ligand-exchange reaction are derived. The fifth axial water molecule seems to be weakly bound and has to have a residence time of the order of $10^{-11}$ sec.

While this work was almost completed a proton and deuterium relaxation study of vanadyl(IV) sulfate solutions appeared, in which rate constants for hydrogen exchange of the order of $1.0 \times 10^4$ sec$^{-1}$ were reported.[19] Neglecting contributions of the exchange reactions of the axial water molecule, the authors conclude that the hydrogen lifetime in the first coordination shell of the $VO^{2+}$ ions is determined by chemical proton exchange processes (protolysis) of the equatorial water molecules and that the residence time of a whole water molecule should be greater. These conclusions are confirmed by the present results.[20]

**Acknowledgment.**—We wish to thank Professor S. Alexander for his kind interest and helpful discussions.

(19) R. K. Mazitov and A. I. Rivkind, *Dokl. Akad. Nauk SSSR*, **166**, 654 (1966). This article may serve as a key to previous literature on proton relaxation in vanadyl(IV) solutions.

(20) NOTE ADDED IN PROOF.—We wish to acknowledge a recent exchange of preprints with K. Wüthrich and R. E. Connick [*Inorg. Chem.*, **6**, 583 (1967)]. They have measured $^{17}O$ relaxation in solutions of vanadyl(IV) perchlorate and obtained results which are in good agreement with those reported here.

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# Nuclear Magnetic Resonance Relaxation of Oxygen-17 in Aqueous Solutions of Vanadyl Perchlorate and the Rate of Elimination of Water Molecules from the First Coordination Sphere

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An investigation was made of the temperature dependence of the transverse nuclear relaxation time $T_2$ for $O^{17}$ in aqueous vanadyl perchlorate solutions in the range 5–170°. In the major part of this temperature region the relaxation due to the influence of the $VO^{2+}$ ions was found to be controlled by the rate of exchange of water molecules between the first coordination sphere of the metal ions and the bulk of the solution. Values for the rate constant and the activation energy of the water exchange and for the constant which describes the scalar coupling between $VO^{2+}$ and the $O^{17}$ nuclei of the coordinated water molecules have been established. The rate of the water exchange was found to be slow compared to the rates found in corresponding experiments with other doubly charged metal ions. This indicates that the high positive charge of $V^{4+}$ is an important factor not only in the formation of the vanadyl group but also in the bonding of the water molecules in the first coordination sphere. Additional relaxation effects are observed at low temperatures. It is shown that these effects are most likely explained by interactions of the vanadyl ion with $O^{17}$ in water molecules loosely coordinated outside the first coordination sphere.

In aqueous solutions of paramagnetic metal ions a certain number of water molecules are coordinated to each metal ion. Because of the magnetic interactions between the paramagnetic ions and the magnetic moments of the $O^{17}$ nuclei of these coordinated water molecules, the transverse nmr relaxation time of these oxygens is greatly decreased. For dilute solutions of the metal ion only a single resonance can be observed which corresponds to that of the bulk water modified by the exchange of water molecules in and out of the coordination spheres of the metal ions.

The property observed is the line width of the resonance. Half the width at half-height, $\delta\omega$, expressed in radians per second, is related to the apparent transverse relaxation time $T_2$ by

$$\delta\omega = 1/T_2 \tag{1}$$

The line width arises from the relaxation of the bulk $O^{17}$ nuclei that would occur in the absence of paramagnetic ions, *i.e.*, $1/T_{2H_2O}$, and the contribution from the paramagnetic ions, $1/T_{2p}$, as given by

$$\frac{1}{T_2} = \frac{1}{T_{2H_2O}} + \frac{1}{T_{2p}} \tag{2}$$

Analysis of $1/T_{2p}$ in terms of the properties of the dissolved paramagnetic ions has been used in earlier studies to evaluate the water exchange rate and various parameters which characterize the relaxation in aqueous solutions of a series of 3d metal ions.[1] In the present paper the application of the nmr technique to the study of aqueous vanadyl perchlorate solutions is described.

## I. Theory

The shape of the nmr spectrum of a chemically stable system is described by the Bloch equations.[2] A modification of the Bloch equations by McConnell[3] which includes the possibility of chemical exchange has been extended by Swift and Connick[1] to the conditions present in dilute aqueous solutions containing paramagnetic metal ions. They found that the effect

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(1) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

(2) F. Bloch, *Phys. Rev.*, **70**, 460 (1946).

(3) H. M. McConnell, *J. Chem. Phys.*, **28**, 430 (1958).

of the paramagnetic ions on the relaxation of the $O^{17}$ nuclei in a solution where the water may exchange between the bulk of the solution and one kind of coordination sites on the metal ions can be given by eq 3. $\tau_{H_2O}$

$$T_{2p}^{-1} = \tau_{H_2O}^{-1}\left[\frac{(1/T_{2M}^2) + (1/T_{2M}\tau_M) + \Delta\omega_M^2}{[(1/T_{2M}) + (1/\tau_M)]^2 + \Delta\omega_M^2}\right] \tag{3}$$

and $\tau_M$ are the lifetimes with respect to chemical exchange for the water molecules in the bulk of the solution and on the coordination sites of the metal ions, $T_{2M}$ is the transverse relaxation time of the $O^{17}$ nuclei in the first coordination sphere of the metal ions, and $\Delta\omega$ is the difference in the precessional frequencies of the $O^{17}$ nuclei of the bulk water and those of the coordinated water molecules.

