line copper benzoylacetonate, to gauge the effect of weak axial coordination of copper to the π orbital of an aromatic carbon.

At this juncture, one cannot say why the copper compound packs in one way and the palladium one in another. However, we emphasize that the geometries of the two chelate rings are, within experimental error, identical. Furthermore, the difference in the twist of the phenyl ring out of the mean chelate plane is probably determined by the basic difference in mode of packing. Therefore, we are inclined to attribute the packing difference to a special stability of z axis coordination to the copper ion. This opinion is influenced by the fact that the same sort of packing, involving close axial approach of an aromatic carbon atom, recurs in other crystalline copper chelates—*e.g.*, copper acetylacetonate and copper dibenzoylmethanate.[8]

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CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Oxovanadium(IV) Tartrates. Characterization and Evidence for Intermetallic Coupling in Anionic Species[1]

BY ROBERT E. TAPSCOTT AND R. LINN BELFORD

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A study of physical properties of VO^{2+} with active and racemic tartaric acids in 1:1 aqueous solutions shows that these two acids give 1:1 complex anions, in the region of pH 7, differing in stability, optical spectra, and electron spin resonance spectra. The data indicate that each anionic complex is a dimer containing two VO^{2+} ions bridged by two tetranegative tartrate groups. The first electron spin resonance spectrum to show hyperfine splitting by two equivalent vanadium nuclei is reported for the racemic complex. Magnetic susceptibilities of two of the several solid salts isolated imply that the V–V exchange coupling is less than 50 cm^{-1}, as one would expect for the proposed geometries.

Introduction

The vanadyl(IV)[2] tartrate system has been extensively studied[3] although little information has been recorded on the structures of the species involved. In solution, vanadyl(IV) ion coordinates with tartrate anion to give various complexes depending upon the pH of the solution and the relative amounts of vanadyl(IV) and tartrate present.

Of particular interest is the anionic species formed in solutions containing a 1:1 ratio of vanadyl(IV) and tartrate ions at pH 7. The formation of this complex is indicated by a sudden change in color and, with optically active tartrate, the appearance of a four-peak optical spectrum[4] as the pH of the vanadyl(IV) tartrate solution is increased. Ducret's studies[5] indicate that with racemic tartrate the anionic species is a 1:1 complex containing a tetranegative tartrate ion in which all alcoholic and carboxylic hydrogens are removed. Jørgensen[6] has assumed, as have most authors implicitly, that this complex is mononuclear consisting of a vanadyl(IV) ion surrounded by four coordinating oxygens of the tetranegative tartrate ion. Our molecular models, however, indicate that such a system would be highly strained for any reasonable geometry about the vanadyl(IV) ion. Jones and Larsen,[7] on the other hand, have assumed that this system contains polynuclear species by analogy to the behavior of basic copper tartrate solutions.

The work reported here confirms that the principal anionic complex of vanadyl(IV) tartrate formed in higher pH solutions is not mononuclear. In a recent paper,[8] Dunlop, *et al.*, have also arrived at this conclusion based on one of the observations that we have made—*i.e.*, vanadyl(IV) tartrate solutions at higher pH containing optically active tartaric acid have different spectral properties than those containing the racemic acid. They, however, conclude that several polymeric species are present whereas our data imply that there is primarily one complex present—a tetranegative anion consisting of two vanadyl(IV) ions bridged by two tetranegative tartrate anions. From our work, we infer that with *d*- (or *l*-) tartrate, a dimer is formed having two *d*- (or *l*-) tartrate bridges while with the racemic tartrate, dimers are formed having one *d*- and one *l*-tartrate bridge.

Finally, we present electron spin resonance spectra

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[2] Vanadyl(IV) and oxovanadium(IV) both denote the VO^{2+} ion.

[3] See J. Selbin, *Chem. Rev.*, **65**, 158 (1965), for a list of references.

[4] J. Selbin and L. Morpurgo, *J. Inorg. Nucl. Chem.*, **27**, 673 (1965).

