TABLE IV

KINETIC DATA AND CFAE'S FOR THE DISSOCIATION OF SOME COMPLEXES OF THE FIRST TRANSITION SERIES

System	Complex	$\Delta S^{\ddagger}$, eu	E_a, kcal	CFAE, Dq
d^3	$V(phen)_3^{2+}$ [a]	−8	21.3	2
	$V(bipy)_3^{2+}$ [a]	Slow	. . .	2
d^4	$Cr(bipy)_3^{2+}$	+13	22.6	1.4
d^5	$Mn(phen)_3^{2+}$	Fast	. . .	0
d^6	$Fe(phen)_3^{2+}$	+28	32.1	4
	$Fe(bipy)_3^{2+}$	+17	28.4	4
d^7	$Co(phen)_3^{2+}$	+5	19.4	0
d^8	$Ni(phen)_3^{2+}$	+1	26.2	2
	$Ni(bipy)_3^{2+}$	+2	22.2	2
d^9	$Cu(phen)_3^{2+}$	Fast	. . .	0
d^{10}	$Zn(phen)_3^{2+}$	Fast	. . .	0

[a] This work. For other sources see ref 4, p 150.

The substitution reactions of d^3 systems are also predicted to be slow by valence bond theory.[18] In this approach d^8 systems are predicted to be labile, since they would be ionic or outer-orbital complexes.[18] The slower reactions of V(II) than of Ni(II) somewhat substantiate this conclusion. However, nickel complexes are certainly much less labile than those of Mn(II), high-spin Fe(II), Co(II), Cu(II), and Zn(II), all of which are outer-orbital, or ionic, complexes. The activation energy for dissociation of $Ni(phen)_3^{2+}$ is greater than that for $V(phen)_3^{2+}$ (Table IV). In the case of formation of the monothiocyanate complexes, the activation energy is greater[19] for V^{2+} than for Ni^{2+}.

Acknowledgment.—This work was supported by the National Science Foundation under Grants 3400 and 6341 X to Northwestern University. The authors are indebted to Dr. W. P. Schaefer of the California Institute of Technology for a helpful exchange of information.

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[18] H. Taube, *Chem. Rev.*, **50**, 69 (1952).

[19] J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, **7**, 250 (1968).

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Nuclear Magnetic Resonance Studies of the Coordination of Vanadyl Complexes in Solution and the Rate of Elimination of Coordinated Water Molecules

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The temperature dependence of the O^{17} nmr line width in O^{17}-enriched aqueous solutions of the vanadyl complexes with the chelating ligands ethylenediaminetetraacetate (EDTA), nitrilotriacetate (NTA), 2-picolyliminodiacetate (PIDA), iminodiacetate (IDA), 5-sulfosalicylic acid (SSA), and Tiron (TIR) has been measured. The dependence on temperature of the complex formation equilibria was obtained from esr studies, so that the concentrations of the various paramagnetic species present in solutions of VO^{2+} ions and one of the ligands were known over the whole temperature range studied. The data obtained for $VO(EDTA)^{2-}$ show that a possible exchange of the doubly bonded "vanadyl oxygen" would be too slow to be observed by the O^{17} nmr technique. The exchange of the water molecule in the axial position opposite the vanadyl oxygen in $VO(SSA)_2^{4-}$ and $VO(TIR)_2^{6-}$ contributes at most a very small line broadening which is consistent with a very short lifetime with respect to chemical exchange of the axial water. Large relaxation effects arise from the presence of the 1:1 complexes with IDA, SSA, and TIR which have equatorial positions available for coordination of water molecules. The influence of the ligands in adjoining positions on $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and the first-order rate constant k of the water exchange from the equatorial coordination sites and on the scalar coupling constant A/h of O^{17} in the equatorial positions has been studied. The data obtained from solutions of the complexes with the tetradentate ligands NTA and PIDA can be interpreted in terms of a pyramidal structure of these compounds. The vanadyl oxygen and the four equatorial positions would then be at the corners of a tetragonal pyramid, with V^{4+} somewhat above the plane of the base. In a similar pyramidal structure of the hydrated vanadyl ion one would expect only four waters to be tightly bound, which would be consistent with the experimental data. A comparison of the O^{17} relaxation data with chemical shift measurements and proton relaxation experiments reported by others indicates that, in addition to the effects arising from the chemical exchange from the equatorial positions, the nuclear resonance in the bulk water of VO^{2+} solutions is influenced by the exchange of loosely coordinated waters. This may correspond to weak coordination of water molecules in the axial position opposite the vanadyl oxygen and on the four faces of the pyramid formed by VO^{2+} and the four more tightly bound equatorial waters.

I. Introduction

In dilute aqueous solutions of vanadyl ions a single nuclear magnetic resonance of O^{17} or H^1 can be observed which corresponds to that of the bulk water modified by the exchange of O^{17} and protons in and out of the coordination spheres of V^{4+}. Measurement of the line width of that resonance in metal ion solutions is a convenient method for studying the rate of exchange of O^{17} and H^1 between the bulk water and the coordination spheres of the metal ions, as well as the interaction between the unpaired electrons of the metal ion and the nuclei of the coordinated water molecules.[1] Half the line width at half-height, $\delta\omega$, expressed in radians per second, is equal to the reciprocal of the apparent transverse relaxation time T_2 and is given by

$$\delta\omega = \frac{1}{T_2} = \frac{1}{T_{2H_2O}} + \frac{1}{T_{2p}} = \delta\omega_{H_2O} + \delta\omega_p \qquad (1)$$

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[1] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962); **41**, 2553 (1964).

T_{2H_2O} describes the relaxation of the nuclei in the bulk of the solution that would occur in the absence of paramagnetic ions, and T_{2p}, the relaxation effects arising from the presence of the paramagnetic ions.

The line width of the resonance observed in solutions containing the hydrated vanadyl ion may be influenced by the exchange of nuclei from four kinds of nonequivalent coordination sites (Figure 1), *i.e.*, the site of the doubly bonded "vanadyl oxygen," the four equatorial positions (I), the axial position opposite the vanadyl oxygen (II), and possibly additional coordination sites in a second coordination sphere (III). The observed line broadening arising from the presence of the VO^{2+} ions, $\delta\omega_p$, is then given by eq 2, where all the $\delta\omega_{pi}$ may be different.

$$\delta\omega_p = \sum_i \delta\omega_{pi} \qquad i = V{=}O, I, II, III$$

Experiments designed to distinguish between the exchange reactions from the different nonequivalent coordination sites have been described previously. Reuben and Fiat[2] measured the chemical shift of O^{17} in Dy^{3+} solutions which contained various amounts of $VOSO_4$. They found that four water molecules were tightly bound to the VO^{2+} ion at room temperature. Assuming that no appreciable relaxation effects arise from the exchange of the vanadyl oxygen, they concluded that only the exchange of the water molecules coordinated to the four equatorial positions leads to a marked broadening of the O^{17} resonance, while the extremely fast water exchange involving the axial position and possibly positions in a second coordination sphere leads to a small shift of the resonance. From studies of the O^{17} nmr relaxation in $VO(ClO_4)_2$ solutions[3] two exchange reactions could be distinguished. It was not possible, however, to assign the reactions with certainty to specific ones of the four different kinds of coordination sites. Analysis of the temperature dependence of the proton relaxation in $VOSO_4$ solutions also led to the conclusion that two different exchange reactions contribute to the observed data.[3,4] In the present paper it is shown how the different kinds of coordination sites can be studied separately in a series of vanadyl chelate complexes[5] and how the water exchange from one of the coordination sites can be influenced by the ligands coordinated to adjoining positions.

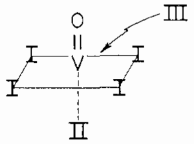

Figure 1.—Nonequivalent coordination sites of V^{4+} in vanadyl complexes.