An analysis of eq 3 reveals two relaxation mechanisms, one involving $\Delta\omega$ and the other involving $T_{2M}$. The "$\Delta\omega$ mechanism"[4] can be of importance if $\Delta\omega$ is sufficiently large so that transverse relaxation can occur through the change in precessional frequency which arises when the nuclei exchange between the bulk of the solution and the coordination sites of the metal ion. The relaxation through $T_{2M}$[5] can be important if the nuclei of the coordinated water molecules undergo fast relaxation because of either scalar or dipolar coupling with the unpaired electrons of the metal ions. In certain cases the mechanism governing $T_{2p}$ can be established from the temperature dependence of $T_{2p}$.[1] The following limiting cases A and B are important for the treatment of the $O^{17}$ nuclear relaxation in $VO(ClO_4)_2$ solutions

$$\text{A.}\quad \frac{1}{T_{2M}^2} \gg \frac{1}{\tau_M^2}, \Delta\omega_M^2;\quad \frac{1}{T_{2p}} = \frac{P_M}{\tau_M} = \frac{1}{\tau_{H_2O}} \tag{4}$$

Relaxation by $T_{2M}$ is fast; $1/T_{2p}$ is controlled by the rate of the chemical exchange which is given by the lifetimes of the water molecules in the different environments. The probability factor $P_M$ is given closely by $n[M]/55.5$, where $[M]$ is the molar concentration of the paramagnetic ion and $n$ is the number of water molecules in the coordination sites characterized by the lifetime $\tau_M$.

$$\text{B.}\quad \frac{1}{T_{2M}\tau_M} \gg \frac{1}{T_{2M}^2}, \Delta\omega_M^2;\quad \frac{1}{T_{2p}} = \frac{P_M}{T_{2M}} \tag{5}$$

Chemical exchange is rapid; $1/T_{2p}$ is controlled by the $T_{2M}$ relaxation process. The possibility that the relaxation is controlled by a change in the precessional frequency, *i.e.*, $\Delta\omega^2 \gg 1/T_{2M}^2$, is no longer included in this discussion, since it can readily be eliminated from consideration: an impossibly high value of the constant which characterizes the scalar coupling between $VO^{2+}$ and the $O^{17}$ nuclei of the coordinated water molecules would be necessary to explain the experimental data in terms of a $\Delta\omega$ mechanism.

The variation of $\tau_M$ with temperature is given by the usual expression for the temperature dependence of the rate of chemical reactions

$$\tau_M = \frac{h}{kT}\exp[(\Delta H^{\ddagger}/RT) - (\Delta S^{\ddagger}/R)] \tag{6}$$

where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy and entropy of activation for the water exchange between the first coordination sphere of the vanadyl ions and the bulk of the solution. The variation of $T_{2M}$ with temperature is determined by the mechanism which interrupts the interaction between $VO^{2+}$ and the $O^{17}$ nucleus. Both, dipolar coupling and scalar coupling, can be interrupted by the relaxation of the unpaired electron and by the rate of elimination of the coordinated water molecule. The dipolar interactions can further be interrupted by the Brownian motion of the molecules.

The transverse relaxation time of the $O^{17}$ nuclei in the first coordination sphere due to scalar coupling is expected to be given by (7),[6] where $A/\hbar$ is the scalar

$$\frac{1}{T_{2M}} = \frac{1}{3}S(S+1)\frac{A^2}{\hbar^2}\tau_e \tag{7}$$

coupling constant in radians per second and $S$ is the electron spin quantum number. The correlation time $\tau_e$ is given by $1/\tau_e = (1/T_{1,el}) + (1/\tau_M)$, where $T_{1,el}$ is the longitudinal relaxation time of the electronic system. Equation 7 corresponds to only the second term of Abragam's[6] eq 127, p 311 (or the first term of eq 122, p 309) being of importance in our case. Since the temperature coefficient for $T_{1,el}$ is usually much smaller than for $\tau_M$, the tendency will be for $T_{2M}$ to be controlled at high temperature by the interruption arising from chemical exchange and at low temperature by the electronic spin flip; *i.e.*, at high temperature the observed line broadening would be due to scalar relaxation of the first kind and at lower temperatures to scalar relaxation of the second kind.[6] In our experiments with $VO(ClO_4)_2$ the temperature never became high enough for chemical exchange to dominate.

For the dipole–dipole coupling induced relaxation in the first coordination sphere only the interruption of the coupling through rotational tumbling of the hydrated vanadyl ions has to be taken into consideration, since the chemical exchange rate and the $T_{1,el}$ process are much slower in aqueous $VO(ClO_4)_2$ solutions. A quantitative treatment given by Solomon[7] assumes that the Brownian motion of the molecules can be described by Stokes' diffusion equation; *i.e.*, the molecules are treated as rigid spheres of radius $r$ moving in a medium of viscosity $\eta$. The result is given by eq 8, where $\gamma_I$ and $\gamma_S$ are the gyromagnetic

$$\frac{1}{T_{2M}} = \gamma_I^2\gamma_S^2\hbar^2 S(S+1)\frac{1}{15d^6}\left\{4\tau_c + \frac{\tau_c}{1+(\omega_I-\omega_S)^2\tau_c^2} + 3\frac{\tau_c}{1+\omega_I^2\tau_c^2} + 6\frac{\tau_c}{1+\omega_S^2\tau_c^2} + 6\frac{\tau_c}{1+(\omega_I+\omega_S)^2\tau_c^2}\right\} \tag{8}$$

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(4) H. M. McConnell and S. B. Berger, *J. Chem. Phys.*, **27**, 230 (1957).

(5) I. Solomon and N. Bloembergen, *ibid.*, **25**, 261 (1956).

(6) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961.

(7) I. Solomon, *Phys. Rev.*, **99**, 559 (1955); see also ref 6.

$$\tau_c = \frac{4\pi r^3}{3k}\frac{\eta}{T}$$

ratios for the $O^{17}$ nucleus and for the unpaired electron in $VO^{2+}$, $S$ is the electron spin quantum number, $d$ is the distance between the interacting spins, $\tau_c$ is the correlation time for the interruption of the dipole–dipole coupling through rotational motion, $\omega_I$ and $\omega_S$ are the Larmor frequencies for the spins of the $O^{17}$ nucleus and the unpaired electron of $VO^{2+}$ in the applied external magnetic field, and $k$ is the Boltzmann constant.

