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The Paramagnetic Influence of Hexaaquochromium(III) Ion in Aqueous Perchlorate Solutions[1]

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Paramagnetic shifts of the nuclear magnetic resonance peak for O^{17} in labile H_2O and in ClO_4^- ion have been observed in aqueous, acidic perchlorate solutions of Cr(III). The data fit a model in which both labile H_2O and ClO_4^- ion experience a paramagnetic influence when they enter a "second sphere" about the $Cr(H_2O)_6^{+3}$ ion.

Connick and Poulson[2] have shown that Cr(III) in aqueous solution is much less effective than other paramagnetic ions in relaxing the O^{17} nuclear spin in H_2O. This implies that the labile H_2O in Cr(III) solutions is at least partially shielded from the paramagnetic Cr(III) by the nonlabile layer of H_2O in the $Cr(H_2O)_6^{+3}$ complex. Though this is undoubtedly true, it was found in the present work that $Cr(H_2O)_6^{+3}$ produces a significant paramagnetic shift in the position of the O^{17} nuclear magnetic resonance in both ClO_4^- ion and labile H_2O in aqueous perchlorate solutions. The shift in the O^{17} resonance in the labile H_2O, though small compared with H_2O^{17} shifts produced by some paramagnetic ions, is large enough to be measured with good precision over a rather wide range of Cr(III) concentrations. The shift by $Cr(H_2O)_6^{+3}$ of the O^{17} resonance in ClO_4^- ion is quite small but can be measured with reasonable precision at higher Cr(III) concentrations.

This paper utilizes measurements of the shifts in the position of the O^{17} nuclear magnetic resonance to draw conclusions concerning the interaction of $Cr(H_2O)_6^{+3}$ with ClO_4^- ion and labile H_2O in aqueous perchlorate solutions of Cr(III).

Experimental

A quantity of Cr(III) perchlorate was prepared by reduction of analytical grade CrO_3 with H_2O_2 in $HClO_4$ solution. The composition of the crystals obtained by evaporation of the resulting Cr(III) solution is expressed by the formula $Cr(ClO_4)_3(H_2O)_{6.43}(HClO_4)_{0.24}$. To make up solutions for n.m.r. investigation, weighed amounts of these crystals were dissolved in weighed amounts of H_2O enriched to ~1% in O^{17}. To avoid possible solvolysis of Cr(III) species at low acidity, a weighed amount of 70.4% aqueous $HClO_4$ was added to each solution to make it ~1.5 *m* in H^+.

The n.m.r. shifts were measured at 8 Mc. using a Varian wide-line spectrometer. The samples were contained in 17-mm. o.d. spherical Pyrex bulbs provided with 4-mm. i.d. stems for filling. The stem was closed off at the top by a greased standard-taper stopper. All measurements were made at ambient temperature (~20°).

Results

The resonance shifts of O^{17} in ClO_4^- and labile H_2O, along with the pertinent solution composition variables, are listed in Table I. Hunt and Taube[3] have shown that in aqueous perchlorate solutions of Cr(III), the chromium species is $Cr(H_2O)_6^{+3}$, which exchanges H_2O very slowly with the unbound water in the system. In principle, the O^{17} n.m.r. spectrum in such solutions should then display two H_2O peaks, one for the H_2O in the $Cr(H_2O)_6^{+3}$ complex and one for the unbound or labile H_2O. In fact, only the peak for the labile H_2O is observed and it is presumed that the peak due to the H_2O in the $Cr(H_2O)_6^{+3}$ complex is so strongly shifted and broadened as to escape detection by the methods employed in this work. It is further observed that the position of the O^{17} resonance in the labile H_2O in these solutions is shifted paramagnetically from its position in pure H_2O. The amount of this shift is the quantity δ_{H_2O} listed in Table I. Since δ_{H_2O} increases with increasing Cr(III) concentration, one is led to the conclusion that the labile H_2O experiences a paramagnetic influence whenever it finds itself in a "second sphere" around the $Cr(H_2O)_6^{+3}$ ion. If ClO_4^- ion were excluded from this "second sphere," then the observed shifts in the H_2O^{17} resonance would be proportional to the ratio of $Cr(H_2O)_6^{+3}$ to labile H_2O, *i.e.*, column 10 in Table I should be constant. This is clearly not the case. Moreover, the fact that the O^{17} resonance in ClO_4^- ion experiences a paramagnetic shift which increases with increasing Cr(III) concentration indicates that ClO_4^- ion is coming in close contact with the $Cr(H_2O)_6^{+3}$ ion. One must then consider a model in which both ClO_4^- ion and labile H_2O can come into the immediate vicinity of the $Cr(H_2O)_6^{+3}$ species.

