *J. Am. Chem. Soc.*, **75**, 2726, 3770 (1953).

TABLE I

THERMODYNAMIC DATA FOR PYRIDINE COMPLEXES

25°, 1 $M$ $NaClO_4$, values of $\Delta F_i$ and $\Delta H_i$ in kcal./mole; $\Delta S_i$ in e.u.

| | $-\Delta F_1$ | $-\Delta F_2$ | $-\Delta F_3$ | $-\Delta F_4$ | $\Delta H_i$ (av.) | $\Delta S_1$ | $\Delta S_2$ | $\Delta S_3$ | $\Delta S_4$ |
|---|---|---|---|---|---|---|---|---|---|
| Mn(II) | 2.54 | 2.17 | 1.22 | 0.82 | 2.39 | 0.5 | −1.5 | −3.9 | −5.3 |
| Ni(II) | 2.90 | 2.26 | 1.53 | 0.89 | 2.65 | 0.8 | −1.3 | −3.8 | −5.9 |
| Cu(II) | 3.35 | 2.66 | 1.73 | 1.15 | 2.95 | 1.3 | −1.0 | −4.1 | −6.0 |
| Zn(II) | 2.84 | 2.31 | 1.40 | 0.87 | 2.58 | 0.9 | −0.9 | −4.0 | −5.7 |

aminetetraacetate complexes *vs.* the iminodiacetates and discussed the favorable entropy change which stabilized the chelated species. Adamson[5] pointed out that the chelate effect is largely due to asymmetry in the choice of standard thermodynamic states. Thus far heterocyclic nitrogen complexes have not been studied with respect to the chelate effect. Since the formation of tetradentate heterocyclic nitrogen chelates in the case of the porphyrins and phthalocyanines appears to give unusually stable complexes, it is important to investigate the chelate effect of the bidentate analogs of these systems.

In this paper data are reported on $\Delta F_i$, $\Delta H_i$, and $\Delta S_i$ of formation for the pyridine complexes of the transition metals Mn(II), Ni(II), Cu(II), and Zn(II). The chelate effect is evaluated by calculations with bipyridine data obtained under identical conditions. The unitary and cratic portions of the chelate effect are discussed. Also the use of electron spin resonance to study the thermodynamics of complex ion formation is presented.

## Experimental

**Materials.**—Pyridine was obtained as reagent grade material. It was purified by refluxing over KOH and distillation with a boiling range of 0.5°. Dilute solutions were titrated with standard $HClO_4$ to determine the concentration of pyridine in the equilibrium studies.

**Determination of Thermodynamic Quantities.**—The methods were detailed in an earlier paper.[2] Formation constants were determined by potentiometric titrations and $\Delta H_i$ by calorimetry.

**Electron Spin Resonance.**—A spectrometer at a microwave frequency of 9100 Mc. was used. The derivative of the detected signal was recorded as a function of the magnetic field. Millimolar aqueous Mn(II) solutions were used in quartz tubes of 1 mm. i.d. A series of solutions was made up with varying concentrations of pyridine and bipyridine, holding the concentration of Mn(II) constant. To prevent the formation of hydroxy complexes at high pH values, the pH of the solutions was maintained by using a 0.1 $M$ acetate buffer. Samples of each solution were placed in quartz tubes of identical bore. The klystron power and the detecting crystal current were optimized with Mn(II) water solution in the cavity. Using a power of 7 d.b., adjusting the iris screw at the cavity so that the crystal current measured 100 μa., using maximum 100 kc./sec. modulation and a fixed attenuation, each sample was run under the same conditions at room temperature. It was not necessary to retune the klystron between samples. The spectra were measured in arbitrary units of height. The sweep rate was adjusted so that the area of the resulting signal could be obtained at approximately 1% precision on a width measurement. To check the instrument a series of $Mn(ClO_4)_2$ solutions over a tenfold concentration range from $1 \times 10^{-4}$ to $1 \times 10^{-3}$ $M$ was measured. The sum of the heights of the six hyperfine lines gave a linear plot against concentration.

