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The Electron Spin Resonance of Binuclear Vanadyl Tartrates

Akinori Hasegawa, Yoshio Yamada, and Masaji Miura
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima

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The ESR spectra of aqueous solutions of binuclear vanadyl tartrates remarkably varied with their pH values. This variation was found to be directly correlated with the change in the form of the carboxyl group, *i.e.* whether it was dissociated or acidic. Thus, the frozen solution spectra were observed in water-ethylene glycol at 77°K and analyzed in terms of several magnetic parameters containing the parameter of magnetic dipolar interaction, *D*. From these *D* values, the intramolecular V···V distances were estimated to be *ca.* 4.2, 5.2, and 6.5Å in the solutions at pH 9, 4.8, and 2.8 respectively. Such a remarkable change in the V···V distances as interpreted to be caused by the dissociation of the coordinate bonds between the vanadium atom and the carboxyl oxygen atom and the change in the molecular structure of the tartrates, brought about the change in the form of the carboxyl groups.

The aqueous solutions of vanadyl tartrates give ESR spectra characteristic of a dimeric structure with two unpaired electrons coupled with a spin-exchange interaction.[1] Although the dimeric structure in an aqueous solution had been doubted because of the specific ESR linewidth variation,[2] it has been confirmed by the observations of pairs of satellite lines caused by singlet-triplet transitions, which were allowed because of the mixing of the singlet and the triplet levels.[3–5]

The ESR spectrum of the aqueous vanadyl tartrate solution changes according to the change in the pH value. As to the aqueous solution of vanadyl *dl*-tartrate, fifteen triplet lines were observed, but no satellite lines appeared above pH 6.[1] Two kinds of considerably complicated triplet-state spectra accompanied by satellite lines were observed in the pH ranges from 5 to 3 and from 3 to 2. The values of the spin exchange interaction, *J*, have been determined to be 1.071×10^{-1} and 5.62×10^{-2} cm^{-1} on the basis of the analysis of the satellite lines for the dimeric species in the pH 3—5 and 2—3 ranges respectively.[4,5] In these two pH ranges, no difference was observed between the aqueous-solution spectrum of vanadyl *dl*-tartrate and that of vanadyl *dd*-tartrate, but a remarkable difference appeared between them above pH 6.[3]

Frozen-solution spectra of vanadyl *dl*- and *dd*-tartrates were observed at pH 7 in a water-ethylene glycol mixture.[6] Their spectra consist of the lines attributable to $\Delta M_s=\pm1$ transitions at $g\approx2$ and to $\Delta M_s=\pm2$ transitions at $g\approx4$, and they are interpreted in terms of the parameter of the magnetic dipolar interaction, *D*, and the anisotropies of the *g* value and the hyperfine coupling constant.

However, no interpretation has been given to the structural change of the complex caused by the change in pH. In the present paper, therefore, we attempted to investigate the structural change in these dimeric species by means of ESR, IR, pH titration, and a molecular model.

Experimental

Vanadyl *dl*-tartrate ($Na_4[(VO)_2(d\text{-tart}),(l\text{-tart})]\cdot11H_2O$) and vanadyl *dd*-tartrate ($Na_4[(VO)_2(d\text{-tart})_2]\cdot6H_2O$) were prepared by the method of Tapscott and Belford.[1] pH titrations of the aqueous solutions of these vanadyl tartrates, the pH value of which had been previously adjusted to 2.7 with HCl, were carried out by addition of the aqueous solution of NaOH. The ESR spectra of the solutions of vanadyl *dl*- and *dd*-tartrates at different pH values were measured in the frozen and liquid solution states; the frozen spectra

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[1] R. E. Tapscott and R. L. Belford, *Inorg. Chem.*, **6**, 735 (1967).

[2] R. H. Dunhill and T. D. Smith, *J. Chem. Soc., A*, **1968**, 2189.

[3] R. H. Dunhill and M. C. R. Symons, *Mol. Phys.*, **15**, 105 (1968).

[4] P. G. James and G. R. Luckhurst, *ibid.*, **18**, 141 (1970).

[5] L. C. Dickinson, R. H. Dunhill, and M. C. R. Symons, *J. Chem. Soc., A*, **1970**, 922.