While scalar coupling is expected to influence appreciably only nuclei of water molecules in the first coordination sphere, we have to include the possibility of dipole–dipole coupling between $VO^{2+}$ and the nuclei in outer coordination spheres. We distinguish between two possible cases: (1) If the lifetime of the water molecules in a second coordination sphere is long compared to the correlation time arising from the rotational motion of the molecules $VO(H_2O)_n(H_2O)_m{}^{2+}$, where $n$ and $m$ denote the number of water molecules in the first and in the second coordination sphere, we have formally the same system as for the treatment of the dipolar coupling between $VO^{2+}$ and the $O^{17}$ nuclei in the first coordination sphere, and the relaxation effects are given by eq 8. (2) If the lifetime of the water molecules in the second coordination sphere of the complex is short compared to the rotational correlation time, the interruption of the dipole–dipole coupling is controlled by the relative translational motions of $VO(H_2O)_n{}^{2+}$ and the $O^{17}$ nuclei in the bulk water. Assuming that the rate of the translational motions is diffusion controlled, a quantitative treatment[8] of this case leads to expression 9 for the evaluation of the relaxation effects to be expected, where

$$\frac{1}{T_{2p}} = \frac{16\pi^2}{15}N_{Me}\gamma_I{}^2\gamma_S{}^2\hbar S(S+1)\frac{\eta}{kT}\frac{4r_1r_2}{(r_1+r_2)^2} \qquad (9)$$

$N_{Me}$ is the concentration of paramagnetic ions expressed in $cm^{-3}$, $r_1$ is the radius assumed for the rigid sphere representing $VO(H_2O)_n{}^{2+}$, and $r_2$ the radius of the sphere representing $H_2O$. Note that (9) gives directly the experimentally observable relaxation time $T_{2p}$ and not a quantity corresponding to $T_{2M}$ as in (7) and (8). Equation 9 is only valid in the above form in the case of "extreme motional narrowing," *i.e.*, if $(6\pi\eta/kT)\cdot(r_1+r_2)r_1r_2\omega << 1$ for all of the spins involved, where $\omega$ is the Larmor frequency of the spins. When this condition does not hold, the numerical factor in (9) can become as small as $28\pi^2/75$.

A comparison of expressions 6–9 shows that a study of the temperature dependence of $T_{2p}$ should enable us to distinguish between relaxation controlled by chemical exchange, by scalar relaxation of the first kind, by scalar relaxation of the second kind, and by relaxation through dipole–dipole coupling.

The first term in (2) which includes the relaxation time $T_{2H_2O}$ for $O^{17}$ nuclei in pure water has been studied by Meiboom.[9] In acidic solution $T_{2H_2O}$ is believed to be mainly due to interactions between the spin moment and the quadrupolar moment of the $O^{17}$ nucleus interrupted by rotational tumbling of the water molecules. For the case of "extreme motional narrowing," which is a good approximation for the treatment of the $O^{17}$ relaxation in water, the transverse relaxation time due to quadrupolar coupling is given by (10),[10] where it is assumed that the Brownian motions of the molecules can be described by Stokes' diffusion equation. In eq 10, $I$ is the nuclear spin quantum number, $\zeta$ is the

$$\frac{1}{T_{2H_2O}} = \frac{3}{40}\frac{2I+3}{I^2(2I-1)}\left(1+\frac{\zeta^2}{3}\right)\left(\frac{eQq}{\hbar}\right)^2\frac{4\pi r^3\eta}{3kT} \qquad (10)$$

asymmetry parameter, $Q$ is the nuclear quadrupole moment, $q$ is the electric field gradient, $r$ is the radius assumed for a sphere which represents the water molecule, and $\eta$ is the viscosity of the solution under consideration.

## II. Experimental Section

Employing the side-band detection technique[11] we recorded the $O^{17}$ nmr spectra with a modified Varian Associates Model V-4200 wide-line spectrometer, operated with a fixed-frequency unit V-4311 at 8.134 Mc. A further modification, the use of a PAR lock-in amplifier Model HR-8, made it possible to vary the modulation frequency continuously in the range 1–4000 cps. Samples of *ca.* 0.5 cc in volume were studied in tubes of 7–8-mm outer diameter.

For studies at variable temperature an nmr probe with an all-glass dewar insert which contained the sample tube and the receiver coil was used. Heated or cooled nitrogen was then passed through the probe and the resulting temperature was measured simultaneously outside and at the center of the sample tube. The temperature range covered was 275–450°K.

The following chemicals were used: water enriched to 3.5 and 10% in $O^{17}$ obtained from the Weizmann Institute of Science, $VOSO_4\cdot 5H_2O$ obtained from Fairmont Chemical Co., $BaCO_3$ ACS reagent and $HClO_4$ 70% ACS reagent obtained from Allied Chemicals. The $O^{17}$ nmr spectrum of the water was measured in the temperature range of interest and the obtained $T_{2H_2O}$ values were in good agreement with earlier data.[12] Vanadyl perchlorate solutions were made from $VOSO_4\cdot 5H_2O$, $BaCO_3$, and $HClO_4$. Through evaporation of the water under vacuum, the $VO(ClO_4)_2$ solutions were concentrated to *ca.* 2.5 *M*. The vanadyl perchlorate concentration was determined through titration with $KMnO_4$. The samples for the nmr experiments were prepared by adding known volumes of the concentrated $VO(ClO_4)_2$ solution and of 70% $HClO_4$ with micropipets to the $O^{17}$-enriched water. Since $T_{2p}$ decreases very much with increasing temperature in the major part of the temperature region examined, the vanadyl concentration was lowered in several steps from 0.83 *M* for the experiments at room temperature to 0.016 *M* for measurements above 390°K in order to have line widths appropriate to the side-band technique. The samples contained 0.1 or 0.3 *M* $HClO_4$ and *ca.* 0.01 *M* $Ba(ClO_4)_2$.

In order to check relaxation effects which might arise from paramagnetic impurities the $VO(ClO_4)_2$ solutions used in our experiments were analyzed spectrochemically. The analyses were made by G. V. Shalimoff of the Lawrence Radiation Laboratory on a Baird 3-m grating spectrograph. None of the elements known to form ions which influence the $O^{17}$ nuclear relaxation in aqueous solutions could be detected and the following upper limits, given in weight per cent metal relative to vanadium as metal, could be established: Mn, <0.001; Cu, <0.001; Ni, <0.005;

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(8) See ref 6, p 304.

(9) S. Meiboom, *J. Chem. Phys.*, **34**, 375 (1961).

(10) See ref 6, p. 314.

(11) J. V. Acrivos, *J. Chem. Phys.*, **36**, 1097 (1962).

(12) C. W. Merideth, Thesis; Lawrence Radiation Laboratory Report UCRL-11704, University of California, Berkeley, Calif., 1965.

