line widths were much less than those for systems having free-spin d electrons (usually 15–25 G);[16–18] (3) the spectroscopic splitting factor was very small and was less by a factor of two orders than for systems having free-spin d electrons.[19] Oxyvanadium(V) ions have a higher charge to radius ratio than Ti^{4+} ions. Therefore, the $HO_2\cdot$ radicals may be attached laterally with oxyvanadium(V) ions in solution and linearly or angularly with Ti(IV) species.[20] For vanadate ions the radical end of $HO_2\cdot$ may interact strongly with t_{2g} orbitals of these ions which results in generating an eight-line spectrum, $I = {}^7/_2$ for ^{51}V. For Ti^{4+} ions, if the radical ligands are linearly or angularly attached, the interaction of the radical site with the t_{2g} orbitals would be weak, and no hyperfine splitting would occur.[9]

The oxyvanadium(V)–free-radical complex was unstable and decayed as a first-order reaction, probably by interaction of the complex with the solvent, as shown in Figure 4. For the Ce^{4+}–H_2O_2 system shown, $k = -6.2\ sec^{-1}$ and $t_{1/2} = 0.1$ sec.

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Triplet State of Vanadyl Tartrate Binuclear Complexes and Electron Paramagnetic Resonance Spectra of the Vanadyl α-Hydroxycarboxylates[1]

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Abstract: The oriented single-crystal epr spectra of tetrasodium divanadyl *d*-tartrate *l*-tartrate dodecahydrate and the liquid (pH ~7) and frozen solution epr spectra of vanadyl ion complexed with *d*- and *dl*-tartrate, glycolate, mandelate, and benzilate anions (both hydroxyl and carboxyl protons removed) were investigated. Within experimental error $g_\parallel = 1.953$ and $g_\perp = 1.983$ for all the α-hydroxycarboxylate complexes, except the glycolate complex. Observation of the half-field ($g \sim 4$) "forbidden" transitions for both tartrate complexes confirms the existence of triplet-state binuclear species in solution. Their spectra are interpreted in terms of the usual axially symmetric $S = 1$ spin Hamiltonian, axial symmetry being a better approximation for the *d*-tartrate than the *dl*-tartrate complex. The D values (0.0335 cm^{-1}, *d*-tartrate, frozen solution; 0.0334 and 0.0338 cm^{-1}, *dl*-tartrate, frozen solution and single crystal) are accounted for by simple magnetic dipole calculations. An unusual frequency dependence in the room-temperature solution spectra of the *d*-tartrate is reported. Assignments of the ligand-field transitions in the α-hydroxycarboxylates are discussed utilizing the epr results.

The anionic complexes of VO^{2+} ion with α-hydroxycarboxylate anions, in which both hydroxyl and carboxyl protons are removed, exhibit novel structural, optical, and magnetic properties. Three of their structures, monomeric sodium tetraethylammonium bis(benzilato)oxovanadium(IV) di-2-propanolate,[2] binuclear tetrasodium divanadyl(IV) *d*-tartrate *l*-tartrate dodecahydrate,[3] and binuclear tetraammonium divanadyl(IV) bis(*d*-tartrate) dihydrate[4] have been determined by X-ray methods. In the solid, the active and racemic tartrate complexes consist of two VO^{2+} ions bridged by two tetranegative tartrate anions, $O_2CC(O)H\cdot C(O)HCO_2{}^{4-}$, with *trans* and *cis* arrangements about the vanadyl group, respectively. The brown *cis-dl* isomer exhibits a three-band optical spectrum in solid and solution,[5] in contrast to the four bands displayed by both the purple *trans-dd* isomer[5,6] and *trans*-vanadyl bisbenzilate chelate.[2]

A 15-line X-band epr spectrum of the *dl*-tartrate complex in aqueous solution at pH ~7 and a similar but more complicated X-band spectrum of the *dd*-tartrate complex (Figures 2 and 3) were reported from this laboratory.[5] We attributed the 15-line spectrum to electron exchange between two vanadium metal nuclei (^{51}V, $I = {}^7/_2$). Seven- and 15-line solution spectra of some copper[7] ($I = {}^3/_2$) and cobalt[8] ($I = {}^7/_2$) chelates have been presented as evidence for dimers in solution; however, these were mixed valence complexes in which only one unpaired electron was shared by both metal nuclei. In addition to the epr results, osmometer formula weight determinations and potentiometric titrations as well as the strikingly different optical spectra for active and racemic tartrate complexes led us to conclude that dimeric species also exist in solution.[5]