[5] L. P. Ducret, *Ann. Chim.* (Paris), **6**, 705 (1951).

[6] C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 73 (1957).

[7] K. M. Jones and E. Larsen, *ibid.*, **19**, 1210 (1965).

[8] J. H. Dunlop, D. F. Evans, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc., Sect. A*, 1260 (1966).

to show that intermetallic coupling occurs in the *dl*-tartrate dimer and to give some indication that coupling also occurs with the *d*-tartrate dimer. These are the first vanadyl(IV) complexes reported where hyperfine splitting has given unambiguous indications of such coupling.

Experimental Section

Preparation of Solid Salts of Vanadyl(IV) Tartrate Anions.—These salts have the formula $M_4[(VO)_2(d\text{-tartrate})_2]\cdot xH_2O$ or $M_4[(VO)_2(d\text{-tartrate})(l\text{-tartrate})]\cdot xH_2O$ where M is a univalent cation (or $M'_2[(VO)_2(\text{tartrate})_2]\cdot xH_2O$ where M′ is divalent). They were prepared by reduction of V_2C_5 (Fisher technical grade) with an excess of either the optically active or racemic tartaric acid followed by addition of the base MOH to the vanadyl(IV) tartrate obtained. Racemic and *l*-tartaric acids were obtained from Aldrich Chemical Co. and *d*-tartaric acid from both Aldrich and Fisher. Alternatively, vanadyl(IV) tartrate can be prepared and stored and the necessary base added to it for preparation of a particular salt.

Barium, sodium, potassium, ammonium, tetramethylammonium, and rubidium vanadyl(IV) tartrate salts were prepared. Only the sodium salt was used to prepare solutions for work reported in this paper and this compound was particularly well characterized. The other salts were prepared for characterization and future work on the solid state of these compounds. The tetramethylammonium and rubidium salts of vanadyl(IV) *d*-tartrate and solid salts of vanadyl(IV) *dl*-tartrate have not been reported before. We were unable to obtain crystalline salts using cesium, strontium, lithium, or tetraethylammonium cations, possibly because of their high solubilities; only glasses were obtained.

With the exception of the barium salts, which are nearly insoluble, all are highly soluble in water and form well-defined crystals. The sodium salts are among the least soluble (except for barium) and the tetramethylammonium the most soluble in water. Only the latter are soluble in nonaqueous solvents. The vanadyl(IV) *dl*-tartrate salts are varying shades of brown which dissolve in water to give red-brown solutions whereas the salts of vanadyl(IV) *d*- (or *l*-) tartrate are shades of violet which dissolve to give violet or purple solutions, depending upon the concentration.

Vanadium pentoxide was slurried with a minimum of water and heated on a steam bath. Solid tartaric acid was slowly added to the hot solution using 2.2 moles of tartaric acid per mole of V_2O_5. The mixture was heated with evolution of CO_2 gas until a blue solution, sometimes containing a suspension of vanadyl(IV) tartrate, was obtained (about 0.5 hr). Four equivalents of base per mole of V_2O_5 was then added (carefully, to avoid splattering!) to the hot solution, which was filtered hot to remove traces of a black residue which occasionally formed and any unreacted vanadium pentoxide. Crystals of the salt formed when the solution was cooled and were filtered off. Nitrogen was bubbled through the reaction mixture during the preparation to decrease oxidation, to which the vanadium(IV) is particularly susceptible following addition of the base. We have observed no oxidation in the dried salts. The over-all reaction is presumably

$$5V_2O_5 + 20MOH + 11C_4H_6O_6 = 5M_4[(VO)_2(C_4H_2O_6)_2] + 33H_2O + 4CO_2\uparrow$$

Another procedure is preferable for the relatively insoluble barium salt. Barium chloride solution was added slowly, with stirring, to a hot solution of the sodium salt in stoichiometric proportions. Poorly defined crystals formed slowly over a period of 1–2 hr. Small changes in the procedure and conditions often gave an immediate precipitate which did not analyze well. The barium salts were not recrystallized.