Co, <0.005; Fe, <0.005. Using these limits and the data on relaxation effects arising from the presence of the paramagnetic ions formed by these metals[1] it is seen that none of them can contribute appreciably to the relaxation effects observed in $VO(ClO_4)_2$ solutions, except for $Mn^{2+}$ which could cause at most one-third of the "additional relaxation effects" (Figure 4, curve c) observed at low temperatures.

## III. Results

The $O^{17}$-enriched aqueous solutions used for the nmr studies contained various concentrations of $VO(ClO_4)_2$, $HClO_4$, and traces of $Ba^{2+}$ ions. In eq 2 we assumed that the relaxation of the $O^{17}$ nuclei in pure water and the relaxation arising from the presence of the paramagnetic ions are two independent processes. On the basis of expression 4, 5, or 9 we expect the line widths $\delta\omega = (1/T_{2H_2O}) + (1/T_{2p})$ to be linearly dependent on the metal ion concentration. In Figure 1 this was found to be the case for $VO(ClO_4)_2$ solutions. Further experimental checks showed that $\delta\omega$ is independent of the perchloric acid concentration in the range 0.1–0.5 *M*. As would be expected, no change in $\delta\omega$ was observable after addition of various amounts of $Ba(ClO_4)_2$.

The temperature dependence of that part of the over-all transverse relaxation time for the $O^{17}$ nuclei arising from the presence of the $VO^{2+}$ ions is given in Figure 2. The data indicate that $T_{2p}$ is controlled by the rate of exchange of water molecules between the bulk of the solution and the first coordination sphere of $VO^{2+}$ in the temperature range 330–390°K, since $T_{2p}$ decreases with increasing temperature. It has been shown by X-ray studies[13] that the $VO^{2+}$ ion in solid $VOSO\cdot 5H_2O$ binds four water molecules and one sulfate oxygen in the first coordination sphere. Presumably in aqueous solution each $VO^{2+}$ will have four equivalent oxygens of water in the equatorial plane and one water oxygen in the axial position opposite the vanadyl oxygen.[14] One expects the bonding of the axial water molecule to be different from the bonding of the equatorial waters. Thus the number *n* of the coordinated $H_2O$ molecules which take part in the exchange reaction observed by nmr is not known *a priori*. Therefore, we cannot yet characterize the exchange reaction numerically but rather by the stoichiometry (11) and the expressions in Table I which include *n*.

$$VO(H_2O)_{5-n}(H_2O)_n^{2+} + nH_2O^* \rightleftarrows VO(H_2O)_{5-n}(H_2O^*)_n^{2+} + nH_2O \quad (11)$$

The reaction rate constant *k* is the first-order rate constant for the loss from the first coordination sphere of a particular one of the exchanging waters. Its value at room temperature, $k(298°)$, has been calculated from $k(333°)$ and $\Delta H^{\ddagger}$.

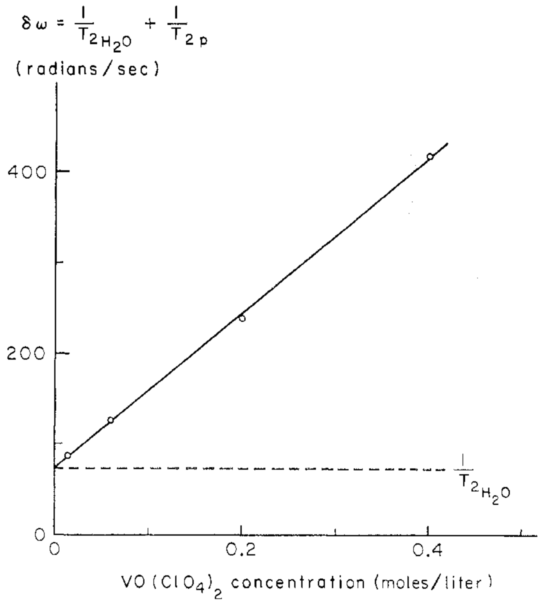

Figure 1.—Variation of the $O^{17}$ nmr line widths with vanadyl ion concentration at 345°K.

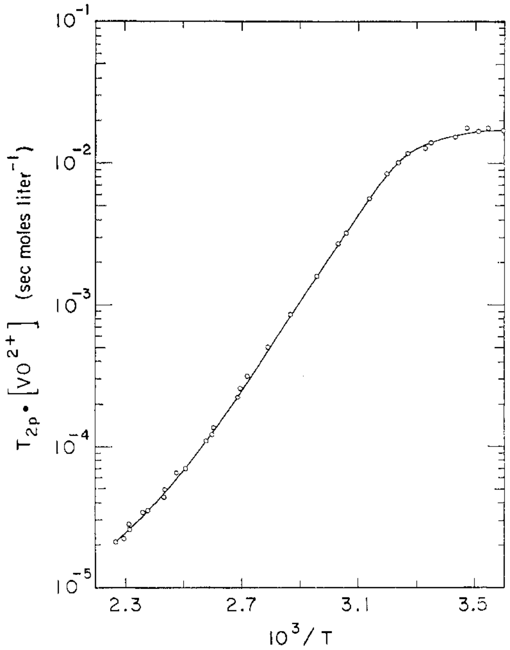

Figure 2.—Dependence on reciprocal of temperature of log $T_{2p}$ in solutions of $VO(ClO_4)_2$.

Table I

Parameters for Exchange of $O^{17}$ between the First Coordination Sphere of $VO^{2+}$ and Bulk Water

| Quantity | Value |
|---|---|
| $\Delta H^{\ddagger}$ | 13.7 kcal mole$^{-1}$ |
| $k(333°K)$ | $(1/n)(2.3 \times 10^4)$ sec$^{-1}$ |
| $k(298°K)$ | $(1/n)(2.0 \times 10^3)$ sec$^{-1}$ |
| $\Delta S^{\ddagger}$ | $(2.2 - 4.6 \log n)$ eu |
| $A/h$ | $(1/\sqrt{n})(7.6 \times 10^6)$ cps |

Above 390°K the temperature dependence of $T_{2p}$ deviates from the slope found for the exchange-controlled region. This implies that at high temperatures the relaxation is in part controlled by the $T_{2M}$ process, since, as mentioned earlier, the observed results cannot be explained by a $\Delta\omega$ mechanism. Using the data given in Table I it is found that $\tau_M \cong T_{2M}$ is of the order of magnitude of $n \times 10^{-6}$ to $n \times 10^{-7}$ sec in the temperature region considered here. It is easy to show by inserting suitable numbers into eq 8 and 9 that such a small value for $T_{2M}$ cannot be explained by dipole–dipole

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(13) M. B. Palma-Vittorelli, *et al.*, *Nuovo Cimento*, **3**, 718 (1956).