II. Theory

Nmr Relaxation Studies.—A thorough discussion of the transverse nuclear relaxation in dilute aqueous solutions of paramagnetic metal ions has been given by Swift and Connick.[1] They found that two relaxation mechanisms may contribute to the observed line-broadening $\delta\omega_p$, the "$\Delta\omega$ mechanism" involving relaxation 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,[6] and the "T_{2M} mechanism"[7] involving the fast relaxation of the coordinated nuclei. It has been shown that the $\Delta\omega$ mechanism is not of importance in solutions of vanadyl ions.[3] The effect of the exchange of nuclei between the ith kind of coordination sites of the vanadyl ion and the bulk water on the nuclear relaxation in the solution is then given by

$$\frac{1}{T_{2pi}} = \frac{P_{Mi}}{\tau_{Mi} + T_{2Mi}} \tag{3}$$

τ_{Mi} is the lifetime with respect to chemical exchange of a nucleus in the ith coordination site, T_{2Mi} is the transverse relaxation time of a nucleus in the ith coordination site, and the probability factor P_{Mi} is given closely by $n_i[VO^{2+}]/55.5$, where $[VO^{2+}]$ is the vanadyl ion concentration, and n_i is the number of water molecules in the coordination sites of type i. Two limiting cases may be distinguished, *i.e.*, where $1/T_{2pi}$ is controlled entirely by τ_{Mi} or by T_{2Mi}.[3]

The variation of τ_{Mi} with temperature will be that of rate constant (eq 6 of ref 3). The temperature dependence of T_{2Mi} is determined by the interactions between the coordinated nuclei and vanadyl ion. Three types of interaction might be of importance: scalar coupling between the nuclear spins and the unpaired electron, dipole–dipole coupling between the nuclei and the unpaired electron, and interaction of the nuclear quadrupole moment with the electric field in its vicinity. The limiting forms of equations applicable to the present systems are: scalar coupling[3,8]

$$\frac{1}{T_{2Mi}} = \frac{1}{3}S(S+1)\frac{A_i^2}{\hbar^2}\tau_{ci}; \quad \frac{1}{\tau_{ci}} = \frac{1}{T_{1e}} + \frac{1}{\tau_{Mi}} \tag{4}$$

dipole–dipole coupling[3,9]

$$\frac{1}{T_{2Mi}} = \frac{\gamma_I^2\gamma_S^2\hbar^2 S(S+1)}{15d_i^6}\left[7\tau_{ci} + \frac{13\tau_{ci}}{1+\omega_s^2\tau_{ci}^2}\right]; \qquad \frac{1}{\tau_{ci}} = \frac{1}{\tau_r} + \frac{1}{\tau_{Mi}} \tag{5}$$

and quadrupole coupling[3,10,11]

$$\frac{1}{T_{2Mi}} = \frac{3(2I+3)}{40I^2(2I-1)}\left(1 + \frac{\zeta_i^2}{3}\right)\left(\frac{eQq_i}{\hbar}\right)^2\tau_{ci}; \qquad \frac{1}{\tau_{ci}} = \frac{1}{\tau_r} + \frac{1}{\tau_{Mi}} \tag{6}$$

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(2) J. Reuben and D. Fiat, *Inorg. Chem.*, **6**, 579 (1967).

(3) K. Wüthrich and R. E. Connick, *ibid.*, **6**, 583 (1967).

(4) R. K. Mazitov and A. I. Rivkind, *Dokl. Akad. Nauk SSSR*, **166**, 654 (1966).

(5) K. Wüthrich and R. E. Connick, paper presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

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

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

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

(9) I. Solomon, *Phys. Rev.*, **99**, 559 (1955); see also ref 8.

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

(11) See ref 8, p 314.

Here A_i is the scalar coupling constant, d_i is the distance between the two dipoles, ω_s is the electronic Larmor frequency, τ_{ei} is the correlation time, τ_r is the correlation time for rotational tumbling, and T_{1e} is the longitudinal electronic relaxation time. The other symbols have their usual meaning.[3] In each case the temperature dependence of $1/T_{2Mi}$ is expected to arise from the correlation time only.

Chemical Shift Measurements.—The chemical shift in radians per second of the nuclear resonance in the bulk water relative to that in pure water is given by[1]

$$\Delta\omega_{H_2O} = -\sum_i \frac{P_{Mi}\Delta\omega_{Mi}}{\left(\frac{\tau_{Mi}}{T_{2Mi}} + 1\right)^2 + \Delta\omega_{Mi}^2\tau_{Mi}^2} \qquad (7)$$

$\Delta\omega_{Mi}$ is the chemical shift relative to pure water of a nucleus in the ith position and is given by[12]

$$\Delta\omega_{Mi} = \omega S(S + 1)\frac{\gamma_S}{\gamma_I}\frac{A_i}{3kT} \qquad (8)$$

where ω is the Larmor frequency of the nucleus considered. When chemical exchange is fast compared to relaxation, *i.e.*, $1/\tau_{Mi}^2 \gg 1/(T_{2Mi}\tau_{Mi}) + \Delta\omega_{Mi}^2$, the contribution to the chemical shift of the bulk waters becomes

$$\Delta\omega_{H_2Oi} = -P_{Mi}\Delta\omega_{Mi} \qquad (9)$$

Esr Studies of the Complex Formation.—In general, the complex formation of VO^{2+} with a chelating ligand will occur stepwise, as given by

$$VO(L)_{n-1}{}^{p+} + LH_q \rightleftharpoons VO(L)_n{}^{(p-q)+} + qH^+ \qquad (10)$$

Under given conditions a solution may contain two, three, or more different paramagnetic species, which may contribute to the nuclear relaxation in the bulk water through water exchange from up to four kinds of nonequivalent coordination sites (see Figure 1). The observed line-broadening due to the presence of the VO^{2+} ions would then be given by

$$\delta\omega_p = \sum\sum_i \delta\omega_{pij} \qquad (i = V{=}O, I, II, III;$$
$$j = VO, VO(L), VO(L)_2, \text{etc.}) \qquad (11)$$

For an interpretation of the nmr data of solutions of vanadyl complexes we therefore have to know the concentrations of the various species present.

Electron spin resonance measurements have been shown to be a convenient method to investigate the complex formation reactions in vanadyl ion solutions[13] and can easily be applied over the whole temperature range used for the nmr experiments. The esr signal of a vanadyl complex in solution is given by the spin Hamiltonian[14]

$$\mathcal{H}_S = g_0\beta HS_z + a\vec{S}\cdot\vec{I} \qquad (12)$$

g_0 is the isotropic spectroscopic splitting factor, β the Bohr magneton, H the applied external magnetic field in the z direction, and a the isotropic hyperfine coupling constant of V.[51] The eigenvalues of eq 12 to second order are given by[15]

$$H(m_I) = H_0 - am_I - \frac{a^2}{2H_0}(I(I + 1) - m_I^2); \quad H_0 = \frac{h\nu}{g_0\beta} \qquad (13)$$

where m_I are the eigenvalues of I_z and a is given in gauss. The signal consists of eight hyperfine components ($I = {}^7/_2$ for V^{51}). g_0 is only slightly different for different complexes, but the distances between the eight hyperfine components, which are essentially determined by the parameter a (see (13)), are greatly influenced by the ligands coordinated to VO^{2+}. Therefore different complexes which are present in the same solution can be distinguished.[13] This is illustrated in Figure 2 which shows the esr spectrum of a solution of VO^{2+} and Tiron at various temperatures. The positions of the eight hyperfine components of the signals corresponding to VO^{2+}, $VO(TIR)^{2-}$, and $VO(TIR)_2{}^{6-}$ are given at the bottom of Figure 2.[16] The lines corresponding to the signals of these three species are then easily identified in the high-field and low-field parts of the spectra recorded at various temperatures. It is seen that the relative intensities of the three signals vary greatly with temperature. $VO(TIR)_2{}^{6-}$ can hardly be detected in the spectrum at 25°, but it is the predominant species at 125°. These variations of the relative concentrations of the three complexes are fully reversible; *i.e.*, one gets the original spectrum back after cooling the solution from 125 to 25°.

For all of the ligands discussed in this paper, g_0 and a of the 1:1 and, where applicable, the 1:2 complexes with VO^{2+} are known,[13,16] and the line widths of the eight hyperfine components in solutions containing various concentrations of the complexes have been measured at different temperatures. Assuming that the shape of the resonance is Lorentzian, the esr signals of the vanadyl complexes have been reconstructed with eq 13 from these parameters on a CDC 6600 computer. From the calculated signals we computed for the various ligands the esr spectra of solutions containing variable relative concentrations of VO^{2+}, VO^{2+}-(L), and $VO^{2+}(L)_2$. The experimental spectra of the samples used for our experiments were then compared with the calculated spectra of corresponding solutions, and the relative concentrations of the different species were determined from the best fit. Since the total VO^{2+} concentration in the samples was known, we thus obtained the concentrations of VO^{2+}, $VO^{2+}(L)$, and $VO^{2+}(L)_2$.

These esr experiments further show that the lifetime in the first coordination sphere of the chelating ligands used for these studies is long compared to that of the coordinated water molecules. At temperatures above *ca.* 140° where the lifetimes of the water molecules in the first coordination sphere of some of the complexes are short compared to both the electronic relaxation

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[12] N. Bloembergen, *J. Chem. Phys.*, **27**, 595 (1957).

[13] K. Wüthrich, *Helv. Chim. Acta*, **48**, 779 (1965).

[14] H. M. McConnell, *J. Chem. Phys.*, **25**, 709 (1956).

[15] R. N. Rogers and G. E. Pake, *ibid.*, **33**, 1107 (1960).

[16] K. Wüthrich, *Helv. Chim. Acta*, **48**, 1012 (1965).