Recently, Dunhill and Smith[9] reported epr spectra of

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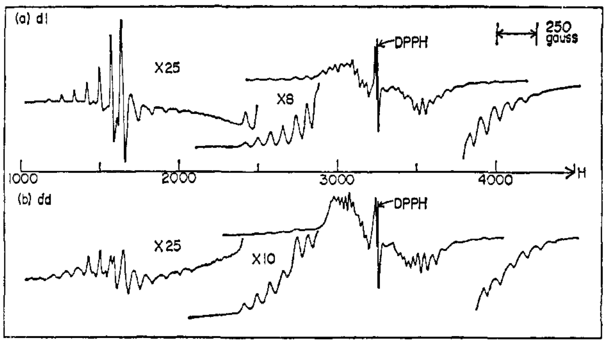

Figure 1. X-Band epr spectra of (a) $Na_4[(VO)_2$(*d*-tart *l*-tart)]·$12H_2O$ and (b) $Na_4[(VO)_2$(*d*-tart)$_2$]·$6H_2O$ in ethylene glycol-water solution at 77°K. First derivatives are plotted.

vanadyl tartrate solutions in the pH range 2 to above 6, at room temperature and 77°K. Their spectra were not well resolved for either of the tartrates and were unlike our previous room-temperature results. Moreover, at 77°K in frozen solution, they did not observe the $g \sim 4$ transitions expected for a triplet-state species. They concluded that epr measurements are unable to confirm the existence of dimers in solution. Later, some additional weak satellite lines, observed only in the *low* pH spectrum, were attributed to triplet states.[10]

We have investigated the epr spectra of (1) an oriented single crystal of vanadyl *dl* tartrate and (2) a number of vanadyl α-hydroxycarboxylate chelates in liquid (pH ~7) and frozen solutions; our results are quite different from those of Dunhill and Smith.[9] Accordingly, we report here conclusive evidence for triplet-state vanadyl tartrate dimers in solution and epr parameters for the interpretation of the optical spectrum.

Experimental Section

Vanadyl Tartrate Solutions. The methods for preparation of the vanadyl tartrate salts have been previously described.[5] Saturated solutions of pure crystalline tetrasodium divanadyl(IV) *d*-tartrate *l*-tartrate dodecahydrate and tetrasodium divanadyl bis-*d*-tartrate hexahydrate in ethylene glycol-water solution (1:1 by volume) were prepared and frozen quickly for the 77°K spectrum. Aqueous solutions were used for the room-temperature spectra.

Vanadyl Bismandelate and Bisglycolate Solutions. Aqueous solutions of 0.05 *M* $Na_2VOL'_2$ + excess 0.2 *M* NaL (L and L′ = mono- and dinegative α-hydroxycarboxylate anions) were prepared by dissolving 0.0075 mol of the appropriate acid (*dl*-mandelic, $(C_6H_5)CHOHCO_2H$, or glycolic acid, CH_2OHCO_2H, supplied by E. H. Sargent and Co. and Matheson Coleman and Bell, respectively) in 3.33 ml of 3 *N* sodium hydroxide. Then 3.12 ml of 0.4 *M* vanadyl sulfate, $VOSO_4$, was added dropwise with stirring and the pH was adjusted to approximately 7 with dilute (~0.1 *M*) sodium hydroxide and sulfuric acid solutions. The resultant solution was diluted to 25 ml with approximately 15 ml of sodium tetraborate-perchloric acid-ascorbic acid buffer, pH 7.52 at 25°. The final measured pH values were 7.85 and 7.88 for the mandelate and glycolate solutions, respectively. An excess of ligand was used to establish equilibrium favorable to the parent species,[3] but this prevented complete buffering of the solution. To inhibit oxidation, all solutions were purged with nitrogen before and during the mixing procedures. The samples were immediately chilled in ice and used within 2 hr.

Vanadyl Bisbenzilate Solution. The aqueous solution was prepared as above from benzilic acid, $(C_6H_5)_2COHCO_2H$ (supplied by Eastman Kodak); the vanadyl sulfate solution was diluted threefold before use to avoid precipitating the ligand. The final pH was 8.55, a lower pH not being obtainable because benzilic acid precipitates at pH ~7.