(14) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

coupling and therefore most likely arises from scalar coupling. The interruption of the coupling will occur essentially entirely from the longitudinal electronic relaxation since the chemical exchange is much slower than the $T_{1,\mathrm{el}}$ process in the temperature region examined. Only the transverse relaxation time $T_{2,\mathrm{el}}$ of vanadyl perchlorate in aqueous solution and its temperature dependence are known above 400°K: the average value for $T_{2,\mathrm{el}}$ for the esr spectrum of a $10^{-2}$ *M* aqueous vanadyl perchlorate solution is *ca.* $1.0 \times 10^{-8}$ sec at 400°K and is to a good approximation independent of temperature between 400 and 450°K.[15] From work done by Myers and McCain[16] at room temperature and in a magnetic field of 1000 gauss, $T_{1,\mathrm{el}}$ for $VO^{2+}$ ions in aqueous solution appears to be only slightly longer than $T_{2,\mathrm{el}}$. In going to 14,000 gauss, the magnetic field used for the $O^{17}$ nmr experiments, and *ca.* 430°K, it seems still a good approximation to set $T_{1,\mathrm{el}}$ equal to $T_{2,\mathrm{el}}$, since the estimated value for $\omega_S\tau$, where $\omega_S$ is the electron spin resonance frequency and $\tau$ the correlation time in aqueous solution, probably does not vary greatly through this change of experimental conditions.

Following the above discussion we would expect $T_{2M}$ to be essentially independent of temperature in the region of interest. Neglecting the terms including $\Delta\omega$ in eq 3 we find that $T_{2p}$ is given by

$$T_{2p} = \frac{1}{P_M}(\tau_M + T_{2M}) \qquad (12)$$

The data in Figure 3 for $T_{2p}$ measured in a 0.016 *M* $VO(ClO_4)_2$ solution are well approximated by adding to the contributions of the chemical exchange as calculated from Table I a temperature-independent value $T_{2M}/P_M = 6 \times 10^{-4}$ sec, which corresponds to $T_{2M} = n(1.7 \times 10^{-7})$ sec. Inserting this value and $T_{1,\mathrm{el}} \approx T_{2,\mathrm{el}} = 1.0 \times 10^{-8}$ sec into eq 7 we find for the scalar coupling constant $A/h$ the value given in Table I.

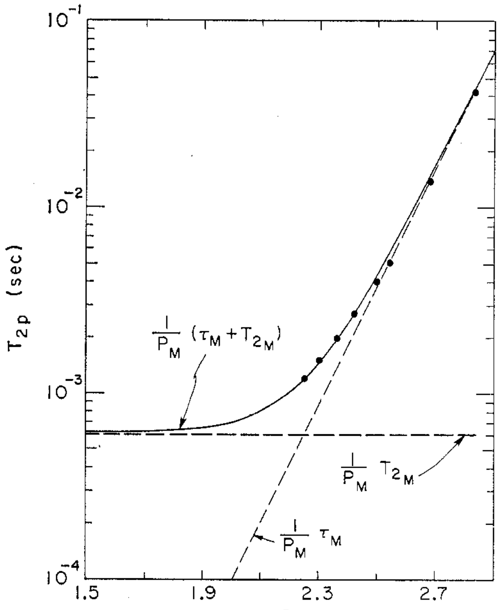

Figure 3.—Dependence on reciprocal of temperature of log $T_{2p}$ for a $1.6 \times 10^{-2}$ *M* $VO(ClO_4)_2$ solution above 390°K with the lines resulting from the curve fitting. Dots indicate experimental values.

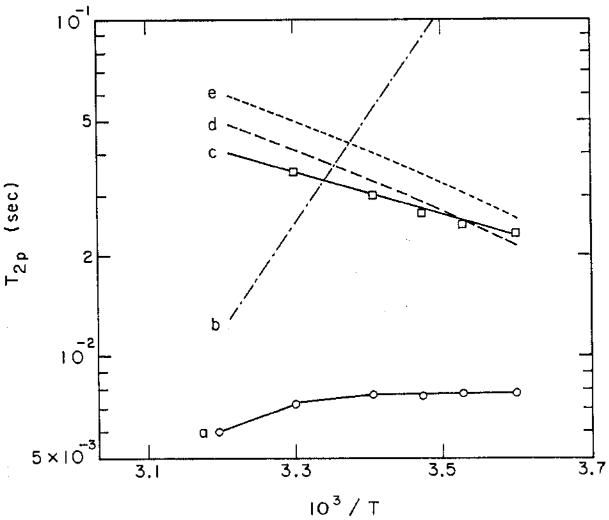

Figure 4.—Dependence on reciprocal of temperature of log $T_{2p}$ for a 0.83 *M* $VO(ClO_4)_2$ solution below 310°K: (a) experimental data using $T_{2H_2O}$ of pure water in eq 2; (b) contribution of the chemical exchange (11) calculated from Table I; (c) data given in curve a after subtraction of curve b and correction of the water blank for the high viscosity in 0.83 *M* $VO(ClO_4)_2$ (calculated using eq 10 and the following data: at 280°, $1/T_{2H_2O} = 251$ radians/sec, $\eta_{H_2O} = 1.43 \times 10^{-2}$ poise, $\eta_{0.83\,M\,VO(ClO_4)_2} = 1.93 \times 10^{-2}$ poise; at 290°, $1/T_{2H_2O} = 188$, $\eta_{H_2O} = 1.08 \times 10^{-2}$, $\eta_{VO(ClO_4)_2} = 1.54 \times 10^{-2}$; at 300°, $1/T_{2H_2O} = 151$, $\eta_{H_2O} = 0.85 \times 10^{-2}$, $\eta_{VO(ClO_4)_2} = 1.24 \times 10^{-2}$; this viscosity correction has been included in the values for $T_{2p}$ plotted in Figure 2); (d) calculated relaxation effect from dipolar coupling with the nuclei of eight water molecules bound with a lifetime longer than *ca.* $10^{-10}$ sec in a second coordination sphere in $VO(H_2O)_{13}{}^{2+}$; (e) calculated relaxation effect from dipolar coupling with one rapidly exchanging (lifetime *ca.* $10^{-10}$ sec) water molecule in the first coordination sphere of $VO(H_2O)_5{}^{2+}$.