[6] R. L. Belford, N. D. Chasteen, H. So, and R. E. Tapscott, *J. Amer. Chem. Soc.*, **91**, 4675 (1969).

were obtained at 77°K in water-ethylene glycol (1 : 1 in volume), and the aqueous solution spectra, at room temperature. The specimens submitted to IR measurements were prepared by freeze-drying the aqueous solutions, the pH values of which had been adjusted to 9, 4.8, and 2.8. The ESR spectra were measured by a spectrometer described elsewhere,[7] and the IR spectra, by the KBr disk method, using a Hitachi EPI-G3 IR spectrometer.

Results and Discussion

The ESR spectra of aqueous vanadyl tartrate solutions depend remarkably upon their pH values, as has been pointed out by several authors.[2-5] Thus, pH titrations of the aqueous solutions were carried out; two inflection points appeared at pH 4.8 and 9, in the pH titration curve of vanadyl *dl*-tartrate, as can be seen in Fig. 1. The same result was also obtained in the case of vanadyl *dd*-tartrate. The amount of NaOH consumed between these two inflection points corresponded to just twice the number of moles of vanadyl tartrate used. All of the four carboxyl groups in a vanadyl tartrate molecule are known to dissociate at pH 9.[1] These facts suggest that, at pH 4.8, two of the carboxyl groups have the acidic form, and the other two have the dissociated form. In the same manner, all of the groups are suggested to have the acidic form at pH 2.8. The change in the ESR spectrum of the aqueous solution was found to be closely correlated with the change in the form of the carboxyl group; different kinds of spectra were observed at pH 2.8, 4.8, and 9, and each of them turned to another upon the pH change in exactly the same manner as was to be expected from the pH titration curve.

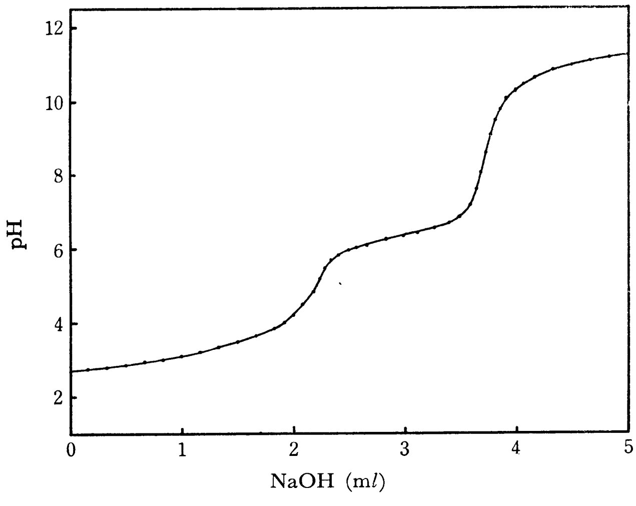

Fig. 1. pH titration curve of 0.085 g vanadyl *dl*-tartrate with aqueous solution of 0.15 N NaOH.

The ESR spectra of the aqueous solutions at pH 2.8, 4.8, and 9 have been well investigated by several authors.[2-5] However, the ESR spectra of the frozen solutions have been studied only at pH 7,[6] where most of carboxyl groups take the dissociated form. Thus, the ESR frozen solution spectra of vanadyl *dl*- and *dd*-tartrates were observed in water-ethylene glycol at pH 9, 4.8, and 2.8; the results are shown in Figs. 2(a)—(d). A difference between the ESR spectrum of vanadyl *dl*-tartrate and that of vanadyl *dd*-tartrate was found in the frozen solution state only at pH 9, as in the case of the aqueous solution state. The spectrum at pH 2.8 is complicated by the presence of hyperfine lines both from the complex corresponding to that obtained at pH 4.8 and from a complex containing a single vanadium nucleus,