Epr Spectra. All spectra were recorded with a Varian V-4502 spectrometer operating at 9 GHz (X-band) or 35 GHz (Q-band). The magnetic field was read directly from the "Fieldial" accessory; a bit of powdered DPPH served as a *g*-marker with its isotropic *g* value taken as 2.0036.[11] Each sample for the frozen solution measurement was introduced into a 3-mm i.d. quartz tube, stoppered, and then immersed in a liquid nitrogen dewar located in the X-band cavity. A glass capillary, formed from the thin section of a disposable pipet, containing saturated aqueous solution, was used for the Q-band spectra. Frequently, difficulty was encountered in tuning the instrument for Q-band aqueous solution measurements, but with much manipulation we obtained a reproducible resonance. All other spectra were collected by standard procedures.

Results and Discussion

A. Frozen Solution Spectra of the Tartrate Chelates.

The ethylene glycol-water frozen solution spectra of both the vanadyl *d*-tartrate and *dl*-tartrate chelates are shown in Figure 1. Contrary to Dunhill and Smith's results,[9] the half-field, $\Delta M_S = 2$ transitions ($g \sim 4$) are clearly seen at $H \sim 1600$ G. We believe that this discrepancy arises from different methods of sample preparation, their samples being prepared in solution with tartaric acid and vanadyl ion, whereas *pure crystalline* compound is needed for optimum results.

We assume an axially symmetric system and write the appropriate $S = 1$ spin Hamiltonian as follows

$$\mathcal{H} = \beta[g_{\parallel}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] + D[S_z^2 - S(S+1)/3] + AS_zI_z + B(S_xI_x + S_yI_y) \quad (1)$$

where all symbols have their usual meaning.

The spectrum at $H \sim 3500$ G consists of the overlapping low- and high-field parallel and perpendicular components, with the high- and low-field parallel lines separated by approximately $2D$.

We determined the $g_{\parallel}$, A, and D values from parallel lines through Bleaney's equation[12] for the field direction along the symmetry axis

$$\omega_0 = g_{\parallel}\beta H + 2D\left(M_S - \frac{1}{2}\right) + AM_I + (B^2/\omega_0)[I(I+1) - M_I^2 + (2M_S - 1)M_I] \quad (2)$$

where $I = 7$; $M_S = 1, 0$; $M_I = \pm7, \pm6, \ldots, 0$; and ω_0 is the radiation frequency. The resultant epr parameters are given in Table I

Table I. Epr Parameters of the Vanadyl α-Hydroxycarboxylates

	dl-Tartrate	*d*-Tartrate	Benzilate	Mandelate	Glycolate
g^a	1.972	1.973	1.974	1.973	1.974
a^b	38.3	40.8	77.7	81.0	83.0
$g_{\parallel}^c$	1.953	1.950	1.954	1.953	1.944
$g_{\perp}^c$	1.982	1.984	1.985	1.984	1.989
A^b	72.3	73.2	150.5	152.5	166.6
B^b	21.3	24.6	41.5	45.3	41.3
D^d	334 (2), 338 (8)	335 (4)	...	...	...

[a] Estimated errors are ±0.004 for the tartrates, ±0.001 for the other complexes. [b] Values are given in units of 10^{-4} cm^{-1} with estimated errors of 0.8, 1.0, 2.0 × 10^{-4} cm^{-1} for *a*, *A*, and *B*, respectively. [c] Estimated errors are ±0.002 in $g_{\parallel}$ and ±0.006 in $g_{\perp}$ of the tartrates and half as much for the other complexes. [d] Units are in 10^{-4} cm^{-1} with errors in the last digit given in parentheses. The second value in *dl*-tartrate is from the single-crystal spectrum.

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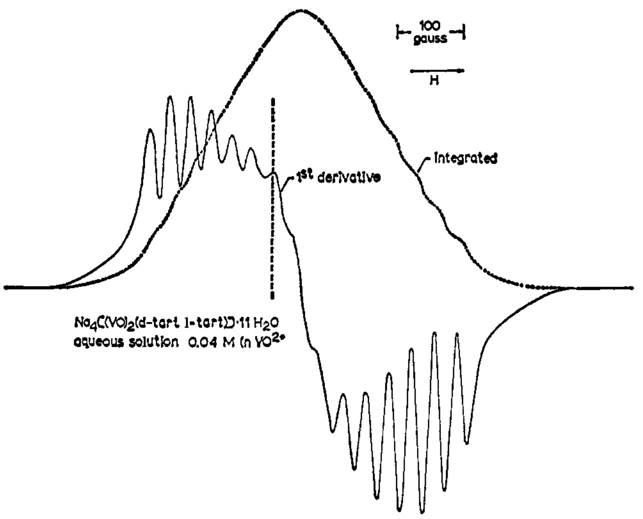

Figure 2. X-Band epr spectrum of sodium vanadyl(IV) *dl*-tartrate at room temperature. Vertical dashed line locates DPPH resonance. First derivative and absorption curves are plotted.