At temperatures below *ca.* 310°K the line broadening of the nmr spectrum of $O^{17}$ from the presence of $VO(ClO_4)_2$ is small and varies only little with temperature. Figure 4 shows the results of a study in 0.83 *M* $VO(ClO_4)_2$ solution. In evaluating $T_{2p}$ from $T_2$ through eq 2 it is necessary to correct the pure water values of $T_{2H_2O}$ for the increased viscosity of a 0.83 *M* $VO(ClO_4)_2$ solution (see eq 10). The data then show that an additional relaxation path is important at low temperature: after subtracting from the values of curve a the contributions arising from the high viscosity and from chemical exchange (calculated from Table I), there is left a small relaxation effect given by curve c which must be due to other interactions between $VO^{2+}$ and the $O^{17}$ nucleus. In order to check whether interactions with the nuclei in water molecules outside the first coordination sphere could be responsible for this effect, we calculated the line broadening to be expected from different possible mechanisms: (i) inserting suitable numbers into eq 9, we found that contributions to the relaxation arising from dipolar coupling between $VO(H_2O)_n{}^{2+}$ and the bulk water interrupted by the translational motion of the particles would be negligibly

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(15) K. Wüthrich, unpublished results.

(16) D. C. McCain and R. J. Myers, *J. Phys. Chem.*, **71**, 192 (1967).

small. (ii) We assumed that a molecule $VO(H_2O)_5(H_2O)_8^{2+}$ with a lifetime which is long compared to the correlation time characteristic for its rotational tumbling exists in the solutions at lower temperatures. The eight water molecules bound in a second coordination sphere might be thought of as residing on the faces of the tetragonal bipyramid formed by $VO(H_2O)_5^{2+}$ (Figure 5). Using the parameters $r$ = 5 A and $d$ = 3.5 A for this species and the viscosities determined experimentally for 0.83 $M$ $VO(ClO_4)_2$ solutions at various temperatures, one calculates the curve d (Figure 4) for the relaxation effects to be expected from dipolar coupling with the $O^{17}$ in the second coordination sphere. (iii) We have further calculated the relaxation effect which would arise if one of the five water molecules in the first coordination sphere were exchanging rapidly and subject to dipolar coupling only, assuming $r$ = 4.5 A and $d$ = 2.4 A. Figure 4, curve e, shows that a result very similar to the result for $VO(H_2O)_{13}^{2+}$ is obtained.

## IV. Discussion

As mentioned earlier it is believed that complexes of the form $VO(H_2O)_5^{2+}$ exist in aqueous solutions of vanadyl ions.[14] The most striking feature of the $VO(H_2O)_5^{2+}$ molecule is the multiple bond between $V^{4+}$ and one of the ligand oxygens which implies a strong axial symmetry in the molecule (Figure 5). A detailed discussion of the electronic structure of the hydrated vanadyl ion has been given by Ballhausen and Gray.[14] It is seen from Figure 6 that they give the configuration $[(Ia_1)^2(IIa_1)^2(b_1)^2(e_\sigma)^4(IIIa_1)^2(e_\pi)^4(b_2)^1]$ for the ground state of the molecule, whereby the unpaired electron is believed to be in a mainly nonbonding orbital of $b_2$ symmetry. From the symmetry of the molecule it follows that the bonding of the four equatorial water molecules should be equivalent, while different wave functions are involved in the bonding of the axial water molecule. Experimental evidence for the equivalence of the four equatorial coordination sites has been found from X-ray data[13] and from esr measurements.[17]

From the present knowledge of the properties of the hydrated vanadyl ion it appears most likely that the number $n$ of exchanging water molecules in reaction 11 is 1 or 4, perhaps even 5. $n$ = 1 corresponds to the case where the four equatorial water molecules would exchange too slowly to influence the $O^{17}$ relaxation of the nuclei in the bulk water, and thus only the effect of the exchange of the axial water molecule would be observable. For the case $n$ = 4 only the effect of the water exchange in the equatorial positions would be observable, the scalar coupling of $O^{17}$ in the axial position being too small for the exchange of the axial water, which may occur at a high rate, to contribute appreciably to the relaxation in the bulk water. The case $n$ = 5 would correspond to all of the coordinated water molecules having a uniform scalar coupling constant of $O^{17}$ and exchanging at the same rate despite the differences in the bonding. The rate constants and the scalar coupling constants calculated for these possible cases are given in Table II.

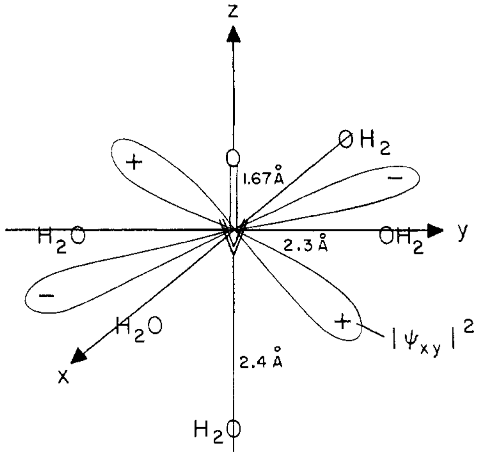

Figure 5.—Structure of $VO(H_2O)_5^{2+}$. $|\psi_{xy}|^2$ outlines the areas of high unpaired electron density for the ground state of the molecule.