The salts (except barium) were recrystallized from water three to five times. Ethanol brings them out of solution but was not used during the final crystallization because it occasionally caused a slightly low vanadium content, possibly owing to inclusion of some ethanol in the crystals. The crystals were washed with 50% ethanol, absolute ethanol, and acetone and were dried over $CaCl_2$ under vacuum for 7–10 days. Depending upon the drying conditions, one can obtain salts with varying water contents. The sodium salts failed to reach a definite stoichiometric composition over P_2O_5. The yields ran about 50% depending upon the solubilities and the number of recrystallizations.

EDTA titrations, using a $ZnCl_2$ back titration and xylenol orange indicator, gave excellent analyses for the vanadium in these compounds (Table I). The titrations were run in acetic acid–sodium acetate pH 6 buffered solutions containing ascorbic acid as a reducing agent. Analysis for vanadium(IV) using ceric ion failed owing to interference by the tartrate anion.

TABLE I

	Analyses, %				
	Calcd	Found		Calcd	Found
$VO(dl\text{-tart})\cdot 3H_2O$[a]			$VO(d\text{-tart})$		
Light blue, finely divided solid			No solid obtained, dark blue in solution		
C	17.86	17.75			
H	3.75	3.80			
$Na_4[(VO)_2(d\text{-tart})(l\text{-tart})]\cdot 11H_2O$			$Na_4[(VO)_2(d\text{-tart})_2]\cdot 6H_2O$		
Large, lustrous, red-brown crystals			Lustrous, well-formed, violet crystals		
V	14.23	14.20 ± 0.06[b]	V	16.28	16.09 ± 0.15
C	13.42	13.63, 13.26	C	15.35	15.48, 15.25
H	3.66	3.76, 3.86	H	2.58	2.46, 2.55
$K_4[(VO)_2(d\text{-tart})(l\text{-tart})]\cdot 3H_2O$			$K_4[(VO)_2(d\text{-tart})_2]\cdot 3H_2O$		
Brown crystals			Lustrous, violet crystals		
V	16.01	16.07 ± 0.17	V	16.01	15.88 ± 0.08
C	15.10	15.76	C	15.10	15.43
H	1.58	1.29	H	1.58	1.66
$Ba_2[(VO)_2(d\text{-tart})(l\text{-tart})]\cdot 7H_2O$			$Ba_2[(VO)_2(d\text{-tart})_2]\cdot 7H_2O$		
Violet-brown flakes			Violet clusters		
C	11.62	11.64	C	11.62	11.85
H	2.19	2.32	H	2.19	2.28
$(NH_4)_4[(VO)_2(d\text{-tart})(l\text{-tart})]\cdot 2H_2O$			$(NH_4)_4[(VO)_2(d\text{-tart})_2]\cdot 2H_2O$		
Dark brown crystals			Well-defined, purple crystals		
C	17.99	18.49 ± 0.13	C	17.99	17.96
H	4.53	4.62 ± 0.04	H	4.53	4.76
N	10.49	10.60 ± 0.13	N	10.49	11.64
$[N(CH_3)_4]_4(VO)_2(d\text{-tart})(l\text{-tart})]\cdot 6H_2O$			$[N(CH_3)_4]_4[(VO)_2(d\text{-tart})_2]\cdot xH_2O$		
Light violet-brown, irregular crystals			Light violet, dendritic crystals not analyzed		
C	34.70	35.56			
H	7.77	7.88			
N	6.75	6.74			
$Rb_4[(VO)_2(d\text{-tart})(l\text{-tart})]\cdot 2H_2O$			$Rb_4[(VO)_2(d\text{-tart})_2]\cdot 2H_2O$[c]		
Chocolate-brown crystals			Well-defined, purple crystals		
C	11.95	12.11	C	11.95	11.98
H	1.00	1.13	H	1.00	1.38

[a] Throughout this paper, "tart" denotes the $C_4H_2O_6^{4-}$ anion. [b] Mean absolute deviation from average of several analyses. [c] Prepared by B. Bersted. The rubidium salt crystallizes in the tetragonal system with dimensions similar to those of the ammonium salt which belongs to space group $P4_12_12$, eight vanadium atoms per unit cell with approximate dimensions $a = b = 7.98$ A, $c = 31.63$ A.