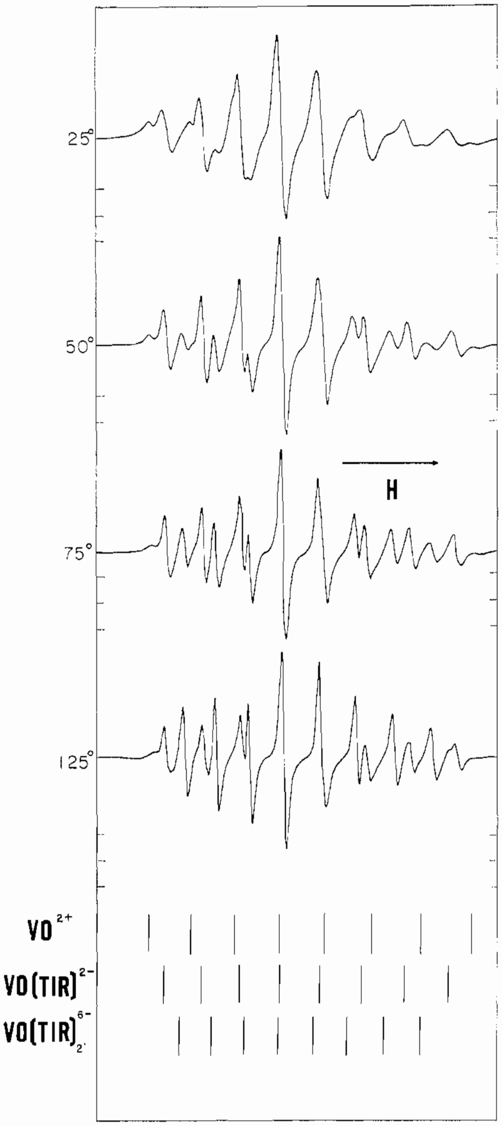

Figure 2.—Esr spectrum of an aqueous solution of 0.11 *M* $VO(ClO_4)_2$ and 0.26 *M* Tiron at various temperatures, pH (25°) 3.0. The line patterns at the bottom indicate the positions of the hyperfine components corresponding to the different complexes present. This solution was chosen to illustrate the sensitivity of the method for detecting several species and did not correspond to any of the nmr solutions.

time and the reciprocal of the difference between the *a* values corresponding to the various complexes present, one still observes the separate esr signals of the different chelate complexes.

Esr Relaxation Studies.—To calculate the scalar coupling constants from nmr relaxation measurements one has to know the longitudinal electronic relaxation time T_{1e} of the paramagnetic ion (see (4)). T_{1e} has been measured in $VO(ClO_4)_2$ solutions at room temperature,[17] but it is not known for any of the vanadyl complexes at high temperatures. As discussed previously[3] the experiments done by McCain and Myers[17] imply that it is a fairly good approximation to set $T_{1e} = T_{2e}$ for vanadyl ions under the experimental conditions of the nmr relaxation experiments at high temperatures. The value of T_{2e} used in this approximation was that corresponding to the average of the transverse relaxation times of the eight hyperfine components. The transverse relaxation times of the individual components were obtained from measurements of the separation of the positive and negative peaks in the first-derivative spectrum.

III. Experimental Section

Each experiment with one of the vanadyl complexes involved the following steps. (i) Known amounts of $VO(ClO_4)_2$ and one of the chelating ligands were dissolved in O^{17}-enriched water. (ii) Through addition of NaOH a certain pH value was established at room temperature. (iii) The O^{17} nmr spectrum was recorded at various temperatures. (iv) A corresponding solution in nonenriched water was analyzed by esr measurements for the species present at the temperatures where the nmr spectrum was recorded. From these esr spectra we also obtained the transverse electronic relaxation times.

The following chemicals were used: water enriched to 11% in O^{17} obtained from Oak Ridge National Laboratories, *ca.* 2.5 *M* $VO(ClO_4)_2$ solutions which were analyzed for paramagnetic impurities as described previously,[3] disodium ethylenediaminetetraacetate (EDTA) obtained from Fisher Scientific Co., nitrilo-acetic acid (NTA) and iminodiacetic acid (IDA) from Eastman Organic Chemicals, Tiron (TIR, 1,2-dihydroxybenzene-3,5-disulfonic acid, disodium salt) from Baker Chemical Co., 5-sulfosalicylic acid (SSA) from Merck Chemical Co., 2-picolyliminodiacetic acid (PIDA) obtained from Professor S. Fallab at the University of Basel, Basel, Switzerland, and NaOH from Allied Chemicals.

The $VO(ClO_4)_2$ concentration in the stock solution 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 weighed amounts of the ligands to a known volume of O^{17}-enriched water. By addition of very small amounts of concentrated NaOH or $HClO_4$ a certain pH value was then established at room temperature, using a combination glass–reference electrode especially designed for these experiments.[18] The solutions were finally degassed and then studied in sealed nmr tubes. The solutions of some of the complexes tend to decompose after standing for a few days. Therefore all of the experiments were done with freshly prepared solutions. It was checked with esr measurements that no irreversible changes occurred on heating the solutions up to the temperatures needed for the nmr relaxation studies.

All of the O^{17} nmr measurements were made at 8.134 Mc. The nmr spectrometer and the sample tubes used for the O^{17} relaxation studies were described previously.[3] For the O^{17} chemical shift measurements the solutions of the VO^{2+} complexes were studied in spherical bulbs and the spectra were compared to the resonance of pure water recorded in similar sample tubes. The esr measurements were done on a Varian V-4500 X-band spectrometer with 100-KHz field modulation, using a standard Varian V-4500 temperature controller for the experiments at high temperatures. The solutions were studied in sealed capillaries of *ca.* 1.5-mm outer diameter. The proton nmr experiments were done with a Varian A-60 spectrometer equipped with the standard Varian V-6031 variable-temperature probe.

IV. Results

The following VO^{2+} complexes have been studied: $VO(H_2O)_n{}^{2+}$ in $VO(ClO_4)_2$ solutions;[3] the 1:1 complexes, $VO^{2+}(L)$, with ethylenediaminetetraacetate (EDTA), nitrilotriacetate (NTA), 2-picolyliminodiacetate (PIDA), iminodiacetate (IDA), 5-sulfosalicylate (SSA), and Tiron (TIR, 1,2-dihydroxybenzene-3,5-disulfonic

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

(18) The combination glass–reference electrode was constructed for us by Gebr. Möller, Glasblässerei, Zürich, Switzerland.

TABLE I

ESR STUDIES OF THE COMPLEX FORMATION EQUILIBRIA AND AVERAGE TRANSVERSE ELECTRONIC RELAXATION TIMES

Complex studied	$[VO^{2+}]_{tot}$, M	$[L]_{tot}$, M	pH (at 25°)	T, °C	% of $[VO^{2+}]_{tot}$ $[VO^{2+}]$	$[VO^{2+}(L)]$	$[VO^{2+}(L)_2]$	$\bar{T}_{2e}$, sec
VO(IDA)	0.040	0.040	4.3	25	10	90	. . .	6.3×10^{-9}
				60	7	93	. . .	7.4×10^{-9}
				100	5	95	. . .	7.4×10^{-9}
				140	3	97	. . .	7.0×10^{-9}
$VO(SSA)^-$	0.010	0.011	3.8	25	$<4^a$	$>89, \leqslant 100$	$<7^a$	6.2×10^{-9}
				60	$<2^a$	$>94, \leqslant 100$	$<4^a$	9.3×10^{-9}
				100	$<2^a$	$>94, \leqslant 100$	$<4^a$	10.2×10^{-9}
				140	$<2^a$	$>94, \leqslant 100$	$<4^a$	10.0×10^{-9}
$VO(TIR)^{2-}$	0.010	0.020	4.0	25	20	$>75, \leqslant 80$	$<5^a$	6.0×10^{-9}
				60	15	$>80, \leqslant 85$	$<5^a$	8.3×10^{-9}
				100	10	85	5	9.7×10^{-9}
				140	7	86	7	9.7×10^{-9}

[a] The signal of that species was not observed. The numbers correspond to the limits of detection in the calculated spectra.

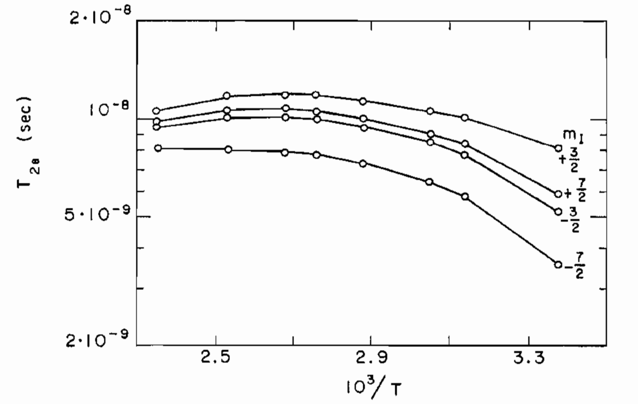

Figure 3.—Dependence on the reciprocal of temperature of log T_{2e} for four of the hyperfine components of the esr spectrum of a 0.01 M aqueous solution of $VO(SSA)^-$.

acid); and the 1:2 complexes $VO(SSA)_2^{4-}$ and $VO(TIR)_2^{6-}$.