## Results and Discussion

Table I contains thermodynamic data for the pyridine complexes. It may be noted that only four constants are reported for each metal ion. Under the concentrations used (0.06 $M$ pyridine) the addition of further moles of pyridine to the metal ions was not observed except with Cu(II). The appearance of the formation curves above a level corresponding to four pyridines per metal ion did not give confidence to any calculations in this area. Subscripts refer to stepwise thermodynamic quantities. An additional non-significant digit is carried in the $\Delta H$ and $\Delta S$ columns to avoid rounding off errors in later calculations.

TABLE II

FORMATION CONSTANTS FOR PYRIDINE COMPLEXES[a]

25°, 1 $M$ $NaClO_4$

| | log $k_1$ | log $k_2$ | log $\beta_2$ | log $k_3$ | log $k_4$ | log $\beta_4$ |
|---|---|---|---|---|---|---|
| Mn(II) | 1.86 | 1.59 | 3.45 | 0.90 | 0.60 | 4.95 |
| Ni(II) | 2.13 | 1.66 | 3.79 | 1.12 | .65 | 5.56 |
| Cu(II) | 2.46 | 1.95 | 4.41 | 1.27 | .84 | 6.52 |
| Zn(II) | 2.08 | 1.69 | 3.77 | 1.03 | .64 | 5.44 |

[a] $pK_a$ pyridine = 5.15.

Table II contains the formation constants of the complexes. The $k_i$ values represent individual formation constants; $\log \beta_i = \log k_1 + \ldots + \log k_i$. These constants for Cu(II) agree well with data reported by Bjerrum,[6] Bruehlmann,[7] and Leussing.[8] However, the results for Ni(II) and Zn(II) are higher than those of Bjerrum[6] and Nyman.[9]

The chelate effect can be shown for the reactions

$$M(py)_2 + bipy \rightleftharpoons M(bipy) + 2py \qquad (1)$$

$$M(py)_4 + 2bipy \rightleftharpoons M(bipy)_2 + 4py \qquad (2)$$

Table III presents values of $\Delta F$, $\Delta H$, and $\Delta S$ for both of these reactions. The subscripts refer to the replacement of pyridine ligands with 1 and 2 moles of bipyridine. The chelate effect is most noticeable with Ni(II) and Cu(II) due to the contribution of a large enthalpy term. The consistency of the entropy portion of the chelate effect is remarkable when one excludes Cu(II). With this ion the low entropy change of the bis chelate is closely related to the low values of entropies observed earlier with Cu(II) bipyridine complexes.[2] The chelate effect for both Mn(II) and Zn(II) is made up solely of

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(5) A. W. Adamson, *J. Am. Chem. Soc.*, **76**, 1578 (1954).

(6) J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950).

(7) R. T. Bruehlmann and F. H. Verhoek, *J. Am. Chem. Soc.*, **70**, 1401 (1948).

(8) D. L. Leussing and R. C. Hansen, *ibid.*, **79**, 4270 (1957).

(9) C. J. Nyman, *ibid.*, **75**, 3575 (1953).

Table III

The Chelate Effect for Bipyridine and Pyridine

| | $\Delta F_1$, kcal./mole | $\Delta F_2$, kcal./mole | $\Delta H_1$, kcal./mole | $\Delta H_2$, kcal./mole | $\Delta S_1$, e.u. | $\Delta S_2$, e.u. |
|---|---|---|---|---|---|---|
| Mn(II) | −0.82 | −3.94 | +0.48 | +0.96 | +5.1 | +17.2 |
| Ni(II) | −4.11 | −10.50 | −2.77 | −5.54 | +4.5 | +16.6 |
| Cu(II) | −3.46 | −8.41 | −2.43 | −4.86 | +3.4 | +11.9 |
| Zn(II) | −1.52 | −5.50 | −0.11 | −0.22 | +4.7 | +17.7 |

an entropy effect. This difference between Zn(II) and Cu(II) chelates was first pointed out by Spike and Parry[4] in the ethylenediamine–methylamine system. If one considers the $\Delta H$ contribution to the chelate effect from a crystal field approach an explanation is possible. The spectroscopic $Dq$ is greater for bipyridine than for pyridine complexes. Therefore Cu(II) and Ni(II) chelates of bipyridine can be stabilized with respect to pyridine complexes through crystal field effects. Mn(II), having a half-filled d-shell, cannot be stabilized because of its cubic symmetry. Zn(II) cannot be stabilized because of its filled d-shell.