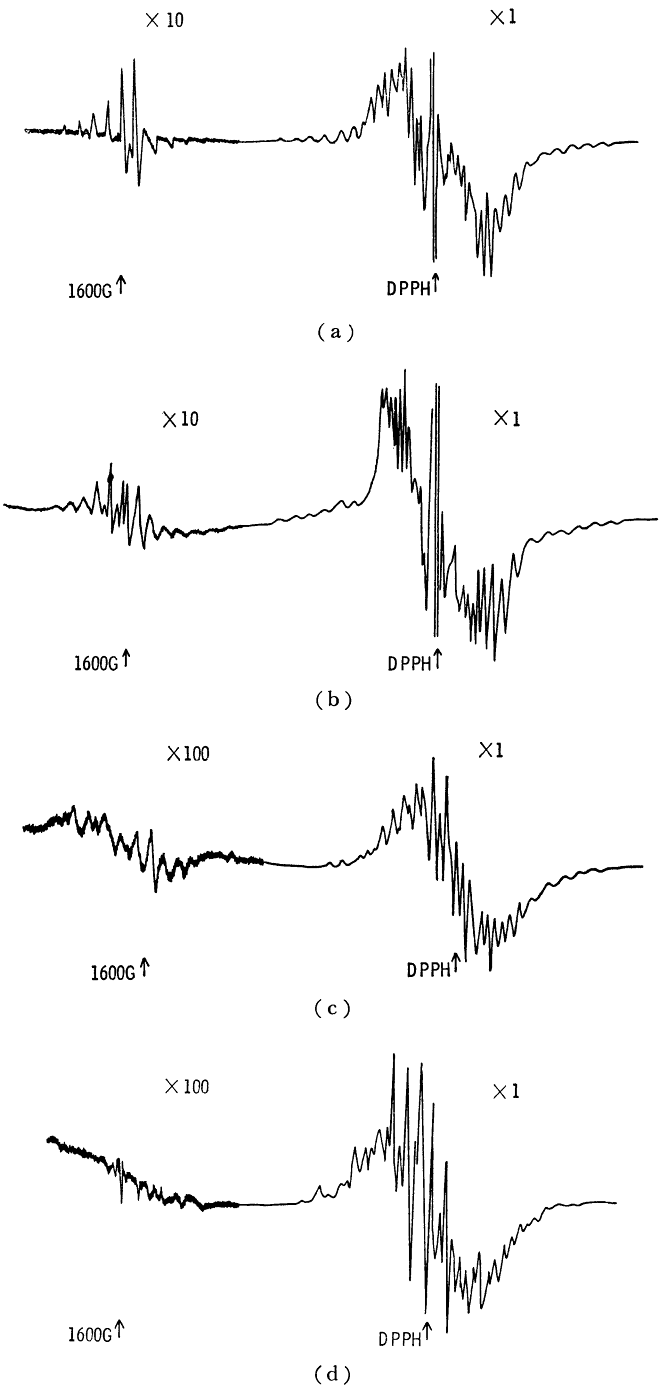

Fig. 2. ESR spectra of frozen solution of vanadyl *dl*-tartrate at (a) pH 9, (c) pH 4.8, and (d) pH 2.8 and of vanadyl *dd*-tartrate at (b) pH 9. Spectra of vanadyl *dd*-tartrate at lower pH values are respectively the same as those of vanadyl *dl*-tartrate.

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[7] A. Hasegawa and M. Miura, This Bulletin, **40**, 2553 (1967).

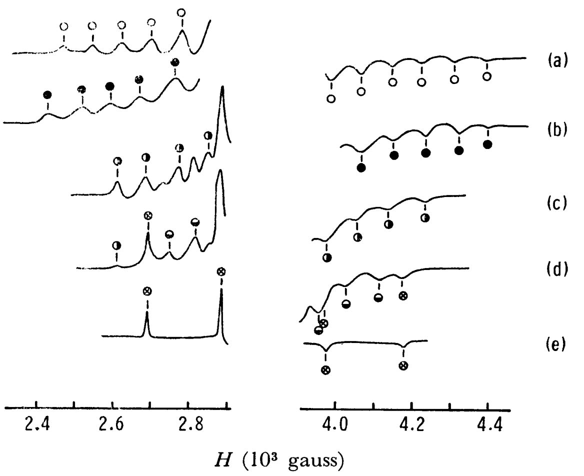

Fig. 3. Expanded view of ESR spectral lines near the both sides of the $\Delta M_s = \pm 1$ transitions of vanadyl *dl*-tartrate at (a) pH 9, (c) pH 4.8, (d) pH 2.8, and (e) pH 1.5 and of vanadyl *dd*-tartrate at (b) pH 9. Letters, (a)~(d), in the following figures have the same meaning as those in this figure. Several symbols in this figure are used to show the assignment of the spectral lines.