Esr Measurements.—Table I gives the results of the esr studies of three typical solutions used for the nmr studies of the 1:1 complexes of VO^{2+} with SSA, TIR, and IDA. For all the other complexes examined it was possible to prepare solutions in which only the esr signal of a single species was observed over the whole temperature region of interest. The temperature dependence of the transverse electronic relaxation times of the complexes used in our experiments follows qualitatively the behavior of T_{2e} of vanadyl acetylacetonate in toluene described by Wilson and Kivelson.[19] The data for $VO(SSA)^-$ are given in Figure 3, which shows a plot of log T_{2e} *vs.* $1/T$ for the four hyperfine components corresponding to $m_I = -^7/_2, -^3/_2, +^3/_2, +^7/_2$. It is seen that in the semilogarithmic plot, which is generally used to present the nmr relaxation data, T_{2e} appears to be essentially independent of temperature between *ca.* 60 and 150°. The values of $\bar{T}_{2e}$ in the last column of Table I correspond to the average of the transverse relaxation times of the eight hyperfine components.

O^{17} Nmr Relaxation Studies.—The experimental data are summarized in Figure 4, which shows plots of log T_{2p} *vs.* $1/T$ for some of the complexes, and in Table II. It is seen that some of the chelate complexes give relaxation effects which are very small compared to those observed in $VO(ClO_4)_2$ solutions, while for other species T_{2p} is much shorter than that of $VO(ClO_4)_2$ in a part of the temperature region examined. A better understanding of the meaning of these data is obtained when one considers the schematic structures of the various complexes given in Figures 5 and 6.

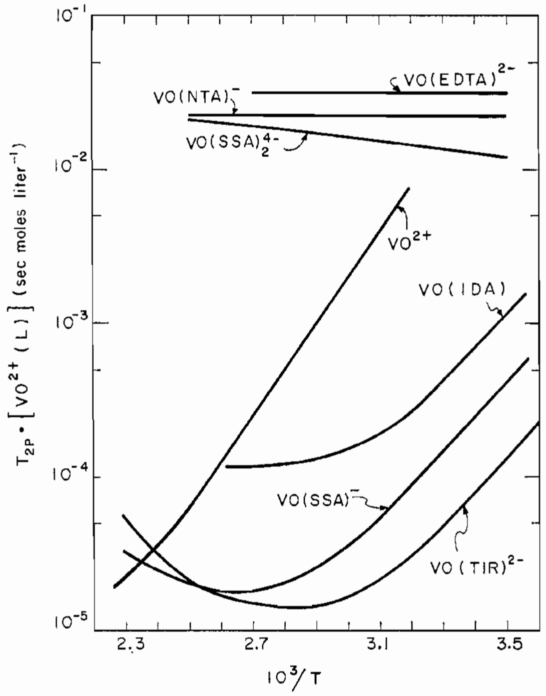

Figure 4.—Dependence on the reciprocal of temperature of log T_{2p} of O^{17} in aqueous solutions of various vanadyl chelate complexes.

Evidence has been found by others[20] that the coordination of protons and metal ions to EDTA occurs preferentially at the nitrogen atoms. Figure 5A appears then from model considerations to be the most likely structure of the VO^{2+}–EDTA complex. Figure 5A is also consistent with the stoichiometry of the complex formation reaction, if one assumes that the de-

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(19) R. Wilson and D. Kivelson, *J. Chem. Phys.*, **44**, 154 (1966).

(20) See R. J. Kula, Thesis, University of California, Riverside, Calif., 1964, wherein further references are given.

TABLE II

EXPERIMENTAL DATA ON THE O^{17} NMR RELAXATION IN AQUEOUS SOLUTIONS OF VANADYL COMPLEXES

Complex	Structure	Experimental observations (see Figure 4)	Parameters obtained[b]
VO^{2+} [a]	Figure 1 (I, II, III = H_2O)	Large $\delta\omega_p$, chemical exchange controlled in the major part of the temperature region 5–170°	$k = 5.0 \times 10^2$ sec^{-1} $\Delta H^{\ddagger} = 13.7$ kcal mol^{-1} $\Delta S^{\ddagger} = -0.6$ eu $A/h = 3.8 \times 10^6$ cps
		Small additional $\delta\omega_p$ at low temperatures, due to fast exchange of loosely bound waters (not given in Figure 4; see ref 3)	
$VO(EDTA)^{2-}$ $VO(EDTAH)^-$	Figure 5A	Very small $\delta\omega_p$ from 5 to 100°	k(vanadyl oxygen) < 20 sec^{-1}
$VO(SSA)_2{}^{4-}$	Figure 5B	Very small $\delta\omega_p$ from 5 to 130°	
$VO(Tiron)_2{}^{6-}$	Figure 5B	Very small $\delta\omega_p$ from 5 to 130°	
$VO(IDA)$ [c]	Figure 5C	Large $\delta\omega_p$, chemical exchange controlled from 5 to 50°; at higher temperatures T_{2M} controlled	$k = 1.2 \times 10^5$ sec^{-1} $\Delta H^{\ddagger} = 11.7$ kcal mole^{-1} $\Delta S^{\ddagger} = +3.9$ eu $A/h = 2.8 \times 10^6$ cps[d]
$VO(SSA)^-$ [c]	Figure 5D	Large $\delta\omega_p$, chemical exchange controlled from 5 to 50°; at higher temperatures T_{2M} controlled.	$k = 1.5 \times 10^5$ sec^{-1} $\Delta H^{\ddagger} = 10.8$ kcal mol^{-1} $\Delta S^{\ddagger} = +1.2$ eu $A/h = 4.5 \times 10^6$ cps[d]
$VO(Tiron)^{2-}$ [c]	Figure 5D	Large $\delta\omega_p$, chemical exchange controlled from 5 to 50°; at higher temperatures T_{2M} controlled	$k = 5.3 \times 10^5$ sec^{-1} $\Delta H^{\ddagger} = 11.8$ kcal mole^{-1} $\Delta S^{\ddagger} = +7.0$ eu $A/h = 4.9 \times 10^6$ cps[d]
$VO(NTA)^-$	Figure 6E *or* F	Very small $\delta\omega_p$ from 5 to 130°	
$VO(PIDA)$	Figure 6E *or* F	Very small $\delta\omega_p$ from 5 to 100°	
$VO(NTA)(OH)^{2-}$	Figure 6G	Very small $\delta\omega_p$ from 5 to 100°	
$VO(PIDA)(OH)^-$	Figure 6G	Very small $\delta\omega_p$ from 5 to 100°	

[a] Studied in $VO(ClO_4)_2$ solutions.[8] [b] k is the first-order rate constant at 25° for the loss from an equatorial position of the first coordination sphere of a particular one of the exchanging nuclei. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy and entropy of activation of the O^{17} exchange from the equatorial positions. A/h is the scalar coupling constant of O^{17} in the equatorial positions. Where only limits could be obtained for the concentration of $VO^{2+}(L)$ (Table I), the values of $[VO^{2+}(L)]$ used in the calculation of the reaction parameters were those which correspond to the average of the upper and the lower limits. [c] Solution composition is the same as in Table I. [d] Calculated using the approximation $T_{1e} = T_{2e}$.

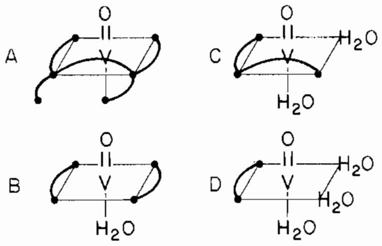

Figure 5.—Coordination of vanadyl complexes with chelating ligands.

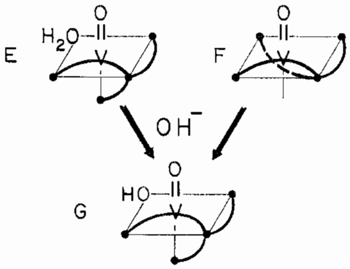

Figure 6.—Coordination of vanadyl complexes with tetradentate ligands.

protonation at pH *ca.* 3.0[21] involves the nonbonded carboxylic acid group. This would then explain that this deprotonation has no effect on the esr signal[13] and on the O^{17} relaxation in the bulk water as was found from a comparison of the O^{17} resonance in solutions of the protonated and the deprotonated EDTA complex. In the structure of Figure 5A only the vanadyl oxygen could possibly be involved in an O^{17} exchange between the first coordination sphere of the V^{4+} and the bulk water. The lack of any observable relaxation effects in $VO(EDTA)^{2-}$ solutions might be due to either very fast or very slow exchange of the vanadyl oxygen. We only consider the possibility of slow exchange and find the upper limit for the rate constant given in Table II. In the calculation of this limit we have used the datum that $T_{2p}[VO(EDTA)^{2-}] > ca.\ 3.0 \times 10^{-2}$ sec at 100° (Figure 4) and have assumed that the activation enthalpy for this reaction would be equal to or greater than that observed for the O^{17} exchange in $VO(ClO_4)_2$ solutions, *i.e.*, 13.7 kcal mol^{-1}.