Let us assume that around each $Cr(H_2O)_6^{+3}$ ion there exists a "second sphere" with the property that any O^{17} nucleus entering this "sphere" is subjected to a paramagnetic influence. We will assume that this "second sphere" contains r sites and that, at any instant, y sites are occupied by H_2O molecules and $(r - y)/n$ sites are occupied by ClO_4^- ions, where n is the number of H_2O sites taken up by one ClO_4^- ion. If we further assume that H_2O molecules are exchanging rapidly in and out of this "second sphere" and that they experience a paramagnetic influence only when they are in the "second sphere," then the shift in the O^{17} resonance in labile H_2O will be given by

$$\delta_{H_2O} = \frac{Kym_{Cr(III)}}{N} \qquad (1)$$

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[2] R. E. Connick and R. E. Poulson, *J. Chem. Phys.*, **30**, 759 (1959).

[3] J. P. Hunt and H. Taube, *ibid.*, **18**, 757 (1950).

TABLE I[a]

Sample	δ_{H_2O}	$\delta_{ClO_4^-}$	m_{H_2O}	$m_{Cr(III)}$	$m_{ClO_4^-}$	N	$M'_{Cr(III)} \times 10^3$	$M'_{ClO_4^-} \times 10^2$	$\dfrac{M'_{Cr(III)}}{\delta_{H_2O}} \times 10^2$	$\dfrac{M'_{Cr(III)}}{\delta_{ClO_4^-}}$
A	0.138	...	133.18	0.6562	5.41	129.24	5.077	4.19	3.67	...
B	0.421	...	136.69	2.079	10.05	124.22	16.73	8.09	3.97	...
C	0.608	...	143.43	3.149	13.43	124.54	25.29	10.8	4.16	...
D	0.610	...	137.46	3.030	13.12	119.28	25.40	11.0	4.17	...
E	0.656	0.20	169.86	3.980	16.27	145.98	27.26	11.1	4.16	0.136
F	0.898	0.29	150.31	4.858	19.27	121.16	40.10	15.9	4.47	0.138
G	0.907	0.29	149.32	4.900	19.84	119.92	40.86	16.5	4.51	0.141
H	1.269	0.40	228.74	10.54	37.38	165.50	63.69	22.6	5.02	0.159

[a] δ_x = measured shift in O^{17} resonance in species x, parts in 10^4. m_x = total no. of millimoles of species x in solution. N = millimoles of labile H_2O in solution = $m_{H_2O} - 6m_{Cr(III)}$. $M'_x = m_x/N$.

where K is a constant related to the specific magnetic field experienced by an O^{17} nucleus in an H_2O molecule in the "second sphere" of Cr(III). The other quantities are defined in the footnote to Table I. To obtain a second equation, we note that the ratio of ClO_4^- to H_2O in the "second sphere" will be related to the ratio of ClO_4^- to H_2O in the bulk solution by the expression

$$\frac{(r-y)/n}{y} = Q\frac{m_{ClO_4^-}}{N} = QM'_{ClO_4^-} \qquad (2)$$

where Q is a constant which indicates the degree to which ClO_4^- ion preferentially seeks the "second sphere" of the $Cr(H_2O)_6{}^{+3}$ ion.