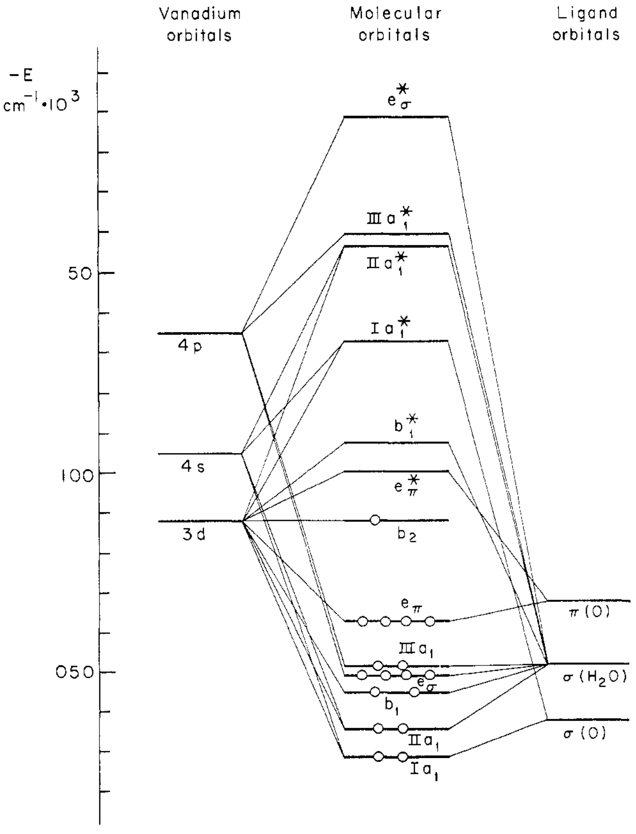

Figure 6.—Energy level diagram for $VO(H_2O)_5^{2+}$, according to Ballhausen and Gray.[14]

The influence of the exchange of the vanadyl oxygen on the $O^{17}$ relaxation in the bulk of the solution has been neglected in this discussion. From various observations it appears that the $VO^{2+}$ entity is very stable in aqueous solution,[18] and therefore one would expect an exchange of the oxygen to be rather slow. This view receives support from experiments with aqueous solutions of various $VO^{2+}$ compounds which showed that, if there is an exchange of the vanadyl

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(17) K. Wüthrich, *Helv. Chim. Acta*, **48**, 1012 (1965).

(18) J. Selbin, *Chem. Rev.*, **65**, 153 (1965).

TABLE II

RATE CONSTANTS AND SCALAR COUPLING CONSTANTS FOR DIFFERENT POSSIBLE VALUES OF $n$ IN REACTION 11

| | $n = 1$ | $n = 4$ | $n = 5$ |
|---|---|---|---|
| $k(298°)$ | $2 \times 10^3$ sec$^{-1}$ | $5 \times 10^2$ sec$^{-1}$ | $4 \times 10^2$ sec$^{-1}$ |
| $\frac{A}{h}$ | $7.6 \times 10^6$ cps | $3.8 \times 10^6$ cps | $3.4 \times 10^6$ cps |

oxygen in these complexes, its rate is too slow to be observed by the $O^{17}$ nmr relaxation technique.[19]

No other measurements exist for the rate of exchange of water molecules in the first coordination sphere of $VO^{2+}$. A comparison with the rates obtained for the water exchange in the first coordination sphere of a series of other doubly charged transition metal ions[1] shows that the exchange in vanadyl perchlorate solutions is comparatively very slow for all the values chosen for $n$. This may be due to a high electrostatic contribution to the bonding of the ligands. The vanadyl ion can be considered as made up of $V^{4+}$ and $O^{2-}$ and it is likely that it acts as a cation with charge of more than +2 not only toward the $O^{2-}$ but also toward the five other ligands. The influence of the high positive charge acting on the coordinated water molecules presumably would also be reflected in the value found for the activation enthalpy $\Delta H^{\ddagger}$ (Table I) which is high compared to $\Delta H^{\ddagger}$ found for the water exchange with other doubly charged metal ions.[1] One would expect that crystal field effects play no important role for $d^1$ systems.[20]

A comparison with earlier results[1] shows that the scalar coupling constant of $O^{17}$ for the $VO^{2+}$ aquo complex is small compared to the values found in corresponding experiments with the hydrated $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, and $Ni^{2+}$ ions. This indicates that scalar interactions of the unpaired electrons with the $O^{17}$ of the coordinated waters occur predominantly *via* $\sigma$ bonding rather than $\pi$ bonding when both possibilities exist: $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, and $Ni^{2+}$ have two half-filled d orbitals available for $\sigma$ bonding, while the unpaired electron of $VO(H_2O)_5{}^{2+}$ is believed to be mainly localized in a molecular orbital of $b_2$ symmetry (Figure 6)[14] which for symmetry reasons cannot contribute appreciably to $\sigma$ bonding of the ligands (Figure 5). From the above-mentioned theoretical considerations[14] of the ground state of $VO(H_2O)_5{}^{2+}$ one might expect scalar interactions to occur *via* $\pi$ bonding (Figure 5). This may be checked by considering the proton scalar coupling constant in $VO(H_2O)_n{}^{2+}$, since $\pi$ bonding has been shown to be primarily responsible for the scalar coupling of protons in hydrated metal ions.[21] From a reinterpretation of Hausser and Laukien's[22] data on the proton nmr relaxation in aqueous $VOSO_4$ solution, $A/h$ of protons in $VO(H_2O)_n{}^{2+}$ was found to be given by $(1/\sqrt{p})3.3 \times 10^6$ cps, where $p$ is the number of coordinated protons. This value is indeed of the same magnitude as the proton scalar coupling constants for $Mn^{2+}$, $Fe^{2+}$, and $Co^{2+}$ [21,23] which also have half-filled d orbitals available for $\pi$ bonding, and it is considerably larger than $A/h$ of protons in the hydrated $Ni^{2+}$ and $Cu^{2+}$ ions[21] which have no half-filled $t_{2g}$ orbitals.

The variation of $T_{2p}$ with temperature between 275 and 310°K (Figure 4) indicates that in this temperature region a large part of $T_{2p}$ (curve c) cannot be explained by the mechanism involving the exchange reaction (11); *i.e.*, a new path for relaxation becomes important. In part III it has been shown that dipole–dipole interactions between $VO^{2+}$ and the $O^{17}$ nuclei of water molecules coordinated to $VO^{2+}$ with a much shorter chemical exchange lifetime than the $n$ ligands characterized by reaction 11 could account for the observed additional line broadening. First, if $n = 4$, the dipolar coupling with a loosely bound water molecule in the axial position of the first coordination sphere could be responsible for the measured relaxation effect (curve e). Second, if the whole effect of the first coordination sphere on the relaxation were accounted for through the mechanism which involves the water exchange (11), dipolar coupling with the nuclei of water molecules bound in a second coordination sphere could explain the line broadening at low temperatures (Figure 4, curve d). The curves 4d and 4e agree as well with the experimental values as can be expected if one takes into consideration the approximation made in describing such systems by Stokes' diffusion equation, as in eq 8.