which is produced at pH values lower than 2. The ESR spectrum of the frozen solution at pH 1.5 was, therefore, measured in order to subtract it from the spectrum at pH 2.8. Except for the spectrum at pH 1.5, each of these spectra consists of the transition lines of $\Delta M_s = \pm 1$ at $g \approx 2$ and of $\Delta M_s = \pm 2$ at $g \approx 4$. If it is assumed that the ligand field around the vanadium atoms is axially symmetrical and that the two V=O axes in a complex molecule are parallel to each other, these ESR spectra of binuclear complexes can be described by the following spin Hamiltonian:[8,9]

$$\mathscr{H} = \sum_{i=1}^{2}\beta\{g_{\parallel}\boldsymbol{H}_z\cdot\boldsymbol{S}_z^{(i)} + g_{\perp}(\boldsymbol{H}_x\cdot\boldsymbol{S}_x^{(i)} + \boldsymbol{H}_y\cdot\boldsymbol{S}_y^{(i)})\}$$
$$+ \sum_{i=1}^{2}\{A_{\parallel}\boldsymbol{I}_z^{(i)}\cdot\boldsymbol{S}_z^{(i)} + A_{\perp}(\boldsymbol{I}_x^{(i)}\cdot\boldsymbol{S}_x^{(i)} + \boldsymbol{I}_y^{(i)}\cdot\boldsymbol{S}_y^{(i)})\}$$
$$+ J\boldsymbol{S}^{(1)}\cdot\boldsymbol{S}^{(2)} + \frac{2}{3}D\Big\{\boldsymbol{S}_{z'}^{(1)}\cdot\boldsymbol{S}_{z'}^{(2)} - \frac{1}{4}(\boldsymbol{S}_{+}^{(1)}\cdot\boldsymbol{S}_{-}^{(2)}$$
$$+ \boldsymbol{S}_{-}^{(1)}\cdot\boldsymbol{S}_{+}^{(2)})\Big\} \qquad (1)$$

where the distinction between z and z' originates from the fact that the V=O axis is not necessarily parallel to the V···V axis and where D is a parameter of the magnetic dipolar interaction.

The resonance condition of the $\Delta M_s = \pm 1$ transition between triplet states is given approximately from this spin Hamiltonian, by modifying the relation derived by Glarum and Marshall[9] with anisotropies of the g value and the hyperfine coupling:[8]

$$h\nu = g\beta H + K(M^{(1)} + M^{(2)}) \pm \frac{1}{2}\Big(J + \frac{2}{3}\gamma D\Big)$$
$$\mp \Big\{K^2(\Delta M)^2 + \frac{1}{4}\Big(2J - \frac{2}{3}\gamma D\Big)^2\Big\}^{1/2} \qquad (2)$$

where $g^2 = g_{\parallel}^2\cos^2\theta + g_{\perp}^2\sin^2\theta$ (3)

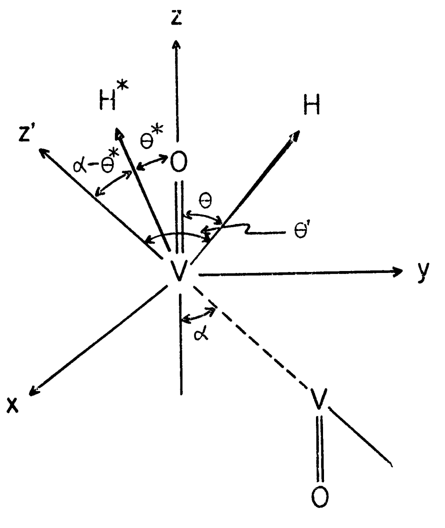

Fig. 1. The relation between two molecular axes and two orientations of the external magnetic field: H is the external magnetic field in a general orientation satisfying Eqs. (2)~(6), and H^*, in the plane containing z and z' axes, is that in the specific orientation giving the maximum resultant splitting satisfying Eqs. (9), (10), and (12).

$$gK = \sqrt{\frac{1}{4}A_{\parallel}^2 g_{\parallel}^2\cos^2\theta + \frac{1}{4}A_{\perp}^2 g_{\perp}^2\sin^2\theta} \qquad (4)$$

$$\gamma = 3\Big(\frac{g_{\parallel}^2\cos^2\alpha + g_{\perp}^2\sin^2\alpha}{g^2}\Big)\cos^2\theta' - 1 \qquad (5)$$

$$\Delta M = |M^{(1)} - M^{(2)}|, \qquad (6)$$

where the angles, θ, θ', and α are defined as is shown in Fig. 4. The external magnetic field is, therefore, oriented at the angle of θ to the symmetrical axis with regard to the g value and the hyperfine coupling, *i.e.*, the V=O direction, and at the angle of θ' to the direction at which the maximum magnetic dipolar splitting can be expected, *i.e.*, the V···V direction.