A comparison of the chelate stabilization for ethylenediamine and EDTA is given in Table IV for $MA_2 + B \rightleftharpoons MB + 2A$, where B represents a chelating ligand which is approximately the dimer of A.

Table IV

Free Energies of Chelation in Various Systems, $\Delta F_1$ in kcal./mole

| | bipy–py | en–$NH_3$[4] | EDTA–iminodiacetate[3] |
|---|---|---|---|
| Ni(II) | −4.1 | −3.7 | −7.2 |
| Cu(II) | −3.5 | −4.3 | −3.2 |
| Zn(II) | −1.5 | −1.6 | −5.2 |

The chelate stabilization of ethylenediamine and ammonia is quite similar to the bipyridine–pyridine system. However, the positions of Cu(II) and Ni(II) are reversed in the two series. EDTA shows even more instability with Cu(II) than bipyridine. This is expected because of the increased distortion produced on the Cu(II) electron system by the chelating ligands as one goes from ethylenediamine to bipyridine to EDTA.

The chelate effect may be examined further after the manner of Gurney[10] and Adamson.[5] Both $\Delta F$ and $\Delta S$ can be separated into a unitary part dependent on the characteristics of particles during a reaction, and a cratic term due to a change in the number of particles during a reaction. The unitary portion can be found most simply (though approximately) by putting $\Delta F$ and $\Delta S$ on a mole fraction concentration basis. At 25° in water this is done by

$$\Delta F' = \Delta F_{(\text{unitary})} - \Delta nRT \ln 55.5$$

$$\Delta S' = \Delta S_{(\text{unitary})} - \Delta nR \ln 55.5$$

Table V

Unitary Chelate Effect

$$\Delta F_i' = \Delta F_i - 2.36\Delta n^a$$

$$\Delta S_i' = \Delta S_i + 7.92\Delta n^a$$

$$\Delta H_i' = \Delta H_i$$

$$M(py)_2 + bipy \rightleftharpoons M(bipy) + 2py \qquad (1)$$

$$M(py)_4 + bipy \rightleftharpoons M(bipy)_2 + 4py \qquad (2)$$

| | $\Delta F_1'$, kcal./mole | $\Delta F_2'$, kcal./mole | $\Delta H_1'$, kcal./mole | $\Delta H_2'$, kcal./mole | $\Delta S_1'$, e.u. | $\Delta S_2'$, e.u. |
|---|---|---|---|---|---|---|
| Mn(II) | +1.54 | +0.78 | +0.48 | +0.96 | −2.8 | +1.4 |
| Ni(II) | −1.75 | −5.78 | −2.77 | −5.54 | −3.4 | +0.8 |
| Cu(II) | −1.10 | −3.69 | −2.13 | −4.86 | −4.5 | −3.9 |
| Zn(II) | +0.84 | −0.78 | −0.11 | −0.11 | −3.2 | +1.9 |

[a] $\Delta n = -1$ for $i = 1$; $\Delta n = -2$ for $i = 2$.

Table VI

E.s.r. Data on Mn(II) Complexes[a]

| | Solvent | Signal height | Uncomplexed Mn(II), moles/l. × $10^3$ |
|---|---|---|---|
| (1) | $H_2O$ | 419.3 | 3.75 |
| (2) | $H_2O$ + 0.1 *M* acetate buffer | 300.0 | 2.68 |
| (3) | (2) + 0.0418 *M* pyridine | 236.0 | 2.11 |
| (4) | (2) + 0.0836 *M* pyridine | 192.3 | 1.72 |
| (5) | (2) + 0.00124 *M* bipy | 183.4 | 1.64 |
| (6) | (2) + 0.00248 *M* bipy | 117.2 | 1.05 |
| (7) | 0.583 *M* pyridine | 218.1 | 1.95 |
| (8) | 0.0218 *M* bipyridine | 36.4 | 0.326 |
| (9) | Pure pyridine | 36.9 | 0.330 |