Apparatus.—The optical spectra were run with monochromatic sample illumination over the region 1300–300 mμ using a Cary Model 14 RI spectrophotometer. A lead sulfide detector was used for the region 650–1300 mμ and a photomultiplier tube at 650–300 mμ. Spectra in these two ranges always coincided (within the thickness of the ink line) at the changeover point.

Electron spin resonance spectra were run on a Varian V-4502 epr spectrometer using 10^5/sec field modulation and an X-band microwave bridge.

All pH values reported were obtained with a Beckman Model G pH meter.

The magnetic susceptibility measurements employed a standard Gouy apparatus using a Sartorius Model 2604 balance and an Alpha AL-7500 electromagnet.

Formula weight determination employed a Mechrolab Model 301A vapor pressure osmometer calibrated with an aqueous sucrose solution.

Procedures. A. pH Titration Curves.—A stock solution of vanadyl (IV) perchlorate was prepared by the method of Jones and Larsen[9] using vanadyl(IV) sulfate (Fisher) and barium perchlorate (GFS Chemical Co.). The solution was standardized by ceric ion titration using ferroin indicator and the results were checked by potassium permanganate titration. Stock solutions of *d*-tartaric acid (Fisher) and *dl*-tartaric acid (Aldrich) were prepared and standardized by titration to a phenolphthalein end point with potassium hydroxide solution. The purity of the *dl*-tartaric acid was checked by melting point determination on three samples: mp 204.5, 204.5–205, 204–205° (lit.[10] 205°). The stock solutions were mixed volumetrically and diluted to give 0.0400 ± 0.0002 *M* 1:1 solutions of vanadyl(IV) perchlorate with *d*-tartaric acid and with *dl*-tartaric acid. These solutions appeared to be indefinitely stable; however, upon addition of base (above pH 5), they exhibit slow oxidation, evidently by dissolved oxygen. To minimize oxidation during the base titration, the water used to prepare the solution was boiled and purged with nitrogen.

Aliquots of 100 ± 0.1 ml of the 0.04 *M* vanadyl(IV) perchlorate–tartaric acid solutions were titrated in a stirred container with 1 *N* potassium hydroxide solution (Acculute) and the pH (±0.04) was recorded as a function of base added (±0.01 ml). The temperature was maintained at 25 ± 0.2° during the titration and all pH measurements were made at 25 ± 0.1°.

B. Optical Spectra.—Two series of spectral curves were run on solutions of both active and racemic sodium vanadyl(IV) tartrate. One series concerned dependence of spectrum upon pH; the other, variation of spectrum with concentration.

For pH dependence, the solutions were prepared by weighing out the sodium salts, dissolving them, adding perchloric acid, and diluting to give a concentration 0.0400 *M* in vanadyl(IV) ion. The pH values were taken within 10 min after dissolving the salts and the spectra within 15 min to minimize any air oxidation.

For concentration variation, the sodium salts of vanadyl(IV) tartrate were weighed out and dissolved in pH 7.51 borax–perchloric acid buffer. The buffer was found necessary to maintain a constant hydrogen ion concentration regardless of the sodium vanadyl(IV) tartrate concentration. That we could observe no difference between spectra of buffered and unbuffered solutions run at the same pH indicates no interference by the buffering ions. All spectra were run at room temperature (24–30°).

C. Electron Spin Resonance.—The esr spectra given were run on 0.0400 *M* solutions of the sodium salts of vanadyl(IV) tartrate at 25° using diphenylpicrylhydrazyl (DPPH) reference.

D. Magnetic Susceptibility.—Magnetic susceptibilities of the solid sodium salts were measured at 23°. $HgCo(CNS)_4$ was used as a standard to calibrate the instrument.