If the assumption,

$$K^2(\Delta M)^2 \ll \Big(J - \frac{1}{3}\gamma D\Big)^2 \qquad (7)$$

is satisfied, Eq. (2) can be simplified as:

$$h\nu = g\beta H + K(M^{(1)} + M^{(2)}) + \gamma D\Big(M_s - \frac{1}{2}\Big) \qquad (8)$$

where $M_s = 1$ or 0. The assumption is satisfied for the frozen solution spectrum at pH 9 because of a large value of J; the J value can be deduced to be about $2\times10^{-1}\,\mathrm{cm}^{-1}$ from the analysis of the linewidth of the triplet spectrum, though the value has not been determined explicitly as yet. The application of Eq. (8) to the spectra at lower pH values is, however, subject to restriction because the J value decreases with the decrease in pH value;[4,5] the derivation of Eq. (8) from Eq. (2) can not be allowed for the transitions corresponding to the large value of $(\Delta M)^2$. Fortunately, even for the spectrum at pH 2.8, the resonance lines due to small values of ΔM, which can be observed near both sides of the $\Delta M_s = \pm 1$ transition spectrum, satisfy the condition of Eq. (7), and the deviation arising from Eq. (8) does not exceed the limits of experimental error. The outermost lines were assigned to the lines of $M^{(1)} = M^{(2)} = \pm 7/2$ with

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[8] B. Bleaney, *Phil. Mag.*, **42**, 441(1951).

[9] S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, **47**, 1374 (1967).

TABLE 1. APPARENT MAGNETIC PARAMETERS

Complex	pH	$\frac{1}{2}A_{\parallel}{}^{*\,\mathrm{a,b)}}$	$D^{*\,\mathrm{a)}}$	$g_{\parallel}{}^{*\,\mathrm{b)}}$	$\frac{1}{2}a_0{}^{\mathrm{a,c)}}$
Vanadyl *dl*-tartrate	9	72.3	334	1.953	38.3
Vanadyl *dd*-tartrate	9	73.2	335	1.950	40.8
Vanadyl *dl*-tartrate	4.8	74.5	180	1.944	47.6
Vanadyl *dl*-tartrate	2.8	70.1	88	1.941	50.6

a) in unit of 10^{-4} cm^{-1}
b) The second order perturbation is involved in the estimation of these values.
c) These values are not apparent but determined ones.

TABLE 2. EVALUATED VALUES FOR VANADYL *dl*-TARTRATE

Complex	pH	$\frac{1}{2}A_{\parallel}{}^{\mathrm{a)}}$	$\frac{1}{2}A_{\perp}{}^{\mathrm{a)}}$	$D^{\mathrm{a)}}$	$R^{\mathrm{b)}}$
Vanadyl *dl*-tartrate	9	76.2	19.3	348	4.16

a) in unit of of 10^{-4} cm^{-1}
b) in unit of Å

a maximum resultant splitting due to hyperfine and magnetic dipolar interaction, where the anisotropy of the g value is assumed to be negligible as compared with the anisotropy of the hyperfine coupling constant and with the angular dependency of the magnetic dipolar splitting. The external magnetic field which gives the outermost lines is defined as being oriented at the angles of θ^* to the direction of V=O and α–θ^* to the direction of the V···V direction, in the plane containing V=O and V···V directions, as can be seen in Fig. 4. The hyperfine coupling constant and magnetic dipolar splitting at this magnetic field direction can be determined approximately from Eq. (8) and from the spectral lines near both the sides of the $\Delta M_s = \pm 1$ transition spectrum, which are shown, with their assignments, in Fig. 3. They are, therefore, shown, neglecting the anisotropy of the g value, by:

$$\frac{1}{2}A_{\parallel}{}^* = \frac{1}{2}\sqrt{A_{\parallel}{}^2\cos^2\theta^* + A_{\perp}{}^2\sin^2\theta^*} \tag{9}$$

and

$$2D^* = D\{3\cos^2(\theta^*-\alpha)\} - 1\} \tag{10}$$

Hereupon, the isotropic coupling constant, $a_0/2$, obtained from the liquid-solution spectrum is connected with the values of $A_{\parallel}$ and $A_{\perp}$ by a well-known relation:

$$\frac{1}{2}a_0 = \frac{1}{3}\left(\frac{1}{2}A_{\parallel} + A_{\perp}\right) \tag{11}$$