Eliminating y between (1) and (2), we obtain the expression

$$\frac{M'_{Cr(III)}}{\delta_{H_2O}} = \frac{nQ}{Kr}M'_{ClO_4^-} + \frac{1}{Kr} \qquad (3)$$

The proposed model and assumptions thus require that a plot of $M'_{Cr(III)}/\delta_{H_2O}$ *vs.* $M'_{ClO_4^-}$ yield a straight line with ratio of slope to intercept = nQ. Such a plot of the data in Table I is shown in Fig. 1 and yields a value of $nQ = 2$.

Using the same model and assuming that ClO_4^- ion is free to exchange rapidly between the "second sphere" and bulk solution, one may derive the following expression relating the shift in the O^{17} resonance in ClO_4^-, $\delta'_{ClO_4^-}$, to $M'_{Cr(III)}$ and $M'_{ClO_4^-}$

$$\frac{M'_{Cr(III)}}{\delta_{ClO_4^-}} = \frac{n}{K'r}M'_{ClO_4^-} + \frac{1}{K'r} \qquad (4)$$

where K' is a constant related to the specific magnetic field experienced by an O^{17} nucleus in ClO_4^- ion while it is in the "second sphere" of Cr(III). This equation is identical in form with eq. 3 and a plot of $M'_{Cr(III)}/\delta_{ClO_4^-}$ *vs.* $M'_{ClO_4^-}$ should yield a straight line from which nQ may be calculated as the ratio of slope to intercept. The reference used for the ClO_4^- shifts listed in Table I was the O^{17} resonance in ClO_4^- ion in a $NaClO_4$–$HClO_4$ solution of about the same acidity and total ClO_4^- ion concentration as the Cr(III) solutions. The plot of the data in Fig. 2 shows that the ClO_4^- shift data are consistent with the proposed model and with a value of $nQ = 2$.

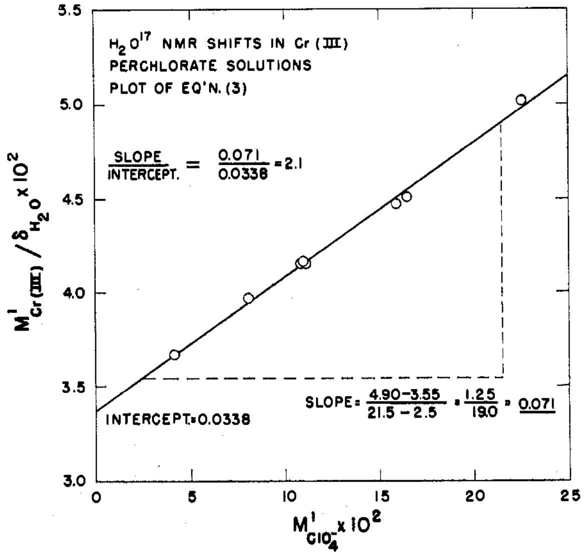

Figure 1.

While the data are consistent with a value of 2 for the product nQ, they do not provide a means for uniquely determining either of the quantities separately. If one assumes that the ratio of ClO_4^- to H_2O in the "second sphere" is the same as it is in the bulk solution (Q = 1), then the number of H_2O sites in the "second sphere" taken up by one ClO_4^- ion is 2 ($n = 2$). This seems a reasonable number. On the other hand, other small numbers for n (*e.g.*, 1 or 3) might also be possible. If one could, on the basis of some other evidence, firmly establish n, then a value for Q could be calculated and one would have a measure of the extent to which either ClO_4^- ion or H_2O preferentially seeks the "second sphere" of the $Cr(H_2O)_6{}^{+3}$ ion.

One further piece of information may be obtained by taking the ratio of the intercept in Fig. 2 to the intercept in Fig. 1. Comparing eq. 4 and 3, it is apparent that this ratio is K/K', and from the plots, its value is ~3. This indicates that the specific magnetic interaction of $Cr(H_2O)_6{}^{+3}$ with "second sphere" H_2O to produce a shift in the O^{17} resonance is about three times as great as its interaction with "second sphere" ClO_4^-. Actually, two effects are operating here. First, ClO_4^- ion has four oxygens and it is unlikely that all of them will experience a magnetic influence when the ion is in the "second sphere." This will serve to make the O^{17} shifts in ClO_4^- smaller than the O^{17} shifts in H_2O. In addition, the strength of the interaction between $Cr(H_2O)_6{}^{+3}$ and a "second sphere" oxygen nucleus will depend to some extent on whether the oxygen nucleus is in an H_2O molecule or in a ClO_4^- ion. The ratio of 3 reported above is thus undoubtedly due to some combination of these effects.