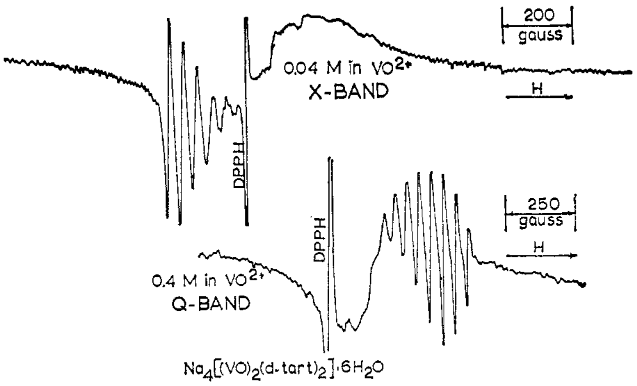

Figure 3. X- and Q-band epr spectra of sodium vanadyl(IV) *d*-tartrate. First derivatives are plotted.

B. Room-Temperature Solution Spectra of the Tartrate Chelates. The $g_\perp$ and B values were obtained from the relations

$$g = (g_\parallel + 2g_\perp)/3 \tag{3}$$

and

$$a = (A + 2B)/3 \tag{4}$$

isotropic g and a being available from the X-band and Q-band room-temperature solution spectra shown in Figures 2 and 3. The g values of the tartrates are very similar to those of all the monomeric complexes except the glycolate (see Table I), and the splitting due to the hyperfine interaction is half of the corresponding splitting in the absence of exchange coupling.[13]

From these and previous results,[5] we have no doubt that dimeric tartrates are the principal species in solution. The poor resolution of the solution spectra is to be expected because of dipole–dipole broadening. If the two unpaired electrons in a triplet system interact strongly, the dipolar broadening is so large that no spectrum is observed in solution.[14] However, if the dipolar interaction is very weak, a complete resolution of hyperfine lines is possible as is exemplified by the distinct five-line spectrum reported for an organic biradical having two nitroxide groups separated by about 10 Å.[15a] Moreover, some Cr^{3+} complexes with zero-field splittings about 0.05 cm^{-1} have line widths as small as 30 G.[15b] The zero-field splittings in the vanadyl tartrates are about 0.03 cm^{-1}, and the line widths range from 20 to 30 G; hence our observation of the hyperfine splitting of ~44 G in the solution spectrum is reasonable.

However, the poor resolution of the solution spectra could also originate in overlapping of various spectra and in some other mechanisms as is implied by the anomalous difference in the Q- and X-band spectra for the *d*-tartrate complex at room temperature (see Figure 3). Surprisingly, in the higher magnetic fields (Q-band), the lower field side of the resonance is poorly resolved, whereas in the lower magnetic fields (X-band), the opposite occurs. Further experiments are underway in an attempt to determine the reason for this reversal.

C. Single-Crystal Spectra. Figure 4 shows the X-band spectra of an oriented single crystal of $Na_4[(VO)_2(d\text{-tart})(l\text{-tart})]\cdot 12H_2O$ with the field direction along the three crystallographic axes. These are the only directions in which the field makes equivalent projections on all four dimers in the unit cell. The spectra along *a* anb *b* exhibit a complicated line shape, while the *c* spectrum appears to be composed of two symmetrical overlapping lines, the splitting between them being independent of frequency (Q- or X-band). If we attribute the splitting (350 G, corrected for overlap of lines) to the D term in the Hamiltonian (1), we calculate a D value of 0.0338 cm^{-1} from the $1 - 3\cos^2\theta$ relation, where $\theta = 82.15°$ is the angle between the V–V and the *c*-axis directions. The gross features of the spectra in the *a* and *b* directions can be interpreted similarly, as is evidenced from their calculated splittings in Figure 4, based on the D value of 0.034 cm^{-1}. Although the D value is in good agreement with the frozen solution result (0.0338 *vs.* 0.0334 cm^{-1}), it may not be valid to ascribe the splitting in the *c* direction solely to the D term, especially in light of the appearance of the spectra in the other directions. Single-crystal measurements on the tetraammonium divanadyl(IV) bis(*d*-tartrate) dihydrate compound of known structure[4] might clarify this point, but thus far we have been unable to obtain single crystals suitable for epr analysis.