X-Ray studies by Dodge, Templeton, and Zalkin[22] showed that the two bidentate ligands in the 1:2 complex of VO^{2+} with acetylacetonate are coordinated to the four equatorial positions of the first coordination sphere. Additional evidence for the correctness of the structures of the complexes with bidentate ligands given in Figure 5B and D has been obtained from esr experiments (see eq 5 and Table III of ref 16). From model

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[21] G. Schwarzenbach and J. Sandera, *Helv. Chim. Acta*, **36**, 1089 (1953).

[22] R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961).

considerations Figure 5C appears to be the most likely structure of the 1:1 complex with IDA. The experiments with $VO(SSA)_2^{4-}$ and $VO(TIR)_2^{6-}$ show that neither the exchange of the vanadyl oxygen nor water exchange from the axial position leads to appreciable broadening of the O^{17} resonance in the bulk water. On the other hand, large relaxation effects are observed in solutions of all of these complexes which have equatorial positions available for the coordination of water molecules (Figures 4 and 5). A comparison of these data with those obtained in $VO(ClO_4)_2$ solutions (Figure 4) implies that only the four equatorial coordination sites are involved in the water exchange which leads to the large $\delta\omega_p$ in $VO(ClO_4)_2$ solutions. The values of k, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ of the water exchange from the four equatorial positions in the hydrated vanadyl ion (Table II) were taken from the data reported previously.[3]

The parameters given for the water exchange from the equatorial positions of the 1:1 complexes with IDA, SSA, and TIR were obtained from the curve-fitting processes given in Figures 7–9. It is easily shown that the observed large relaxation effects cannot arise from dipolar coupling or quadrupolar coupling but must be due to scalar coupling between the unpaired electron and the nuclear spin. Therefore the dependence on temperature of T_{2p} is, through eq 3, determined by the temperature dependence of τ_M (eq 6 of ref 3) and (4), where we assume that $T_{1e} = T_{2e}$ is independent of temperature between 60 and 150° (Table I). In $VO(ClO_4)_2$ solutions τ_M never became short compared to T_{2M} in the temperature region accessible for the nmr experiments, *i.e.*, *ca.* 5–170° (Figure 4). Since the exchange rate of the equatorial waters is greatly enhanced through the influence of the chelating ligands IDA, SSA, and TIR, it was now possible to observe the region where $\tau_M < T_{2M}$ and, in the case of $VO(TIR)^{2-}$, even the region where $\tau_M < T_{1e}$. The values found for A/h will be in error to the extent that T_{1e} differs from $\bar{T}_{2e}$.

Two types of coordination are possible for the complexes of VO^{2+} with the tetradentate ligands NTA and PIDA, which may occupy either the three equatorial positions and the axial position (Figure 6E) or the four equatorial positions (Figure 6F) of the first coordination sphere. Since one would expect the complex given in Figure 6E to give rise to relaxation effects comparable to those in VO(IDA) solutions the O^{17} relaxation experiments indicate that the structure of Figure 6F is more stable in aqueous solutions of these complexes. This structure seems, however, not to be stable in basic solutions, where a hydroxo complex is formed.[13,23] The most likely coordination for the latter seems to be that given in Figure 6G. No appreciable relaxation effects are observed in solutions of these hydroxo complexes, which is consistent with a slow rate of exchange of the OH^- group in the equatorial position.

Chemical Shift Measurements.—The shift of the O^{17} resonance in *ca.* 0.4 *M* solutions of $VO(ClO_4)_2$, $VO(NTA)^-$, $VO(TIR)_2^{6-}$, and $VO(SSA)_2^{4-}$ was studied at 25°. The downfield shift found in the $VO(ClO_4)_2$ solution was in good agreement with the values reported by Reuben and Fiat.[2] No shift or at most very small upfield shifts could be detected in the solutions of the three vanadyl complexes.

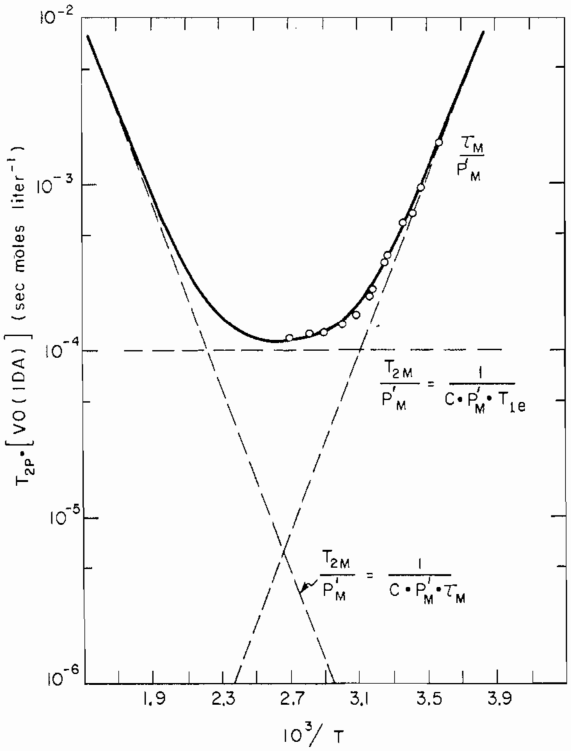

Figure 7.—Dependence on the reciprocal of temperature of log T_{2p} of O^{17} in solutions of VO(IDA) with the lines resulting from the curve fitting; $P_M' = P_M/[VO(IDA)]$.

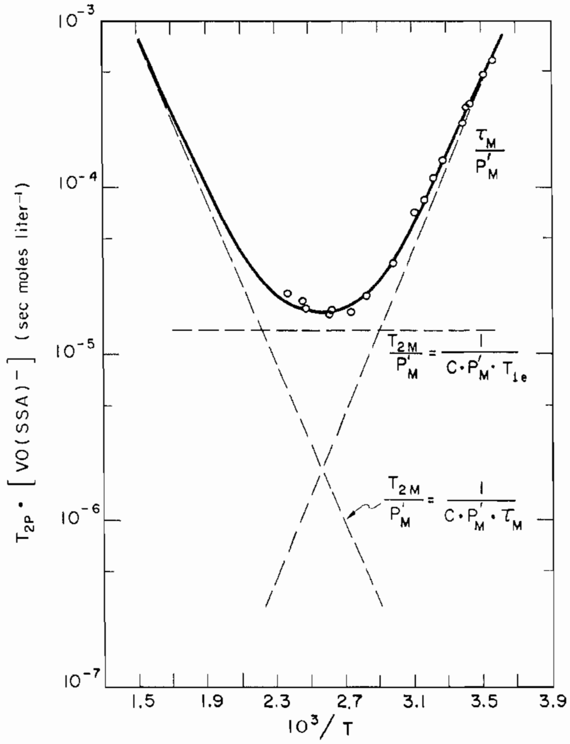

Figure 8.—Dependence on the reciprocal of temperature of log T_{2p} of O^{17} in solutions of $VO(SSA)^-$ with the lines resulting from the curve fitting; $P_M' = P_M/[VO(SSA)^-]$.

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(23) Th. Kaden and S. Fallab, *Chimia*, **20**, 51 (1966).

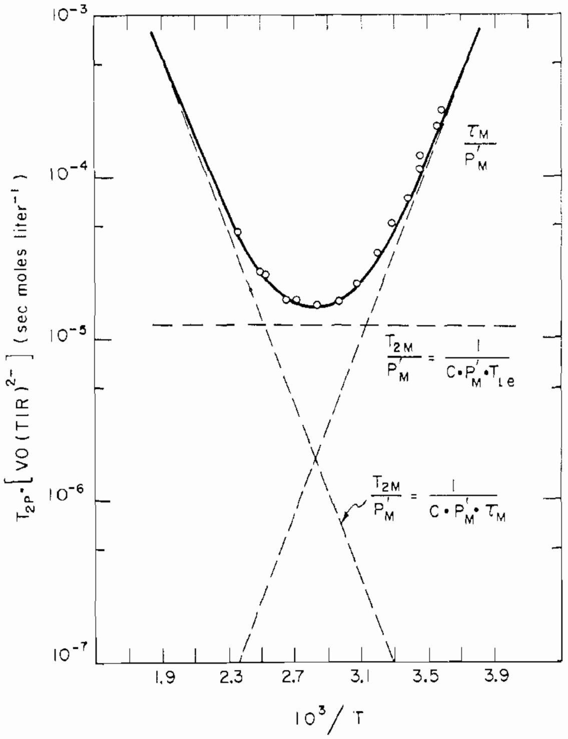

Figure 9.—Dependence on the reciprocal of temperature of log T_{2p} of O^{17} in solutions of $VO(TIR)^{2-}$ with the lines resulting from the curve fitting; $P_M' = P_M/[VO(TIR)^{2-}]$.