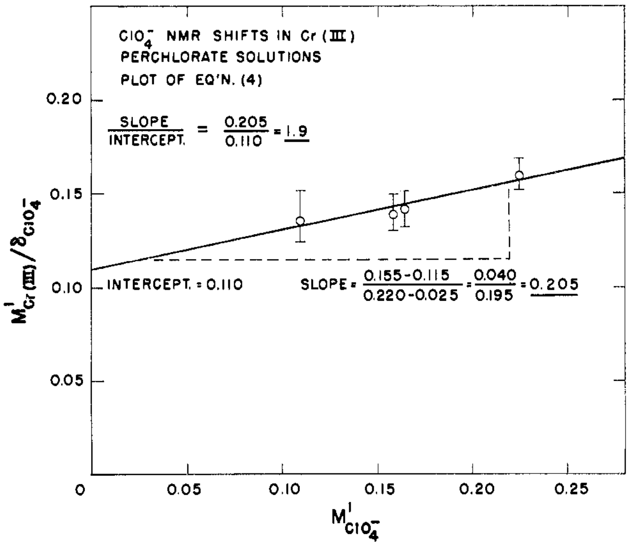

Figure 2.

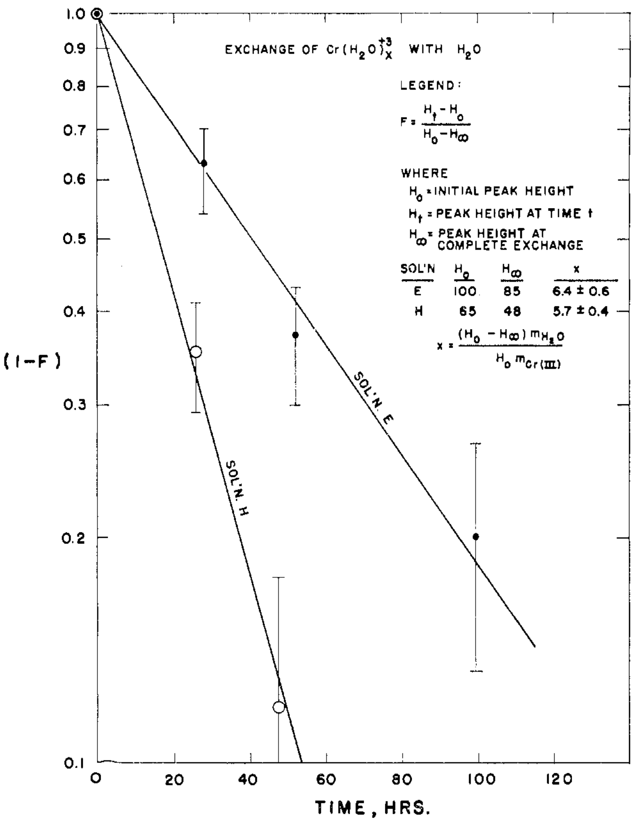

Figure 3.