D. Half-Field Transitions. The "forbidden" $\Delta M_S = 2$ transitions arise when the magnetic field is off the symmetry axis of the molecule by a certain angle, θ. For the *dl* isomer, the hyperfine splitting of the half-field lines is about 3 G greater than that of the full-field parallel lines (82.5 *vs.* 79.3 G), a difference which can occur only if the principal axes of the **g** and **A** tensors are not coincident.

Under the axial-symmetry approximation, the angle θ can be estimated from the relationship[12]

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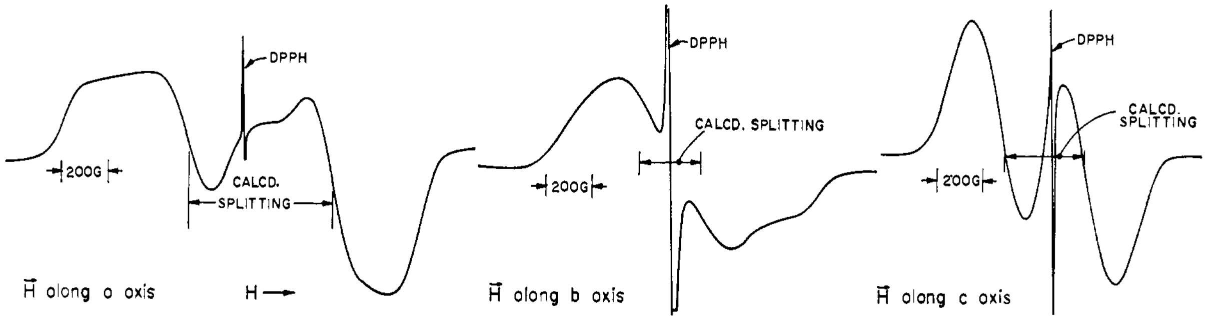

Figure 4. X-Band epr derivative spectrum of a single crystal of $Na_4[(VO)_2(d\text{-tart})(l\text{-tart})]\cdot 12H_2O$ with the field direction along the crystallographic *a*, *b*, and *c* axes; orientation uncertainty, ±5°. The calculated *D* splittings are based on a *D* value of 0.034 cm^{-1}.

$$H = \frac{1}{2g\beta}\left\{\omega_0 - 2KM_I - \frac{B^2}{2\omega_0 K^2}(A_2 + K^2)[I(I+1) - M_I^2] - \frac{1}{\omega_0}\left[\left(\frac{A^2 - B^2}{K}\right)\left(\frac{g_\parallel g_\perp}{g^2}\right)(M_I \sin\theta\cos\theta)\right]^2 - \frac{2D^2 g_\parallel^2 g_\perp^2 \cos^2\theta \sin^2\theta}{\omega_0 g^4} - \frac{D^2 g_\perp^4 \sin^4\theta}{2\omega_0 g^4}\right\} \quad (5)$$

where

$$g^2 = g_\perp^2 \cos^2\theta + g_\parallel^2 \sin^2\theta \quad (6)$$

$$g^2K^2 = g_\parallel^2 A^2 \cos^2\theta + g_\perp^2 B^2 \sin^2\theta \quad (7)$$

Substituting eq 6 and 7 into eq 5 and making use of the appropriate parameters in Table I, we calculate from the $M_I = 0$ line ($H = 1662$ G) for the *d*-tartrate, $\theta = 14°$, and an average hyperfine splitting of 78.1 G in reasonable agreement with the experimental value of 78.6 G.

Because of the severe deviation from axial symmetry (see next section), eq 5 cannot be applied to the *dl*-tartrate.

The *D* value can also be extracted from the half-field transitions through the relationship[16]

$$H_{\min} = [\omega_0^2 - {}^4/_3 D^2]^{1/2}/2g\beta$$

with $H_{\min} = 1651$ and 1662 for the *dl*- and *d*-tartrate complexes, respectively, and $\omega_0 = 0.3048$ cm^{-1}. Setting $g = g_\parallel$ for the *dl* complex and computing *g* from eq 6 with $\theta = 14°$ for the *d* complex, we obtain $D = 0.0412$ (*dl*) and 0.0376 cm^{-1} (*d*). The agreement between these values and the others in the table is reasonable in view of the uncertainty in locating $H_{\min}$.