Results and Discussion

General Observations.—There is a striking difference between the anionic species formed by vanadyl(IV) ion with *d*-tartrate and that formed with *dl*-tartrate at higher pH in solution as evidenced by the color of the solution—the *d*- (or *l*-) tartrate giving a violet or purple solution, and the *dl*-tartrate, a red-brown solution. When equimolar amounts of solutions containing the vanadyl(IV) *d*-tartrate anionic species and the corresponding *l*-tartrate species are mixed, the color changes from violet to red-brown in 1–2 min at room temperature. This indicates that the *dl* complex both has a different spectrum and is more stable.

The spectra of solutions of the vanadyl(IV) tartrates exhibited no dependence on the nature of the compensating cation, whether sodium, potassium, ammonium, or tetramethylammonium. The reflectance spectrum of solid ammonium vanadyl(IV) *d*-tartrate[4] and the crystal absorption spectrum[11] of sodium vanadyl(IV) *dl*-tartrate are not significantly different from the solution spectra.

Formula Weights.—The osmometer determinations of sodium vanadyl(IV) *d*-tartrate and the corresponding *dl*-tartrate salts employed aqueous solutions 0.1 *M* in vanadyl(IV). The empirical formulas for these salts are $Na_2VO(d\text{-tart})\cdot 3H_2O$ and $Na_2VO(dl\text{-tart})\cdot 5.5H_2O$. The apparent formula weights determined were 188 and 232, respectively, before correction for the van't Hoff *i* factor and for nonideality. Let us suppose that the anionic complexes are dimeric, in which case we have five ions in solution for each formula dissolved, and calculate experimental uncorrected formula weights of 940 (188 × 5) and 1160 (232 × 5) for the *d* and *dl* salts. A nonideality correction is essential. It can be estimated from the osmotic coefficients of aqueous 0.05 *M* $K_4Fe(CN)_6$ and $K_4Mo(CN)_8$, for which we obtain about 0.64 by interpolation of reported data.[12] These factors correct the formula weights to 602 (940 × 0.64) and 742 (1160 × 0.64) which agree well with the respective expected formula weights of 626 for $Na_4[(VO)_2(d\text{-tart})_2]\cdot 6H_2O$ and 716 for $Na_4[(VO)_2(dl\text{-tart})_2]\cdot 11H_2O$.

If we assume that a single trimeric species is present so that we have a 6:1 electrolyte and therefore seven ions in solution, we calculate experimental formula weights of 658 and 812 for the *d* and *dl* salts, respectively, as compared with expected values of 939 and 1074 for $Na_6[(VO)_3(d\text{-tart})_3]\cdot 9H_2O$ and $Na_6[(VO)_3(dl\text{-tart})_3]\cdot 16.5H_2O$. A conservatively estimated osmotic coefficient of 0.5 for a 6:1 electrolyte in aqueous solution with a concentration of 0.033 *M* was used. Assumption of a trimeric species thus gives poor agreement between the experimental and calculated formula weights. Computations for higher polymeric species give even poorer agreement (experimental formula weights which are too low).

Similarly, assuming a monomeric species, we calculate formula weights for $Na_2[(VO)(d\text{-tart})]\cdot 3H_2O$ and $Na_2[(VO)(dl\text{-tart})]\cdot 5.5H_2O$ of 482 and 605, respectively, which disagree with expected values of 313 and 358. An osmotic coefficient of 0.87 was taken from data[12] for the 2:1 electrolyte $K_2Cr_2O_7$.

The results, therefore, strongly imply that the

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[9] K. M. Jones and E. Larsen, *Acta Chem. Scand.*, **19**, 1205 (1965).

[10] A. Findlay and A. N. Campbell, *J. Chem. Soc.*, 1769 (1928).

[11] Polarized spectral studies of single crystals are in progress and will be reported later.