All of the foregoing treatment has been based upon the assumption that the Cr(III) species in the solutions studied is $Cr(H_2O)_6^{+3}$ in which the six water molecules exchange very slowly with solvent H_2O. Though the isotopic dilution studies of Hunt and Taube[3] strongly support this assumption, the n.m.r. spectrometer provides a simple means for checking the composition of the Cr(III)–H_2O complex and determining the rate at which the H_2O in the complex exchanges with the remaining H_2O in the system. Thus, if one starts out with a Cr(III) perchlorate solution in H_2O of ordinary O^{17} abundance (0.04%) and adds a large amount of H_2O enriched to ~1% in O^{17}, then initially almost all the O^{17} is in the labile H_2O in the system and the O^{17} content is reflected in the height of the resonance peak for this H_2O. As the H_2O in the Cr(III)–H_2O complex exchanges with the labile H_2O, the net effect is a transfer of O^{17} from the labile H_2O to the H_2O bound in the Cr(III)–H_2O complex and a resulting decrease in the height of the O^{17} resonance peak for the labile H_2O. Thus by measuring the rate of decrease in height of this peak, one has a measure of the rate of exchange of H_2O between the Cr(III)–H_2O complex and the labile H_2O in the system. Moreover, the percentage decrease in peak height from zero to complete exchange coupled with a knowledge of the total H_2O and Cr(III) in the system enables one to calculate the number of H_2O molecules held by each Cr(III). Finally, this over-all procedure has the advantage that the determination of the composition of the Cr(III)–H_2O complex and the measurement of the shifts in the O^{17} resonances in labile H_2O and in ClO_4^- by the complex can all be done in the same solution.

Exchange experiments were performed, in the manner described, on solutions E and H of Table I, and the results are plotted in Fig. 3. The exchange data for solution E are in complete agreement with the results of Hunt and Taube,[3] indicating $6H_2O$ in the Cr(III) complex with $t_{1/2}$ for exchange of ~40 hr. The data from solution H again confirm the composition $Cr(H_2O)_6^{+3}$. The observed decrease in half-life is in agreement with the results of Plane and Taube,[4] who found the rate of the exchange to increase with increasing concentration of anion.

It thus seems quite clear that the magnetic influences noted here are effects extending beyond the H_2O layer in the $Cr(H_2O)_6^{+3}$ complex. It is further evident that both ClO_4^- ion and labile H_2O are influenced and that the specific magnetic effect is ~3 times as great for H_2O as for ClO_4^-.

The observations reported here lend support to the argument of Plane and Taube[4] that the acceleration by anions of the exchange of H_2O with $Cr(H_2O)_6^{+3}$ is due to formation of an activated complex containing both $Cr(H_2O)_6^{+3}$ and anion. The magnetic evidence strongly indicates at least that ClO_4^- ion does indeed come into close contact with the $Cr(H_2O)_6^{+3}$ complex.

With regard to the type of interaction which produces the shifts observed in this work, Shulman[5] has pointed out that because of the symmetry of Cr(III) octahedral complexes, the anisotropic hyperfine and dipolar fields at the ligands vanish when averaged over the rotational coordinates of the complex.[6] One is thus left with the isotropic or contact hyperfine interaction as the source of the shifts observed in this work. This would involve σ-overlap of oxygen sp hybrid orbitals in "second sphere" H_2O or ClO_4^- with Cr(III) t_{2g} orbitals which

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(4) R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

(5) R. G. Shulman, *J. Chem. Phys.*, **29**, 945 (1958).

(6) Since the orbital ground state of Cr(III) is nondegenerate, its octahedral complexes cannot undergo the Jahn–Teller distortion which leads to a nonvanishing average of the anisotropic hyperfine field at the ligands.

contain the magnetic electrons and are directed toward the centers of the 12 edges of the octahedron formed by the $Cr(H_2O)_6^{+3}$ complex.

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Niobium(IV) Compounds Containing Ethoxide: $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ and $Nb(OC_2H_5)_4$

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Further investigations of niobium(IV) solutions in ethyl alcohol have led to the preparation of two diamagnetic compounds, $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ and $Nb(OC_2H_5)_4$. The former is prepared by the addition of pyridine to niobium(IV) chloride solutions in ethyl alcohol. The structure of the dimer is thought to involve chloride bridging on the basis of its chemical properties. $Nb(OC_2H_5)_4$ is prepared by the reaction of $NaOC_2H_5$ with $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$. Both compounds are readily converted to $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$.

Recently, we described[2,3] the preparation and characterization of a series of compounds containing the pentachloroalkoxoniobate(IV) anion. The successful preparation of these compounds has led to a more complete investigation of niobium(IV) solutions in ethyl alcohol and the isolation of two new compounds, dichlorohexaethoxobis(pyridine)diniobium(IV), $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$, and tetraethoxoniobium(IV).