Proton Nmr Relaxation Studies.—The transverse proton relaxation was studied in the bulk water of solutions of $VO(EDTA)^{2-}$. At complex concentrations from 0.05 to 0.5 M no appreciable broadening of the resonance could be observed in the temperature range 5–100°.

V. Discussion

The experiments described in section IV have shown that in most of the solutions of vanadyl complexes studied only one of the many possible contributions to the relaxation of the bulk nuclei given in eq 11 is of importance. It was possible to distinguish between the effects on T_{2p} of the O^{17} exchange from the three nonequivalent kinds of positions in the first coordination sphere of V^{4+} (Figure 1) and to study quantitatively the influence on the rate of the water exchange from the equatorial coordination sites of the ligands coordinated to adjoining positions.

Exchange of the Vanadyl Oxygen.—From the results of previous investigations of vanadyl ion, it was to be expected that the vanadyl oxygen would exchange much more slowly than the oxygens of the water molecules in the other coordination sites of V^{4+}.[24] To our knowledge it has not been established that the vanadyl oxygen exchanges in aqueous solutions of vanadyl complexes. The reaction would certainly be too slow to be studied quantitatively by the O^{17} nmr relaxation technique. The upper limit for the rate constant of a possible vanadyl oxygen exchange given in Table II is probably far too high, because one would expect the enthalpy of activation of this reaction to be considerably greater than that used in the calculation of this limit, *i.e.*, $\Delta H^{\ddagger}$ of the water exchange from the equatorial positions.

Water Exchange from the Equatorial Positions.—The water exchange from the equatorial positions seems to be the only reaction which greatly influences the nuclear relaxation in the bulk of the solution. Its rate and its enthalpy of activation are such that all three limiting cases for the dependence on temperature of T_{2p} predicted by eq 3 and 4 can be observed for some of the complexes (Figures 8 and 9). The rate of the water exchange from one of the equatorial coordination sites can be changed by several orders of magnitude through the influence of the ligands coordinated to adjoining equatorial positions (Table II). A comparison of the water-exchange rates from the first coordination spheres of the hydrated VO^{2+} ion and of other hydrated doubly charged 3d metal ions led to the suggestion that the relatively slow exchange found for VO^{2+} is most likely due to large electrostatic contributions to the bonding of the water molecules.[3] The increase of the exchange rate brought about by the various chelating ligands might then be interpreted in terms of a simple electrostatic picture. Each of the ligands studied, *i.e.*, IDA, SSA, and TIR, occupies two equatorial positions of the first coordination sphere with negatively charged groups which might neutralize part of the high positive charge of V^{4+} effective in the bonding of the water molecules. One might even go further and explain the increase of the exchange rates when going from VO(IDA) to $VO(SSA)^-$ and $VO(TIR)^{2-}$ in terms of the increasing number of negatively charged sulfo groups which are not coordinated to the first coordination sphere of the metal ion. As one would expect, the negative charges of the bonding groups of the ligands would then have a much greater influence on the exchange rates than the charges localized on nonbonding groups. This partial neutralization of the high effective charge of V^{4+} through the chelating ligands presumably would also be reflected in the values found for $\Delta H^{\ddagger}$ (Table II) which appear to be somewhat smaller than $\Delta H^{\ddagger}$ of the water exchange from the hydrated VO^{2+} ion. The values of $\Delta S^{\ddagger}$ of the water exchange from the various complexes are close to 0, as is generally found for the elimination of water molecules from the first coordination sphere of metal ions.[1]

The influence of the ligands in adjoining coordination sites on the scalar coupling constant of the nuclei of waters coordinated to a paramagnetic metal ion has been discussed by Horrocks and Hutchison.[25] Following McConnell and Robertson,[26] they distinguished between two contributions to the observed coupling constant, $A = A_c + A_p$, where A_c is due to Fermi contact coupling and A_p to pseudo-contact interactions. From an analysis of the variations of the scalar coupling constant A of the water protons in a series of mixed

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[24] J. Selbin, *Chem. Rev.*, **65**, 153 (1965).

[25] W. D. Horrocks, Jr., and J. R. Hutchison, *J. Chem. Phys.*, **46**, 1703 (1967).

[26] H. M. McConnell and R. E. Robertson, *ibid.*, **29**, 1361 (1958).

Co^{2+} complexes, they concluded that A_c might to a good approximation be constant for all of the complexes. The dependence of A on the ligands in adjoining positions observed in Co^{2+} complexes would therefore arise mainly from changes of the term A_p, which is closely related to the anisotropy Δg of the g tensor; *i.e.*, for a complex with axial symmetry $\Delta g = g_{\perp} - g_{\parallel}$. The data on VO^{2+} complexes (Table II) suggest that A_c of the nuclei of water molecules might in certain cases also be influenced by the ligands in mixed metal ion complexes. The anisotropy of the g tensor was found to be very small for the hydrated vanadyl ion,[17,19] and from estimates for a series of other vanadyl complexes Δg seems to be very little influenced by the ligands in the equatorial positions.[13] It then appears that the observed ligand influence on the O^{17} scalar coupling constant A/h in vanadyl complexes (Table II) is mainly due to changes of the contact interaction A_c.

The dependence on the ligands of the scalar coupling constants of V^{51} [13] and O^{17} of the coordinated waters indicates that, in addition to purely electrostatic effects, the bonding scheme in VO^{2+} complexes is influenced by the ligands in the equatorial positions. The general trend seems to be that the unpaired electron density at the V^{51} nucleus is decreased when VO^{2+} is coordinated to ligands which are known to form strongly "covalent" bonds in their metal ion complexes.[13,16] Since electrostatic interactions are probably important in all of the complexes studied so far, it has not yet been possible to determine how the water-exchange rates are influenced by the ligand effects indicated in the variations of the scalar coupling constants. Quite possibly these effects could cause the differences in the water-exchange rates from VO^{2+}, VO(IDA), VO(SSA)$^-$, and VO(TIR)$^{2-}$, rather than simple electrostatic interactions. This would not be very surprising, since others have shown that the rate of replacement of H_2O in Ni^{2+} complexes is not in all cases increased by the coordination of negatively charged groups to Ni^{2+}, while on the other hand some electrostatically neutral ligands seem to increase considerably the rate of the water replacement.[27]

Rate of Water Exchange from the Axial Position.—At most very small relaxation effects arise from the water exchange involving the axial position of VO^{2+} (Figure 1, II). Since these relaxation effects appear to be T_{2M} controlled even at low temperatures,[3] they could only come from fast exchange of the axial water molecule. We then have that according to the experimental data for hydrated vanadyl ion[4] the rates of the water exchange at 25° from the axial and the equatorial positions must differ by at least a factor of *ca.* 10^6.

Group theoretical considerations[28] show that different wave functions are involved in the bonding of the four equatorial and the axial ligands of the first coordination sphere of VO^{2+}. One would therefore anticipate that the water-exchange rates from these two kinds of coordination sites might be quite different. Furthermore there is some indication of a tendency for VO^{2+} complexes to form pyramidal molecules in which the V^{4+} would not be in the plane of the four equatorial ligands (Figure 10A), but rather somewhat above this plane (Figure 10B). X-Ray studies[22] have shown that in the solid state of the 1:2 complex of VO^{2+} with acetylacetonate, the vanadyl oxygen and the four equatorial positions are at the corners of a tetragonal pyramid with V^{4+} approximately at its center of gravity. Esr studies[29] imply that in solutions of vanadyl acetylacetonate a solvent molecule is coordinated to the axial position with a very short lifetime, which is at 25° only little longer than the electronic relaxation times of VO(acac)$_2$ in these solutions, *i.e.*, 1.0×10^{-8} to 1.0×10^{-9} sec. For steric reasons one would expect only weak coordination to the axial position in a structure of the type in Figure 10B. Therefore such a short lifetime seems comprehensible if one assumes that VO(acac)$_2$ maintains the pyramidal structure in solution. Further evidence for a pyramidal solution structure of vanadyl complexes comes from the O^{17} nmr experiments which appear to show that the tetradentate ligands NTA and PIDA are coordinated to the four equatorial positions of VO^{2+} (Figure 6F). From model considerations such a coordination of NTA and PIDA appears plausible in a pyramidal structure (Figure 10B), but it would for steric reasons be impossible in a planar structure (Figure 10A). In the pyramidal structure (Figure 10B) the V^{4+} would then be five-coordinated in the complexes with the tetradentate ligands, while for all of the other complexes (Figure 5) at most a weak coordination of a sixth group in the axial position of the first coordination sphere appears likely (Figure 11).

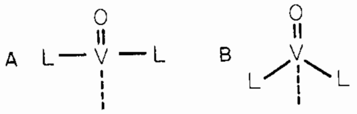

Figure 10.

Axial and Second-Coordination-Sphere Effects.—Two different effects have been found to arise from fast water exchange which could involve either the axial position (Figure 11, L_{ax}) or positions in the second coordination sphere above the triangular faces of the tetragonal pyramid (Figure 11, L_{II}). These are a small chemical shift of the O^{17} resonance in VO^{2+} solutions at room temperature[2] and small contributions to the line width of the O^{17} resonance observed at low temperatures.[3] In this section we discuss some experiments which indicate that two different kinds of interactions between the vanadyl ion and the loosely coordinated water molecules give rise to these two effects on the nuclear resonance in the bulk water.