On the other hand, the θ^* angle must satisfy the following condition, as can be expected from the maximum resultant splitting:

$$\frac{\partial}{\partial\theta^*}\left[14\times\frac{1}{2}\sqrt{A_{\parallel}{}^2\cos^2\theta^* + A_{\perp}{}^2\sin^2\theta^*} + D\{3\cos^2(\theta^*-\alpha)-1\}\right] = 0 \tag{12}$$

As the values of $A_{\parallel}{}^*/2$ and $2D^*$ can be evaluated from the frozen-solution spectrum, and the value of $a_0/2$, from the liquid-solution spectrum, the θ^* value satisfying Eqs. (9)—(12) can be determined unequivocally provided that the value of α is assumed. Thus, the relation between α and θ^* was calculated from the parameters given in Table 1 by using a computer; the results are shown in Fig. 5. From the value of θ^*,

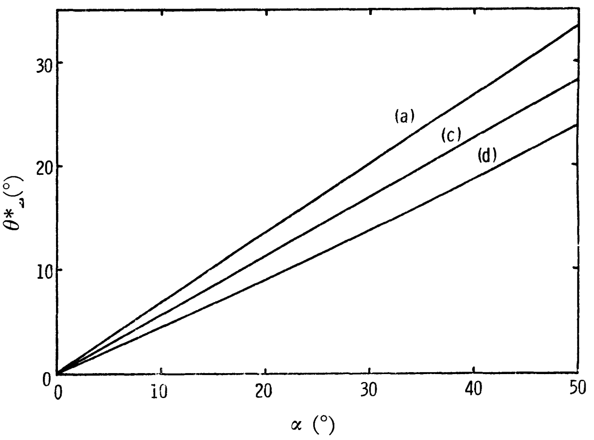

Fig. 5. The relation between α and θ^* for vanadyl *dl*-tartrate. The line for (b) is located slightly higher than that of (a), but almost superimposed with (a) in this figure.

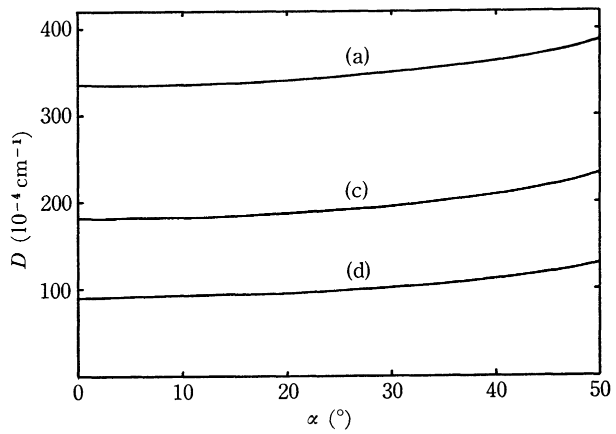

Fig. 6. The relation between α and D for vanadyl *dl*-tartrate. The line for (b) is also located slighly higher than that of (a), but almost superimposed with (a).

in turn, the values of $A_{\parallel}$, $A_{\perp}$, and D were obtained for each value of α. The relation between D and α is shown in Fig. 6.

According to the results of X-ray diffraction,[10] the value of α is 28° for the crystal of vanadyl *dl*-tartrate obtained from the solution at pH 8. When this value is adopted for the complex in the solution of vanadyl *dl*-tartrate at pH 9, the value of θ^* is determined to be 18°58′ from Fig. 5. Thus, the values of $A_{\parallel}/2$, $A_{\perp}/2$, and D determined on the basis of $\alpha=28°$ are given in Table 2. The values of α for other complexes are not yet known but they may be deduced to be not so large.

The intensity ratio of the transition of $\Delta M_s=\pm 2$ to that of $\Delta M_s=\pm 1$ is proportional to the square of the D value:[11]

$$I_{\Delta M_s=\pm 2}/I_{\Delta M_s=\pm 1} = \frac{1}{8}\left(\frac{D\sin 2\theta'}{H}\right)^2 \tag{15}$$

It can, therefore, be checked in terms of this relation whether or not the evaluated D value is reasonable. As the intensities of all the $\Delta M_s=\pm 1$ transitions are roughly equal in Figs. 2 (a)—(c), the intensities of the $\Delta M_s=\pm 2$ transition in these figures may be supposed to be proportional to the square of each D value. The change in the D value evaluated above with the decrease in pH value reasonably explains the observed change in the intensity of the $\Delta M_s=\pm 2$ transition, though the D value is an approximate one because of the uncertainty of the α value.