[12] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworth and Co. Ltd., London, 1959.

vanadyl(IV) tartrate anions are dimeric in these aqueous solutions.

pH Titrations.—The pH titration curves, obtained as described in the Experimental Section, are shown in Figure 1 along with a curve for *d*-tartaric acid in the absence of vanadyl(IV) ion. The free acid in the vanadyl(IV) perchlorate solution was determined by titration of a 1:2 0.04 *M* vanadyl(IV) perchlorate–sodium oxalate solution. Ducret[5] found this method to give good results for determination of the free acid in a vanadyl(IV) solution. Ducret has published a *dl*-tartaric acid–vanadyl(IV) titration curve with which we agree qualitatively but not quantitatively. The curve obtained with *d*-tartaric acid has not been reported before, although Jørgensen[6] reported p*K* values for the addition of H^+ to the anionic species.

The vanadyl(IV) perchlorate–tartaric acid titration curves exhibit two plateaus corresponding to formation of complexes of interest to us. The first falls in the pH range 1.5–5, corresponding to 3 equiv of base added over and above that required to neutralize the initial free acid. The second falls between pH 5 and 7, corresponding to the addition of a fourth equivalent of base. A third plateau at very high pH values indicates the destruction of the anionic vanadyl(IV) tartrate species. It is generally agreed that the first two plateaus represent successive removal of hydrogens from the carboxyl and hydroxyl groups on the tartaric acid.

The tartrate ions are much more stable when complexed; accordingly, their pH titration curves are greatly lowered in the presence of vanadyl(IV).

Of particular interest is the comparison of the curves obtained with the *d*- and the *dl*-tartaric acid complexes. During the addition of the first 3 equiv of base, there is no significant difference between these curves. However, during the addition of the fourth equivalent, there are large changes in color which mark the formation of the vanadyl(IV) anionic complex containing the tetranegative tartrate group. Here, there is a marked difference between the curves for the active and racemic systems. The color in this region changes from dark blue to purple with the *d*-tartaric acid, and to red-brown with the *dl*-tartaric acid.

The difference in the pH values required for formation of the *d* and *dl* anionic complexes was verified in other independent pH titration plots of vanadyl(IV) sulfate–tartaric acid solutions using potassium hydroxide or aqueous ammonia titrants.

The higher stability of the racemic complex is reflected in the lower pH required for formation of the vanadyl(IV) *dl*-tartrate anionic species and also in the higher pH required for the *dl* complex to undergo the process represented by the last plateau (above pH 10). With somewhat more than 4 equiv of base added, presumably hydroxy complexes are formed and the *dl*-tartrate better competes with hydroxide for vanadyl(IV).

The essential equivalence of the vanadyl(IV) *d*-tartrate and *dl*-tartrate curves on the first plateau is good evidence that similar species are formed in both systems before the loss of the last hydrogen by the tartrate anion. In fact, it is also weak evidence (along with the spectra to be discussed) for the absence of other than mononuclear species in the region below pH 5, since one might argue that there would be some differences between species containing both *d*- and *l*-tartrate groups and species containing only *d*-tartrate groups and that such differences could be seen in the pH titration curves and in the spectra.

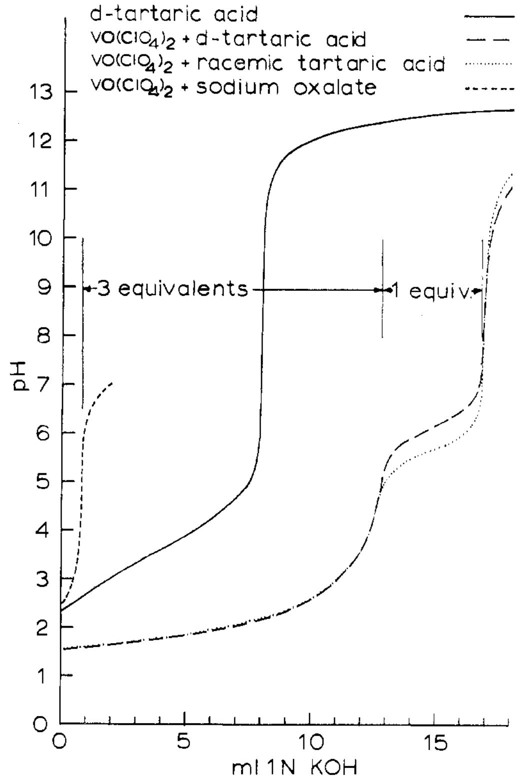

Figure 1. pH titration curves of vanadyl(IV) perchlorate with *d*- and *dl*-tartaric acids. See text for detailed procedure.