The chemical shift of the resonance of the coordinated nuclei is given by (8), where A_i includes contributions from scalar and pseudo-scalar coupling between the un-

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(27) D. W. Margerum and H. M. Rosen, *J. Am. Chem. Soc.*, **89**, 1088 (1967).

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

(29) F. A. Walker, R. L. Carlin, and P. H. Rieger, *J. Chem. Phys.*, **45**, 4181 (1966).

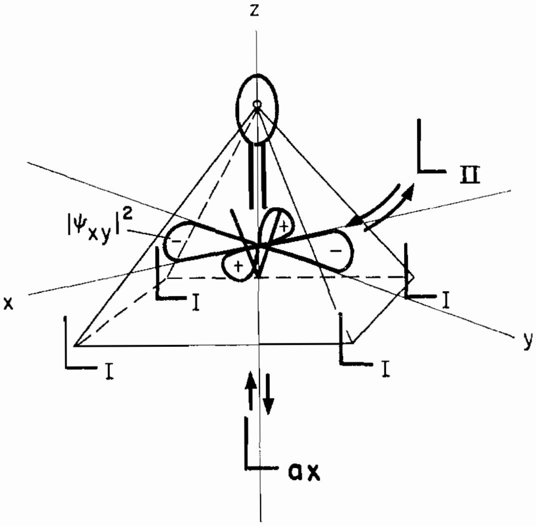

Figure 11.—Pyramidal coordination of the hydrated vanadyl ion. $|\psi_{xy}|^2$ outlines the areas of high unpaired electron density for the ground state of the molecule.

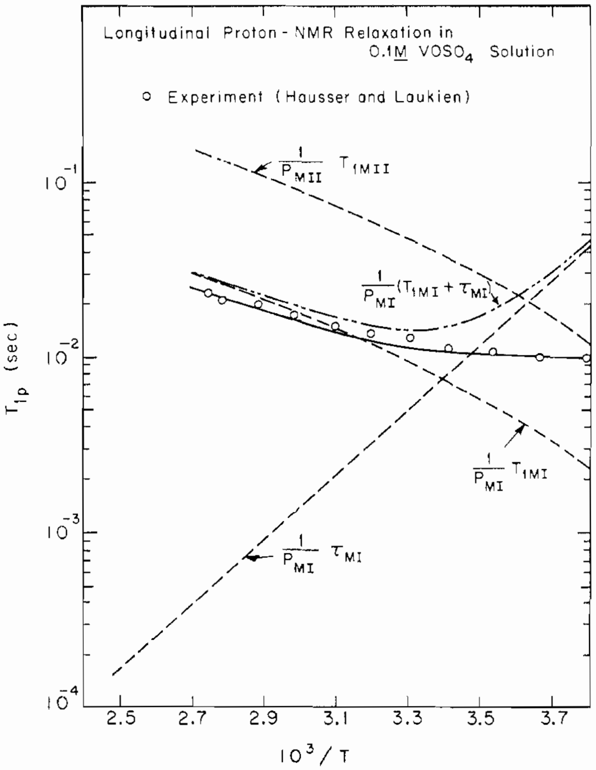

Figure 12.—Dependence on the reciprocal of temperature of log T_{1p} of protons in $VOSO_4$ solutions with the lines resulting from the curve fitting. Subscript I refers to the equatorial coordination sites; subscript II, to the positions which accommodate the labile water molecules. The experimental points which have been obtained from Figure 10 of ref 30 are corrected to 0.1 *M* VO^{2-}.

paired electron and the nuclear spin. Assuming that the shift of the O^{17} resonance in the bulk water (eq 7) is entirely due to fast water exchange from the axial position, Reuben and Fiat[2] found $A/h = 2.06 \times 10^6$ cps for O^{17} of the axial water. Alternatively, if one assumes that the chemical shift arises entirely from four second-coordination-sphere waters residing on the faces of the tetragonal pyramid (Figure 11), $A/h = 5.2 \times 10^5$ cps for O^{17} of these waters.

The enhanced nuclear relaxation could arise from dipolar coupling (eq 5) and quadrupolar coupling (eq 6) as well as scalar coupling (eq 4). To distinguish between the three possible relaxation mechanisms, we have studied the data on the proton nuclear relaxation in solutions of VO^{2+} ions, which have been reported by Hausser and Laukien,[30] and by Mazitov and Rivkind.[4] Mazitov and Rivkind's interpretation, which was unknown to us at the time we treated Hausser and Laukien's data,[5] is based on the same concepts as ours, although it is less detailed. Hausser and Laukien's data are given in Figures 12 and 13, together with our reinterpretation. In Figure 12, log T_{1p} is plotted *vs.* $1/T$. Only dipolar interactions are important for the enhancement of the longitudinal relaxation of the coordinated nuclei.[31] At high temperatures the resulting T_{1MI}, which is the longitudinal relaxation time of the protons of a water molecule coordinated to a position of type I, is long compared to τ_{MI}, but τ_{MI}, which was obtained from Figure 13, increases rapidly on lowering the temperature and controls the relaxation effects arising from exchange from the equatorial positions below *ca.* 25° (eq 3). Additional relaxation effects (T_{1II}/P_{MII}), which must come from fast water exchange from other positions, become important at lower temperatures. The temperature dependence of log T_{2p} (Figure 13) shows the same characteristic features as a similar plot of the O^{17} data.[3] The relaxation of the nuclei in the equatorial positions is due essentially entirely to scalar coupling (T_{2MIsc}/P_{MI}). At high and intermediate temperatures, T_{2p} is controlled by T_{2MI} and τ_{MI} (eq 3), while the relaxation due to the exchange of the labile waters in other positions (T_{2MII}/P_{MII}) becomes dominant below *ca.* 35°. The solid curves in Figures 12 and 13 correspond to the appropriate combinations (eq 2 and 3) of the individual contributions to T_{1p} and T_{2p} shown in the figures.

Protons have no quadrupole moment, and the longitudinal nuclear relaxation time T_{1p} in solutions of VO^{2+} is essentially unaffected by scalar coupling interactions (except for extremely short correlation times and large scalar coupling constants).[31] Therefore the contributions T_{1MI}/P_{MI}) and T_{1MII}/P_{MII} in Figure 12 must come from dipole–dipole coupling with the protons of the coordinated waters. From the curve-fitting process in Figure 13, it is seen that T_{2MII}/P_{MII} is to a good approximation equal to T_{1MII}/P_{MII}. This indicates that dipole–dipole coupling is also responsible for the transverse proton relaxation in the labile water molecules.

If we assume that the labile protons are parts of rapidly exchanging water molecules, we can use the proton data to help interpret the O^{17} data. The proton relaxation in environment II is related to the corresponding oxygen-17 relaxation in that dipole–dipole coupling will be present in both and the rotational and chemical exchange correlation times are presumably

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

(31) See ref 8, pp 309–311.

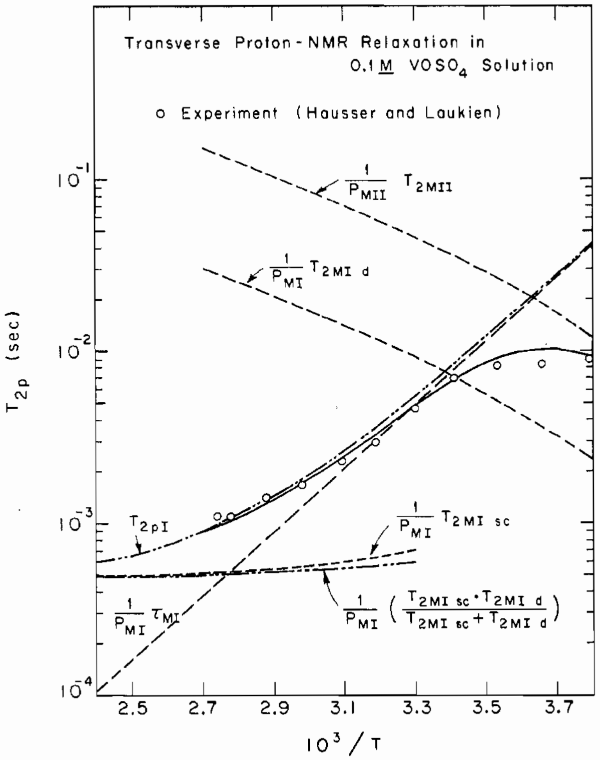

Figure 13.—Dependence on the reciprocal of temperature of log T_{2p} of protons in $VOSO_4$ solutions with the lines resulting from the curve fitting. Subscript I refers to the equatorial coordination sites, II to the positions which accommodate the labile water molecules, sc to scalar coupling, and d to dipolar coupling. The experimental points have been obtained from Figure 10 of ref 30 and are corrected to 0.1 M VO^{2+}. $T_{2MId}/P_{MI} = T_{1MI}/P_{MI}$ has been taken from Figure 12.

the same. The proton T_{1pII} data of Figure 12 were therefore used to estimate the dipole–dipole contribution to T_{2pII} of the oxygen-17 of aqueous vanadyl ion (eq 5).