The splitting due to the magnetic dipolar interaction is also approximately shown by:[12]

$$D = \frac{3}{4}g^2\beta^2\frac{\langle 1-3\cos^2\theta'\rangle_{\max}}{R^3} \tag{16}$$

where R is the V···V distance, the θ', the angle between V···V and the magnetic field directions. The value of D (in cm^{-1}) is, therefore, correlated with the V···V distance, R (in Å), by:[6]

$$D = \frac{0.650}{R^3}g^2 \tag{17}$$

When the $D=348\times 10^{-4}$ cm^{-1} obtained for $\alpha=28°$ was substituted into Eq. (17), the intramolecular V···V distance for the vanadyl *dl*-tartrate at pH 9 was evaluated to be 4.16 Å, where the g value was assumed to be 1.953 (Table 1) as an approximation. The estimated value is very close to the V···V distance determined by means of X-ray diffraction-4.08 Å.[6,10] Although some question is involved in the comparison between the V···V distance in the solution state and that in the crystalline state, the comparison may be significant because a complex molecule is surrounded by eleven water molecules even in the crystalline state.[1] Thus the validity of the procedure for the estimation of the magnetic parameter was confirmed. It is also interesting to compare these results with those which were determined by Belford *et al.* directly from the spectrum observed without such a procedure.[6] The latter values are, by nature, in agreement with those in Table 1. The values of $A_{\parallel}$ and D which were obtained through this procedure, and which are given in Table 2, are larger than those obtained directly from the spectrum.

The relation between R and α was obtained from Fig. 6 and Eq. (16) by the use of the g values in Table 1. The relation depends remarkably upon the value of pH, as can be seen in Fig. 7. The intramolecular V···V distance, which is an approximate value because of the undetermined value of α, changes step by step from *ca.* 4.2 through *ca.* 5.2 to *ca.* 6.5 Å, being closely correlated with the decrease in the pH value, that is, with the change in the form of the carboxyl group.

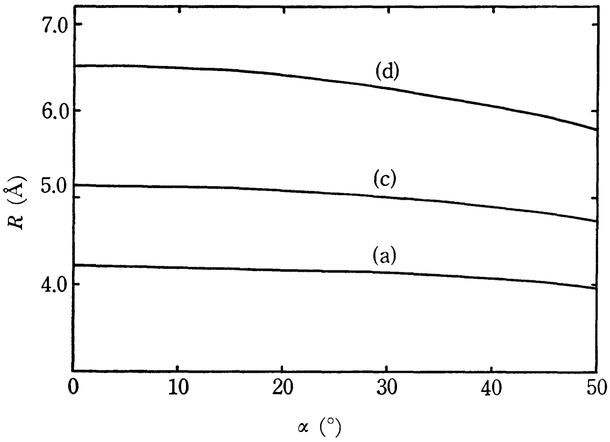

Fig. 7. The relation between α and R for vanadyl *dl*-tartrate. The line for (b) is located a slightly lower than that of (a), but almost superimposed with (a).

When the IR spectra were measured for the complexes in solid forms prepared from solutions of different pH values, the frequency of the absorption due to V=O stretching changed with the change in the pH value; for the vanadyl *dl*-tartrate, 958, 978, and 988 cm^{-1} respectively at pH 9, 4.8, and 2.8, and for vanadyl *dd*-tartrate, 949 cm^{-1} at pH 9, and those at lower pH values were the same as those for vanadyl *dl*-tartrate. Such an increase in the V=O stretching frequency suggests a decrease in the coordination ability of equatorial ligands to the vanadium atom.[13]

It is of great interest to interpret these results in connection with the structural change in these complexes brought about by the change in pH. Such a structural change may be successfully discussed by means of a model of the complex molecule. According to the results of the X-ray diffraction of vanadyl *dl*-tartrate prepared at pH 8,[10] each of two vanadium ions in a molecule of the complex is coordinated with four oxygen atoms, other than the doubly-bonded oxygen atom forming part of the vanadyl ion, two of which are the carboxyl oxygen atom and the alcoholic oxygen atom in a tartrate molecule, and the

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10) R E Tapscott, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, **7**, 356 (1968).