[a] $Mn(ClO_4)_2$ at $3.75 \times 10^{-3}$ *M* in each case.

where $\Delta n$ is the change in the number of particles going from left to right across the reaction. Table V gives the unitary chelate effect for two steps of chelate formation. The elimination of the cratic term gives a negative $\Delta S_1'$ for reaction 1. This is expected since considerably more ordering is necessary to form a chelate ring than the corresponding bis-coördinated complex. The appearance of positive free energies for Mn(II) and Zn(II) complexes indicates that the chelated form is no longer the more stable. Cu(II) and Ni(II) remain stabilized by an enthalpy term. $\Delta S_2'$ for Cu(II) clearly shows the increased ordering necessary to add a second mole of bipyridine.

**Electron Spin Resonance.**—Mn(II) exists in the hexaaquo complex with cubic symmetry, and magnetic susceptibility measurements show that the change in symmetry with complexation does not appear to shift the $^6S$ ground state to a state of lower multiplicity. McGarvey[11] was able to show that the amount of uncomplexed Mn(II) in aqueous solution can be determined by measuring the amplitude of the narrow resonance peak. Decreasing the symmetry causes the hyperfine resonance to disappear. Hexaaquo Mn(II) gives a series of hyperfine lines 30–40 gauss wide, whereas the broad resonance of the pyridine complex is 610 gauss wide. Thus the narrow signal is superimposed on a very broad base, and the intensity of the narrow resonance gives a measure of the uncomplexed Mn(II) concentration.

Calculations of the Mn(II) concentrations from e.s.r. hyperfine spectra were based on $Mn(ClO_4)_2$ in $H_2O$ at a concentration of $3.75 \times 10^{-3}$ *M*. Table VI gives the

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[10] R. W. Gurney, "Ionic Processes in Solution," 2nd Ed., McGraw-Hill Book Co., New York, N. Y., 1953.

[11] B. M. McGarvey, *J. Phys. Chem.*, **61**, 1323 (1957).

data on the sum of the heights of the e.s.r. derivative curve for the six hyperfine lines of Mn(II). The yellow Mn(II)(bipy)$_3$ solution gave an asymmetric spectrum.

Considering ion association due to the Mn(II)-acetate, and complex formation due to the Mn(II)-pyridine, one can calculate

$$\mathrm{Mn(II)} + \mathrm{Ac} \xrightleftharpoons{K_a} \mathrm{Mn(II)Ac}\ \text{(ion association)}$$

$$K_a = \frac{[\mathrm{Mn(II)Ac}]}{[\mathrm{Mn(II)}][\mathrm{Ac}]} = \frac{(0.00375 - 0.00268)}{(0.00268)(0.1)} = 4.0$$

Similar calculations hold for pyridine and bipyridine

$$\mathrm{Mn(II)} + \mathrm{py} \xrightleftharpoons{k_{py}} \mathrm{Mn(II)py}$$

$$\mathrm{Mn(II)} + \mathrm{bipy} \xrightleftharpoons{k_{bipy}} \mathrm{Mn(II)bipy}$$

From (3) and (4), $k_{py} = 6.5$ and 6.8, respectively; from (5) and (6), $k_{bipy} = 3.16 \times 10^3$ and $1.86 \times 10^3$, respectively. Assuming complete complexation for solutions (7) and (8) one calculates $\beta_6$py = 23.3 and $\beta_3$bipy = $1.07 \times 10^6$. The latter value is interesting when compared with Brandt's[12] data from spectrophotometry in the near-ultraviolet: log $\beta_3$ = 6.33; this value (e.s.r.), log $\beta_3$ = 6.03.