The coordinates of the oxygens and protons of the water molecules were calculated from the vanadyl acetylacetonate structure parameters[22] assuming the equatorial water oxygens occupy the average positions of the acetylacetonate oxygens and the axial and second-coordination-sphere waters approach their neighboring oxygens to within the van der Waals distance of 2.80 Å. There are two serious sources of uncertainty: (a) the relative distances from the nuclei to the vanadium (d_i in eq 5 are not known precisely, and (b) it is a poor approximation in eq 5 to represent the unpaired electron by a point dipole at the vanadium nucleus. Using 2.61 and 3.14 Å for the vanadium–oxygen distances of the axial and second-coordination-sphere waters, respectively, and 3.31 and 3.83 Å for the vanadium–proton distances of the axial and second-coordination-sphere waters, respectively, one finds $1/T_{2pII}$ of oxygen-17 to be roughly half dipole–dipole relaxation arising from the axial and second-coordination-sphere waters. It should be noted that this calculation can be made without precise knowledge of the correlation times.

There remain the scalar and quadrupole couplings. The former could come from either the axial water oxygen or the four second-coordination-sphere water oxygens. If the observed scalar coupling is due solely to the axial water, the lifetime for chemical exchange of this water has to be less than 3×10^{-11} sec in order to give rise to no more than half of the observed $1/T_{2pII}$. Such a lifetime seems extremely short for the model chosen, in that the water oxygen approaches the vanadium to within 2.6 Å. Therefore it seems more likely that the scalar coupling is to be attributed primarily to the four second-coordination-sphere waters. Since the unpaired electron of the hydrated VO^{2+} ion is believed to be mainly in the d_{xy} atomic orbital[28] which lies above the plane of the first-coordination-sphere waters (Figure 11), it appears plausible that the four second-coordination-sphere waters on the faces of the tetragonal pyramid could have stronger scalar coupling than the axial water. This origin for the observed paramagnetic shift seems not impossible since scalar interactions of the same kind have been reported for O^{17} in the second-coordination-sphere waters of chromic ion.[32] Because similar electrons are involved (d_{xy} for VO^{2+} and d_{xy}, d_{xz}, and d_{yz} for Cr^{3+}), one might expect similar effects on the O^{17} resonance of water molecules residing on the faces of a pyramid formed by $VO(H_2O)_4{}^{2+}$ and on the faces of an octahedron formed by $Cr(H_2O)_6{}^{3+}$. Again, attributing at most half of $1/T_{2pII}$ of O^{17} to scalar coupling relaxation of the second-coordination-sphere waters sets an upper limit for their chemical exchange lifetime of 1.0×10^{-10} sec.

The quadrupole coupling components of O^{17} in the water molecule can be obtained from the data of Stevenson and Townes[33] for HDO^{17}. Assuming the correlation time is the same as for dipole–dipole coupling, the contribution of quadrupole coupling to the oxygen-17 relaxation should be severalfold that from dipole–dipole coupling—a value which is impossibly large. As will be discussed elsewhere, it seems likely that the quadrupole coupling is reduced by fast rotation of the water molecule around its twofold axis, and such an assumption removes the discrepancy.

The above model for the T_{2pII} relaxation of oxygen-17 on vanadyl ion can be fitted by a variety of combinations of correlation times. If one adopts the rotational lifetime for vanadyl ion found by McCain and Myers[17] by esr studies and corrects it to 25° ($\tau_r = 3.3 \times 10^{-11}$ sec), the exchange lifetime for the second-coordination-sphere waters is *ca.* 3×10^{-11} sec. In the calculation the exchange lifetime for the axial water was assumed to be long compared to τ_r. The scalar coupling from the second-coordination-sphere waters is roughly half the total quadrupole relaxation, which in turn is approximately equal to the total dipolar contribution.

The interpretation is not unique, but appears to be the most plausible one in the light of the present evidence. In any event, it is likely that the low-temperature transverse relaxation of oxygen-17 in a solution of vanadyl ion arises from two kinds of loosely bound

(32) M. Alei, Jr., *Inorg. Chem.*, **3**, 44 (1964).

(33) M. J. Stevenson and C. H. Townes, *Phys. Rev.*, **107**, 635 (1957).

water, *i.e.*, the axial water and water found in a second coordination sphere consisting of four positions on the faces of the pyramidal structure of the hydrated vanadyl ion (Figure 11). Furthermore there is evidence that $1/T_{2pII}$ contains appreciable contributions from dipole–dipole, scalar, and quadrupole coupling.

It would have been nice if the two kinds of loosely coordinated waters could have been studied separately in various chelate complexes, *e.g.*, by comparing the data on VO(NTA)$^-$ and VO(PIDA), where only the loose coordination on the faces of the pyramid could possibly be of importance (Figure 6F), with those on VO(TIR)$_2{}^{6-}$ and VO(SSA)$_2{}^{4-}$, where one would expect to observe the effects of both kinds of labile waters (Figure 5B). Since we are looking for extremely small effects on the nuclear resonance, such experiments have to be done with concentrated solutions of the vanadyl complexes, which seem not to be stable over an extended period of time. Furthermore the viscosity in these concentrated solutions is greatly enhanced compared to that of pure water. Therefore it seems beyond the limits of the method to measure the small enhancement of the relaxation of O^{17} which might arise from a possible exchange of labile waters in solutions of the above-mentioned vanadyl complexes. The small effects shown in Figure 4 for VO(NTA)$^-$, VO(EDTA^{2-}, and VO(SSA)$_2{}^{4-}$ are at about the limit of the experimental accuracy and cannot be taken to establish axial or second-coordination-sphere relaxation. Such relaxation may be appreciably diminished in these complexes through an increase in the rate of water exchange.

Chemical shift measurements appeared to give more reliable data. No measurable shift was observed in the solutions of complexes of the types in Figures 5B and 6F. This indicates that the hydration in the second coordination sphere of these complexes differs appreciably from that in the second coordination sphere of the hydrated vanadyl ion. It therefore appears rather unlikely that one might be able to deduce more information about the coordination of the labile waters in the hydrated vanadyl ion from further studies of vanadyl chelate complexes.

Proton Exchange from the Equatorial Positions.—From the curve-fitting process in Figure 13 we find for τ_{MI} at 25° a value of $n \times 1.15 \times 10^{-5}$ sec, where n is the number of water molecules coordinated to positions of type I. Since the proton exchange from anyone of the coordination sites cannot be slower than the corresponding water exchange, we can immediately exclude the possibility that τ_{MI} in Figure 13 corresponds to exchange from the axial position or from the second coordination sphere. Experiments with solutions of VO(EDTA)$^{2-}$ showed that the transverse proton nuclear relaxation in the bulk water is not affected by the presence of this complex. This is consistent with the assumption that a possible protonation of the vanadyl oxygen is not an important relaxation mechanism in nonacidified solutions. It follows that τ_{MI} in Figure 13 corresponds to the protons of the equatorial waters, as has been anticipated previously,[4] and the proton exchange from these positions can be characterized by $k(25°) = 2.2 \times 10^4$ sec^{-1}, $\Delta H^{\ddagger} = 7.8$ kcal mol^{-1}, $\Delta S^{\ddagger} = -13$ eu, and $A/h = 1.6 \times 10^6$ cps. As was pointed out previously,[3,34] these values clearly indicate that the proton exchange from the equatorial positions is not controlled by the rate of the water exchange (Table II) but by a hydrolysis mechanism.

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Synthesis and Resolution of Heterochelate Metal Complexes of Chromium(III) and Cobalt(III) with the Ligands 2,2′-Bipyridine, 1,10-Phenanthroline, and Oxalate Ion

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New heterochelate complex cations Cr(ox)(bipy)$_2{}^+$, Cr(ox)(phen)$_2{}^+$, Co(ox)(bipy)$_2{}^+$, and Co(ox)(phen)$_2{}^+$ (ox = oxalate ion, bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline) have been prepared as their chloride, perchlorate, or iodide salts and resolved by means of optically active Cr(ox)$_2$phen$^-$. The anionic complexes Co(ox)$_2$bipy$^-$ and Co(ox)$_2$phen$^-$ have also been obtained in combination with either Ba^{2+} or Co(ox)(phen)$_2{}^+$, respectively. All of the optically active cations have been found to racemize in solution and in addition the cobalt(III) complexes were markedly photosensitive.

Introduction

Systematic changes in the nature of the ligands together with changes in the over-all charge of a complex are pertinent in many studies of coordination compounds. The present work was undertaken to provide an interrelated series of optically active chromium(III) and cobalt(III) complexes with the ligands 2,2′-bipyr-

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