As mentioned earlier (part I) eq 8 applies only if the loosely bound water molecules remain coordinated for a time long compared to the rotational correlation time of the hydrated vanadyl ion, *i.e.*, *ca.* $10^{-10}$ sec at 25°. This seems not impossible, particularly in view of the high effective charge of the vanadium as implied by the slow water exchange from the first coordination sphere. It should be pointed out, however, that quadrupolar coupling (10) is also a possible mechanism for the additional relaxation at low temperature. The contributions to $T_{2p}$ arising from quadrupolar coupling would be unimportant if the loosely bound waters were able to rotate as rapidly about their principal axes as unbound waters, since their quadrupolar contribution to the relaxation would then not be influenced by coordination to the vanadyl ions. On the other hand, if the loosely coordinated waters were bound so tightly that they could tumble only through the tumbling of the whole hydrated vanadyl ion, the correlation time $\tau_q$ for quadrupolar coupling would be given by (13), where $\tau_c$ is

$$\frac{1}{\tau_q} = \frac{1}{\tau_c} + \frac{1}{\tau_e} \qquad (13)$$

the correlation time for rotational tumbling of the hydrated vanadyl ion and $\tau_e$ is the lifetime with respect to chemical exchange of the loosely bound waters. $\tau_q$ is also effectively the correlation time for dipole–dipole coupling of eq 8. Therefore the relative contributions from quadrupolar coupling and dipolar coupling will be determined by the ratio of the coupling

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(19) K. Wüthrich, unpublished results.

(20) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 108.

(21) Z. Luz and R. G. Shulman, *J. Chem. Phys.*, **43**, 3750 (1965).

(22) R. Hausser and G. Laukien, *Z. Physik*, **153**, 394 (1959).

(23) B. B. Wayland and W. L. Rice, *Inorg. Chem.*, **5**, 54 (1966).

constants in eq 8 and 10. The quadrupolar effect turns out to be *ca.* 10 times greater. It follows that for this model, *i.e.*, tumbling of the loosely coordinated water molecules only through the tumbling of the whole vanadyl aquo complex, the observed additional relaxation at low temperature would occur primarily through quadrupolar coupling interrupted by chemical exchange with a lifetime of *ca.* $10^{-11}$ sec.

The interpretation of the $O^{17}$ relaxation in $VO^{2+}$ solutions in terms of interactions with water molecules in two different kinds of coordination sites receives support from a comparison with the temperature dependence of the proton nmr relaxation in aqueous $VOSO_4$ solutions: The data by Hausser and Laukien[22] can be explained by an analogous interpretation which assumes that at higher temperature the relaxation is controlled by the exchange of protons from the first coordination sphere, while at lower temperature the contributions from protons of water molecules coordinated to $VO^{2+}$, with a much shorter lifetime than those in the first coordination sphere, become important.

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# Complexes of Cobalt(II). V. A Model for Anomalous Magnetic Behavior

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A strong-field approximation incorporating spin–orbit effects has been used to calculate paramagnetic susceptibilities as a function of temperature and crystal-field strength of cobalt(II) ions in an octahedral environment and in the vicinity of the "crossover" from a high-spin to a low-spin ground level. These calculations predict that the room-temperature magnetic moment should decrease smoothly from high-spin values (>4 BM) to low-spin values (*ca.* 1.7 BM) as the crystal-field splitting increases. A Boltzmann distribution over five levels (3 U′, E′, and E″) can be used to explain anomalous Curie–Weiss behavior reported previously for certain cobalt(II) complexes provided the crystal-field splitting is varied as a function of temperature.

## Introduction

Most six-coordinated octahedral cobalt(II) complexes fall into two classes: those with magnetic moments which lie in the range 4.8–5.6 BM and are referred to as "high-spin" and those with moments in the range 1.73–2.0 BM which are referred to as "low-spin."[1] Recently, however, there have been found a number of six-coordinated cobalt(II) compounds which have room-temperature magnetic moments intermediate between these two classes.[2] Several of these "intermediate-moment" compounds have anomalous magnetic susceptibility curves; that is, they exhibit large deviations from normal Curie–Weiss behavior. In part I of this series,[3] Stoufer, Smith, Clevenger, and Norris listed five such complexes and presented curves of reciprocal susceptibility *vs.* temperature for each. Other cobalt(II) complexes exhibiting similar behavior have subsequently been found by Ramirez[4] and Fisher.[5] A tabulation of most of these compounds and their room-temperature magnetic moments is given in Table I, and plots of $1/\chi$ *vs.* $T$ are shown in Figures 1 and 2 where $\chi$ is the molar paramagnetic susceptibility.

Of various possible qualitative explanations for this "anomalous" magnetic behavior, Stoufer, *et al.*,[3] concluded that the only one consistent with the experimental data involves a model in which there is a distribution of magnetic ions among two or more low-lying electronic levels. The specific idea of an equilibrium between two distinct electronic levels, each having different amounts of spin and orbital angular momenta, has been used in the past to explain unusual magnetic behavior.[6] However, in part I it was shown that, if spin–orbit coupling is introduced into the model, a $d^7$ ion such as Co(II) will have a total of five electronic levels arising from the two lowest terms ($^2E$ and $^4T_1$), all five of which may be accessible at reasonable temperatures and at certain values of crystal-field strength near the point where the $^2E$ and $^4T_1$ terms cross (see Figure 3). It was postulated that a model based on a distribution over the five levels might lead to an explanation of the experimental results. The specific aim of this work is, then, to test this hypothesis in a quantitative fashion by actually calculating paramagnetic susceptibilities as a function of temperature in an attempt to produce theoretical curves similar to those shown in Figures 1 and 2.

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(6) G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 4830 (1964), and references therein.