Thomas[4] has previously attempted the preparation of the tetraalkoxide by the alcoholysis of tetrakis(diethylamido)niobium(IV), but the product was always $Nb(OR)_5$. Bradley[5] has suggested the cause for the instability of the tetraalkoxide in the presence of alcohol, that is

$$2Nb(OR)_4 + 2ROH \longrightarrow 2Nb(OR)_5 + H_2$$

Experimental

Materials.—The source and purification of niobium pentachloride, pyridine, hydrogen chloride, and nitrogen were described previously.[3]

Anhydrous ethyl alcohol was obtained by azeotropic distillation with benzene. Anhydrous benzene was obtained by azeotropic distillation with ethyl alcohol.

Magnetic Susceptibility Measurements.—The measurements were accomplished using the techniques and apparatus previously described.[3]

Spectroscopic Measurements.—The infrared spectra were obtained with Nujol mulls and the use of a Perkin-Elmer Model 21 spectrophotometer. The mulls were prepared under a purified nitrogen atmosphere.

The visible and near-infrared spectra were obtained by the use of a Beckman Model DK-2 spectrophotometer and capped, 1-cm. silica cells which had been dried at 100° for several hours.

Analytical Methods.—Niobium and chloride analyses were performed as with the pentachloroalkoxoniobates.[3] Ethoxide was determined by the method of Bradley.[6]

Pyridine was determined spectrophotometrically at 255 mμ in 0.05 *N* H_2SO_4. Samples were digested in aqueous solutions of H_2SO_4 of known concentration, filtered, and the solutions made up to 1 l. with sufficient H_2SO_4 and water so that the final H_2SO_4 concentration was 0.05 *N*.

Molecular Weight Measurement.—The molecular weight of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ was determined ebullioscopically in $CHCl_3$ by Huffman Microanalytical Laboratories, Wheatridge, Colorado. Due to the sensitivity of this compound to oxidation, the measurement was performed in dry nitrogen atmosphere with a precision of $\pm 10\%$.

Preparation, Properties, and Reaction of Compounds. $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$.—$NbCl_5$ (6.20 g., 0.0229 mole) in 25 ml. of ethyl alcohol saturated with HCl was reduced electrolytically,[3] and the solution was evaporated to dryness. The tacky, dark substance which remained was dissolved in 20 ml. of ethyl alcohol and 5 ml. of pyridine was added. The color of the solution changed from deep purple to an equally deep yellow-red. Crystallization began within 1 hr. and was seemingly complete after another 9 hr. The red compound was collected on a filter under a nitrogen atmosphere and was washed with three 10-ml. portions of cold ethyl alcohol; yield 5.04 g. (64% based on $NbCl_5$). Concentration of the mother liquor produced only a small additional amount of the compound.

Anal. Calcd. for $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$: C_5H_5N, 23.1; Cl, 10.4; Nb, 27.1; molecular weight of dimer, 686. Found: C_5H_5N, 23.2; Cl, 10.3; Nb, 27.1; molecular weight, 674; molecular complexity, 1.97. The infrared spectrum showed that ethoxide was present.

The dimer is very soluble in $CHCl_3$ and slightly soluble in ethyl and isopropyl alcohols at room temperature, but it is insoluble in benzene, ethers, ketones, other halogenated hydrocarbons, dimethylformamide, dimethyl sulfoxide, and glacial acetic acid.

The visible and near-infrared spectrum of the dimer in $CHCl_3$ and ethyl alcohol is simple, consisting only of a shoulder at 365

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(1) To whom correspondence should be directed.

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(3) R. A. D. Wentworth and C. H. Brubaker, Jr., *ibid.*, **2**, 551 (1963).

(4) I. M. Thomas, *Can. J. Chem.*, **39**, 1386 (1961).

(5) D. C. Bradley, R. N. Kapoor, and B. C. Smith, *J. Inorg. Nucl. Chem.*, **24**, 864 (1962).

(6) D. C. Bradley, F. M. Abd-el Halim, and W. Wardlaw, *J. Chem. Soc.*, 3453 (1950).