On the other hand, the divergence of the two curves during formation of the tetranegative tartrate complex makes it obvious that species containing more than one tartrate must exist in this region. We can calculate relative stability constants for these species if we assume that both are formed from the same monomeric complex (*i.e.*, similar species with identical thermodynamic properties) and that they are dimers. The concentration dependence of the spectra (see below) indicates that there is a mononuclear–polynuclear equilibrium in this region and the formula weight determination discussed previously as well as the electron spin resonance spectra strongly indicate that the polynuclear species is a dimer.

Let us assume that the second plateau of the vanadyl(IV) *d*-tartrate titration curves does represent an equilibrium of the form

$$2[(VO)(DH)]^- \rightleftharpoons [(VO)_2D_2]^{4-} + 2H^+ \qquad (1)$$

where DH represents a trinegative *d*-tartrate anion, and D, the tetranegative *d*-tartrate anion. We can use Ducret's method[5] to calculate the relative stability constants for the anionic complexes.

To obtain very accurate pH values at the midpoints of the plateaus, where we hope to assume that half the monomer has been converted to dimer, a back titration was used by adding 0.5 equiv of perchloric acid to the dissolved sodium salts. The solutions were then diluted to give exactly 0.0400 ± 0.0001 M solutions (based on the vanadyl(IV) ion) whose pH was taken within 10 min after dissolving the salts. This procedure was followed to decrease the possibility of inaccurate absolute pH values as read from the pH titration curves as a result of oxidation which could have occurred during the relatively long period of time required for the titration. The pH values thus obtained were 6.46 ($[H^+] = 3.47 \times 10^{-7}\ M$) for the vanadyl(IV) d-tartrate and 5.87 ($[H^+] = 1.35 \times 10^{-6}\ M$) for the corresponding dl-tartrate.

The stability constant is given by

$$K_d = \frac{[(VO)_2D_2][H^+]_d{}^2}{[(VO)(DH)]^2} \frac{f_{(VO)_2D_2}f_{H^+}{}^2}{f_{(VO)(DH)}{}^2} \qquad (2)$$

where the f's are the activity coefficients.

If, at the midpoint of the second plateau, half the vanadyl(IV) is contained in the dimer and half in the monomer, we have $[(VO)(DH)] = 2[(VO)_2D_2]$ and

$$K_d = \frac{[H^+]_d{}^2}{4[(VO)_2D_2]} \frac{f_{(VO)_2D_2}f_{H^+}{}^2}{f_{(VO)(DH)}{}^2} \qquad (3)$$

Similarly, the equilibrium equation and corresponding stability constant for the dl dimer are

$$[(VO)(DH)]^- + [(VO)(LH)]^- \rightleftharpoons [(VO)_2DL]^{4-} + 2H^+ \qquad (4)$$

$$K_{dl} = \frac{[H^+]_{dl}{}^2}{[(VO)_2DL]} \frac{f_{(VO)_2DL}f_{H^+}{}^2}{f_{(VO)(DH)}f_{(VO)(LH)}} \qquad (5)$$

since $[(VO)_2DL] = [(VO)(DH)] = [(VO)(LH)]$.