E. Interpretation of *D* Values. Attributing *D* to the magnetic dipolar interaction between two electronic centers, we can estimate it from the equation[17]

$$D_{\text{calcd}} = \frac{3}{4}g^2\beta^2\left\langle\frac{1 - 3\cos^2\theta}{r_{12}^3}\right\rangle_{\max} \quad (8)$$

where r_{12} is the interelectronic distance and θ is the angle between the r_{12} vector and the magnetic field direction. Assuming that θ equals the angle between the V–V direction and the magnetic field and $1/\langle r_{12}^3\rangle = 1/R^3$, *R* being the V–V distance, we obtain

$$|D_{\text{calcd}}|/\text{cm}^{-1} = \frac{0.325g^2}{R^3}|1 - 3\cos^2\theta|\ \text{Å}^3 \quad (9)$$

From the crystal structure of the *dl* dimer,[3] $R = 4.08$ Å and the V—V=O angle is 152°. Taking $H_\parallel$ to be along the V=O or V—V directions, *i.e.*, $\theta = 28$ or 0°, respectively, one calculates $D_{\text{calcd}} = 0.024$ or 0.037 cm^{-1}, the latter being in better agreement with the value of 0.0334 cm^{-1} from the frozen solution measurements. This would seem to imply that the angle between $g_\parallel$ and the direction in which the dipole interaction maximizes is somewhat less than 28°. (We hasten to point out that such a conclusion is suspect since it is based on an assumption of axial symmetry.) Because of our inability to measure single-crystal *g* and *D* values reliably, we were unable to check this result.

We can perhaps better approximate $\langle(1 - 3\cos^2\theta)/r_{12}^3\rangle$ by calculating the 16 interactions between a quadrupole charge distribution in each half of the dimer, θ being measured from the V—V direction. Here, one-fourth of an electron is placed 0.5 Å from the vanadium atom on each of the four lines perpendicular to the V=O direction and approximately bisecting the ligand oxygen-to-vanadium-to-ligand oxygen angles; the four charges then occupy the four corners of a square with a 1 Å diagonal. The approximate radial distance at which the 3d electron density maximizes for a typical transition-metal ion is 0.5 Å. With the above charge distribution and by taking into account the structural relationship between the two halves of the dimer,[3,4] we calculate $D_{\text{calcd}} = 0.034$ cm^{-1}, in better agreement with the experimental values of 0.0334 and 0.0338 cm^{-1}. A more complete accounting for the electron delocalization is unlikely to change this result by more than a few per cent.

In the case of the *dd* dimer, $R = 4.35$ Å, and the V—V direction deviates from the V=O direction by less than 3° (V—V=O angle = 177.7°). Here, $D_{\text{calcd}} = 0.030$ (simple calculation) or 0.028 cm^{-1} (quadrupole calculation), and $D_{\text{exptl}} = 0.0335$ cm^{-1}.

It is apparent that the primary contribution to the *D* value comes from magnetic dipole interactions between electrons essentially located on the vanadium ions in the dimer; however, it is surprising that the experimental *D* is nearly the same for both isomers in view of the difference in the V–V distances (4.35 *vs.* 4.08 Å).

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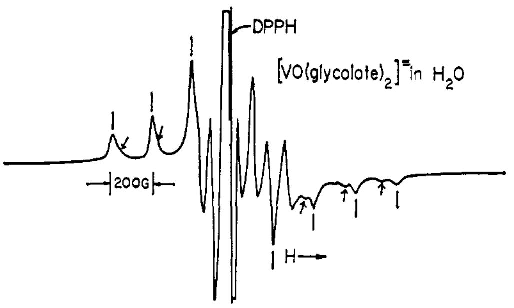

Figure 5. X-Band epr derivative spectrum of sodium vanadyl glycolate plus excess ligand, 0.05 *M* VO^{2+} in H$_2$O, at 77°K. Vertical lines locate parallel components used in $g_{\parallel}$ and *A* determinations. Arrows indicate peaks due to other species.

Since our treatment of the data, eq 2, assumed an axially symmetric system (which appears to be somewhat reasonable for the *dd* dimer but is clearly not the case for the *dl* dimer), any deviation of $g_{\parallel}$ from the principal direction of the dipolar interaction would produce an artifically low experimental *D* value. On the basis of the V–V distance alone, 0.041 cm^{-1} is perhaps a more reasonable number for the *dl* isomer. However, this is not substantiated by the single-crystal measurements (see discussion of single-crystal spectra).