11) Y. Kurita, *Nippon Kagaku Zasshi*, **85**, 833 (1964).

12) K. W. H. Stevens, *Proc. Roy. Soc.* (London), **A214**, 237 (1952).

13) J. Selbin, L. H. Holmes, Jr., and S. P. McGlynn, *Chem. Ind.* (London), **1961**, 746.

other two of which are those in the other tartrate molecule, as can be seen in Fig. 8. The two quadrilaterals, which are made by combining these four oxygen atoms coordinating to a vanadium atom, slide with one another, resulting in the angle of 28° between V=O and V···V directions and in the distance of 4.08 Å between these vanadium atoms.[6] The molecular model also supports such a structure. For vanadyl *dd*-tartrate at pH 9, the molecular model suggests that the V=O direction is almost parallel to the V···V direction that the V···V distance is approximately equal to that for the vanadyl *dl*-tartrate. With the decrease in the pH value, the carboxyl group in tartrate takes an acidic form and the coordination of the oxygen atoms in this group is weakened. The change in V···V distance, 4.2, 5.2, and 6.5 Å, estimated from the ESR spectrum must be interpreted in terms of a drastic change in the molecular structure. However, there is no molecular model which allows such a change in the V···V distance if four oxygen atoms of tartrates are kept coordinating to each vanadium atom.

Finally, the following structural changes may be suggested for the interpretation of the change in the V···V distance with the pH. The coordinate bond between a vanadium atom and an oxygen atom of a carboxyl group breaks down with the change in the form of the carboxyl group from a dissociated to an acidic one, and the water molecules of the solvent, in turn, participate in the coordination with the vanadium atom. At the same time, the bond between the second and the third carbon atoms in the tartrate molecule rotates, and the rotation about the C–O bond, in which the second or the third carbon atom participates, is also allowed. Furthermore, the length of the coordinate bond remaining may also increase. Thus, at pH 4.8, the dissociation of the two coordinate bonds in a vanadyl tartrate binuclear complex brings about the enlargement of the V···V distance to *ca.* 5.2 Å, and at pH 2.8 the following dissociation of the two coordinate bonds to *ca.* 6.5 Å. This separation of 6.5 Å is possible only for the following structure: the two vanadium atoms are coordinated with oxygen atoms bound to the second and the third carbon atoms in tartrates and are extremely remote from one another, two carboxyl groups in each tartrate molecule are projected out and free from the coordination to the vanadium atom, and two hydrogen atoms are bound to carbon atoms orient to the rather inner part, as can be seen in Fig. 9. The value of α is expected to be small for this complex.

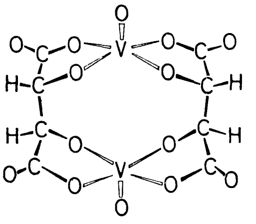

Fig. 8. The structure of the vanadyl *dl*-tartrate in the aqueous solution at pH 9.[1,10]

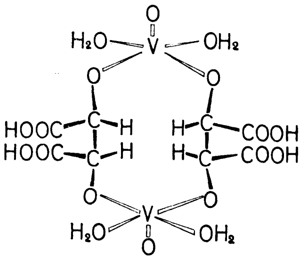

Fig. 9. Proposed structure of the vanadyl *dl*-tartrate in the aqueous solution at pH 2.8.

In such a structure at pH 2.8, two tartrate molecules coordinate to the vanadium atom in the relation of *cis* for vanadyl *dl*-tartrate and of *trans* for vanadyl *dd*-tartrate, as can be expected from the molecular model proposed by Tapscott and Belford.[1,9] If the effect of the difference between the *cis* and *trans* forms on the ESR spectrum is assumed to be weakened by the coordination of the solvent molecules, it can be tentatively accounted for why the ESR spectrum of vanadyl *dl*-tartrate is in close agreement with that of vanadyl *dd*-tartrate at pH 4.8 and 2.8.

In conclusion, the remarkable change in the ESR spectrum of the binuclear vanadyl tartrate complex with the pH has been interpreted in terms of the change in the molecular structure of the complex accompanied by the dissociation of coordinate bonds and the change in the structure of the tartrate molecule.

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