To estimate the chelate effect from the e.s.r. data one may compare log $k$ values for bipyridine and pyridine, respectively. The average values are 3.39 and 0.82, giving a $\Delta F_{chel}$ of $-3.6$ kcal./mole. This compares favorably with the potentiometric value and points out the good possibility of using e.s.r. to obtain reliable data on biological complex stabilities either by direct Mn(II)-ligand interaction or a competition between Mn(II) and another metal ion.

**Acknowledgment.**—We wish to thank Dr. R. H. Sands and Mr. W. Moos for help with the spin resonance experiments.

(12) R. R. Miller and W. W. Brandt, *J. Am. Chem. Soc*, **77**, 1384 (1955).

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# Magnetic Susceptibilities and Dilution Effects in Low-Spin d$^4$ Complexes: Osmium(IV)

BY ROLF B. JOHANNESEN AND GEORGE A. CANDELA

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Magnetic susceptibility measurements were made on a series of hexachloro- and hexabromoösmates, $M_2OsX_6$, and on potassium hexachlororuthenate, $K_2RuCl_6$. The paramagnetism of the Os(IV) complexes is independent of temperature and increases as the osmium ions are separated. It is shown that the effect of dilution is described by the equation $\chi = \chi_\infty/(1 + \lambda d^{-n}\chi_\infty)$, where $\chi_\infty$ is the susceptibility at infinite dilution, $d$ is the average distance between the osmium ions, $\lambda$ is a constant, and $n$ is approximately 2. An intermediate coupling scheme is necessary to explain the experimental results for the 5d$^4$ configuration. The magnetic susceptibility and part of the optical absorption spectrum can be fit to theory by choosing the values of 2100 ± 100 cm.$^{-1}$ for the spin-orbit coupling constant and 2800 ± 100 cm.$^{-1}$ for the Coulomb interaction coefficient.

## Introduction

In 1949 Kotani[1] proposed a theory to explain the magnetic susceptibilities of d$^n$ octahedral complexes for $n$ = 1–5. Kotani made the important assumption that the ligand field is much larger than the Coulomb repulsion between the d-electrons. He calculated energy levels and susceptibilities for the magnetically dilute complexes with the further assumption that the Coulomb interaction coefficient, $3B + C$, was much greater than the spin-orbit coupling constant, $\zeta$. He obtained excellent agreement with experiment for the 3d$^n$ complexes. Kotani predicted that a d$^4$ configuration would have a singlet ground state and a temperature independent paramagnetism given by the equation $\chi = 24N\beta^2/\zeta$ when $\zeta >> kT$, where $N$ is Avogadro's number and $\beta$ is the Bohr magneton. The spin-orbit coupling constant is expected to be fairly large for the 4d and 5d electrons and in 1954 Johannesen and Lindberg[2] reported a temperature independent paramagnetic susceptibility for ammonium hexabromoösmate of (980 ± 20) $\times 10^{-6}$ cm.$^3$ mole$^{-1}$ over the temperature range of 100 to 400°K.[3] Using Kotani's theory and their susceptibility data they estimated a value of 6400 cm.$^{-1}$ for the spin-orbit coupling constant, which is considerably higher than that expected for the free osmium ion.

In 1958 Griffith[4] noted the isomorphism between the octahedral (dt$_2$)$^n$ and p$^{6-n}$ configurations and reported another derivation of the Kotani formulas for susceptibilities of low-spin d$^n$ complexes. At a conference in 1958 Figgis and co-workers[5] reported tem-

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(1) M. Kotani, *J. Phys. Soc. Japan*, **4**, 293 (1949).

(2) R. B. Johannesen and A. R. Lindberg, *J. Am. Chem. Soc.*, **76**, 5349 (1954).

(3) In 1943 the susceptibility of the same complex was reported by D. P. Mellor (*J. Proc. Roy. Soc. N. S. Wales*, **77**, 145 (1943)); however, the measurements were made at room temperature only.

(4) J. S. Griffith, *Trans. Faraday Soc.*, **54**, 1109 (1958).

(5) B. N. Figgis, J. Lewis, R. S. Nyholm, and R. D. Peacock, *Discussions Faraday Soc.*, **26**, 103 and 175 (1959).