It is interesting to apply the dipole model to other dimeric systems of known structure and epr parameters. When Cu^{2+} ions are doped into bis(N-methylsalicylaldimine)nickel(II) in sufficient concentration, a spin-triplet spectrum arises from Cu^{2+} ions occupying adjacent Ni^{2+} sites;[18] $D_{\text{obsd}} = 0.046$ cm^{-1}, $D_{\text{calcd}} = 0.089$ cm^{-1} based on eq 9, and $R = 3.29$ Å (the Ni–Ni distance).[19]

The poor agreement is probably due to a number of factors: a shorter metal–metal distance than in the tartrates, making the *D* value more sensitive to details of the electron distribution, greater covalency of copper compounds over vanadyl compounds, and increased electron exchange interaction. We can approximate the charge distribution in each half of the copper dimer by assuming that the fraction of the unpaired electron in the copper ground state $d_{x^2-y^2}$ is given by $\alpha^2 = 0.774$, α^2 being the metal orbital population determined from the epr parameters.[18] We place a charge $q_{\text{M}} = \alpha^2/4$ on the four metal–ligand bonds at a distance of 0.50 Å from the copper and a charge $q_{\text{L}} = (1 - \alpha^2)/4$ on each of the four chelating atoms, nitrogen or oxygen, at a distance of 1.945 Å (average of the Cu–O and Cu–N bond lengths)[20] from the copper atom. Hence, the spin distribution around each copper is approximated by an octupole consisting of the charges q_{M} and q_{L}; $\langle(1 - 3\cos^2\theta)/r_{12}^3\rangle$ is then calculated from a total of 64 interactions, yielding $D_{\text{calcd}} = 0.060$ cm^{-1}, in fair agreement with experiment. No attempt was made to adjust any of the starting parameters; in light of the uncertainty in α^2 and the somewhat arbitrary choice of the other parameters, we see that we can reasonably account for the *D* splitting with a dipole model.

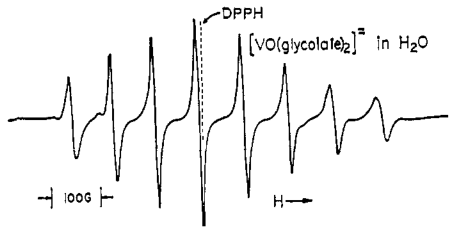

Figure 6. X-Band epr derivative spectrum of sodium vanadyl glycolate plus excess ligand, 0.05 *M* VO^{2+} in H$_2$O, at room temperature.

In the case of dimeric copper acetate monohydrate, $D_{\text{obsd}} = 0.34$ cm^{-1} [21] and $D_{\text{calcd}} = 0.20$ cm^{-1} from eq 9 with $R = 2.64$ Å;[22] introduction of covalency in the calculations will only serve to reduce D_{calcd}. Presumably, the anisotropy in the large exchange interaction in this system dominates and the simple magnetic dipole–dipole calculation is no longer adequate.

Epr Spectra of the Monomers. The Hamiltonian for the monomeric species is the same as eq 1 except that the *D* term is omitted and $S = {}^1/_2$, $I = {}^7/_2$. Representative spectra of frozen and room-temperature specimens are shown in Figures 5 and 6, from which the magnetic parameters were extracted as for the tartrates. All *g* values were corrected for second-order effects.[23]

The average line width of the room-temperature solution spectra of the glycolate, mandelate, and benzilate complexes were 12, 24, and 35 G, respectively, suggesting less complete rotational averaging of *g* and hyperfine tensors for the larger molecules.

In contrast to the mandelate and benzilate, $g_{\parallel}$ and *A* of the glycolate chelate were very sensitive to solution pH in the range 7.5–9.5. The frozen solution spectrum in Figure 5 contains several peaks which were not present in the spectra of the other two complexes. Moreover, the poor resolution and sensitivity of the optical spectra toward pH indicate that substantial amounts of various species are present in the glycolate solutions. The differences between the epr parameters of this complex and the others can be explained on this basis (see Table I).

***g* Values and the Optical Spectrum.** The agreement among the *g* values certainly suggests a similar ordering of the ligand field energy levels for all the vanadyl α-hydroxycarboxylate complexes. The solution spectrum of the *cis-dl*-tartrate has three band maxima at 13.6, 18.7, and 23.8 kK compared to four band maxima for both the *trans-d*-tartrate and bisbenzilate, which occur at 11.1, 17.0, 18.7, and 25.1 kK, and 11.8, 16.7, 18.5, and 24.0, kK, respectively (see introductory section). Previously, a correlation of coordination geometry with band positions together with simple crystal-field considerations prompted us to suggest two possible energy level schemes, one of which was $xy \rightarrow x^2 - y^2$ (~12 kK), $xy \rightarrow xz$, yz(~17–19 kK), and $xy \rightarrow z^2$(~24 kK) for both *cis* and *trans* complexes. While we were tempted to assign the apparent splitting of the second band (*cis-dl*, 18.7 → *trans-dd*, 17.0 and

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18.7 kK) to a separation of *xz*, *yz* orbitals, our epr results are very hard to reconcile with this hypothesis. In an axial system, the shift in the *g* values from the free electron value, 2.0023, is related to the energy levels by

$$\Delta g_{\parallel} = \frac{8\alpha^2\beta^2\lambda}{E_{x^2-y^2}} \text{ and } \Delta g_{\perp} = \frac{2\alpha^2\gamma^2\lambda}{E_{xz,yz}}$$

where α, β, and γ are modified molecular orbital coefficients of the xy, $x^2 - y^2$, and xz, yz orbitals, respectively, λ is the spin-orbit coupling constant, and E_j is the energy of orbital j measured from the ground-state orbital, xy. For the benzilate complex, if we choose $E_{x^2-y^2} = 11.8$ kK and $E_{xz,yz} = (16.7 + 18.5)/2 = 17.6$ kK to fit the above energy level scheme, and reasonably assume $\beta^2/\gamma^2 = 0.8$, we calculate $\Delta g_{\parallel}/\Delta g_{\perp} = 4.8$ in contrast to the experimental value 2.8 ± 0.6. Each of the two other proposed assignments [$xy \rightarrow yz$, $x^2 - y^2$, xz, z^2 (for bands 1–4, respectively)[2] or $xy \rightarrow xz \sim yz$ (first band), $x^2 - y^2$ (second), z^2 (third), and charge transfer (fourth)[6]] produces a calculated $\Delta g_{\parallel}/\Delta g_{\perp}$ within the observed range, 2.8 ± 0.6. At present, particularly as we lack information on the in-plane anistropy, we cannot choose between these two possibilities.[24]

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[24] NOTE ADDED IN PROOF. Another vanadium compound is reported[25] to exhibit a 15-line epr spectrum in solution, and similarly an 11-line spectrum probably characteristic of triplet-state dimers has been observed[26] in solutions of molybdenum(V) glutathione enriched in ^{95}Mo. We have also found $Na_4[Cu_2(d\text{-tartrate})(l\text{-tartrate})]\cdot 10H_2O$ to be binuclear and to exhibit epr evidence of a triplet state similiar to that reported here[27]

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Thermodynamics of Ion Association. XIX. Complexes of Divalent Metal Ions with Monoprotonated Ethylenediaminetetraacetate[1a]

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Abstract: Free energy and enthalpy changes accompanying the protonation of divalent metal–ethylenediaminetetraacetate complexes in the reaction $MY^{2-} + H^+ \rightleftharpoons MHY^-$, where H_4Y represents EDTA, have been measured potentiometrically and calorimetrically at 25° and at an ionic strength maintained at 0.10 *M* with potassium nitrate. The metal ions investigated were Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}. The data are discussed in terms of the extent of coordination of the multidentate ligand with the metal ions, and comparisons are made with the corresponding thermodynamic functions for the formation of related metal complexes.

There is considerable interest in the structures of aqueous metal complexes involving the EDTA anion. In the absence of any unequivocal method for their determination, they have generally been inferred from free energy, kinetic, and spectral measurements. In the solid state, Hoard and his coworkers[2–6] have used X-ray methods to determine the structures of a number of metal–EDTA complexes. Invariably the ligand was bound in a sexadentate structure, and no evidence was found for the presence of an uncomplexed acetate residue. Additional water molecules were bound in the manganous[2] and ferric[3,4] species in seven-coordinate structures. X-Ray studies of the crystalline protonated complexes $Co(OH_2)YH_2$ and $Ni(OH_2)YH_2$ revealed the presence of one unchelated acetate residue with the ligand bound in a quinquedendate manner.[5,6]

In solution, the structures of the EDTA complexes are uncertain. The similarity of the acid dissociation constants[7] of the protonated complexes, $M(OH_2)YH^-$, of a large number of metal ions led Higginson[8] to conclude that this corresponded to the protonation of a free acetate arm and to propose quinquedentate coordination in $M(OH_2)Y^{2-}$ in every case except, perhaps, for manganese(II). On the other hand, the marked changes in the visible spectrum accompanying the protonation of CuY^{2-} and CoY^{2-}[9] indicated that these complexes contain at least a proportion of six-coordinated species. The results of a recent kinetic study,[10] in which cobaltous EDTA solutions at various acidities were allowed to react with rapid outer-sphere oxidants to form the cobatic complex, also indicated the presence

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