Taking the ratio of K_{dl} to K_d and assuming that the corresponding activity coefficients are equal, we find

$$\frac{K_{dl}}{K_d} = 4\frac{[H^+]_{dl}{}^2}{[H^+]_d{}^2} = \frac{(4)(1.35 \times 10^{-6})^2}{(3.47 \times 10^{-7})^2} = 60 = K \qquad (6)$$

This relative stability constant, K, is, of course, the equilibrium constant for the conversion of the two enantiomeric dimers to the racemic dimer

$$0.5[(VO)_2D_2]^{4-} + 0.5[(VO)_2L_2]^{4-} \rightleftharpoons [(VO)_2DL]^{4-} \qquad (7)$$

Optical Spectra.—Figures 2 and 3 illustrate the spectra obtained at various pH values in the active and racemic sodium vanadyl(IV) tartrates. In the regions of lower pH, where 1, 2, and 4 equiv of perchloric acid have been added (corresponding to the first plateau of the pH titration curves), no spectral differences between the d- and dl-tartrate systems can be detected. This again indicates, as did the pH titration curves, that similar species are present in both systems in the lower pH region. When less than 1 equiv of acid is added, however, markedly different spectra for the two systems are obtained. The anionic d-tartrate species gives a four-band[13] spectrum whereas the dl-tartrate complex shows three bands. Another major difference immediately apparent is the large shift in the lowest energy band, which lies at higher wavelengths for the vanadyl(IV) d-tartrate anionic species. On the other hand, the spectra also exhibit striking similarities. In particular, the general shapes of the curves are very similar and the location of the band at approximately 535 mμ is the same for both systems. We hope that future crystal spectra of these complexes will aid in explaining these differences and similarities and thus contribute to an understanding of the electronic structure of vanadyl(IV) complexes.

One might reasonably expect the vanadyl(IV) d-tartrate anionic complex, whose dimeric form is less stable, to show a greater concentration dependence than the dl-tartrate complex anion. This is indeed the case as can be seen in Figures 4 and 5. These spectra exhibit changes with concentration for which, for lack of sufficient data, we can offer only an incomplete explanation. They indicate that the d- and dl-tartrate systems do not form the same single monomeric species upon dilution since their respective spectral curves cross over at several points as the concentration is lowered rather than approaching the same extinction coefficients. Obviously, monomeric species containing only one tartrate ligand will not have different spectra whether containing d- or dl-tartrate anions. We must assume, therefore, that species other than 1:1 monomers are involved. There could be, for instance, formation of 1:2 complexes such as $[VO(d\text{-tart})_2H_n]^{n-6}$ and $[VO(d\text{-tart})(l\text{-tart})H_n]^{n-6}$ which could give different spectra.

It is not within the scope of this paper to examine possible assignments for the visible spectra of the $[(VO)_2(tart)_2]^{4-}$ complex ions. However, one fact essential to any interpretation is clearly established by this work. That is that the four-band spectrum of the active complex and the three-band spectrum of the racemic complex patently are not caused by overlapping spectra of various species in solution, as stated by Dunlop, *et al.*[8] (which is *not* to say that the spectra are uncontaminated by other species, but rather that the principal features of the specrat are reliably those of one dimeric species). First, the molecular weight measurements do not admit a wide range of species in concentrated solutions. Second, the four-band structure in the spectrum of the active form becomes most distinct at high concentrations where (1) hydroxy species are less likely to interfere, (2) the equilibrium is shifted away from possible mononuclear forms such as $[VO(tart)]^{2-}$ or $[VO(tart)_2H_n]^{n-6}$, and (3) the solution spectrum becomes essentially that of the pure crystalline salt. The latter observation is important, for if all ions of the solid are in chemically equivalent sites, then the solid spectrum certainly cannot be attributed to a mixture of species. (For part of this argument we are indebted to L. Morpurgo and J. Selbin in private discussions.)

Electron Spin Resonance.—It is in the electron spin resonance spectra that we find the most interesting aspect of the vanadyl(IV) tartrate system. The lower pH species exhibit the typical eight-peak esr spectra

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[13] The use of the word "band" is not meant to imply that there are only four electronic transitions involved. Better resolution by low-temperature work has often resolved bands which are featureless in solution at room temperatures. For examples of this in vanadyl(IV) complexes, see J. Selbin, T. R. Ortolano, and J. F. Smith, *Inorg. Chem.*, **2**, 1315 (1963), and G. Basu, W. Yeranos, and R. L. Belford, *ibid.*, **3**, 929 (1964).

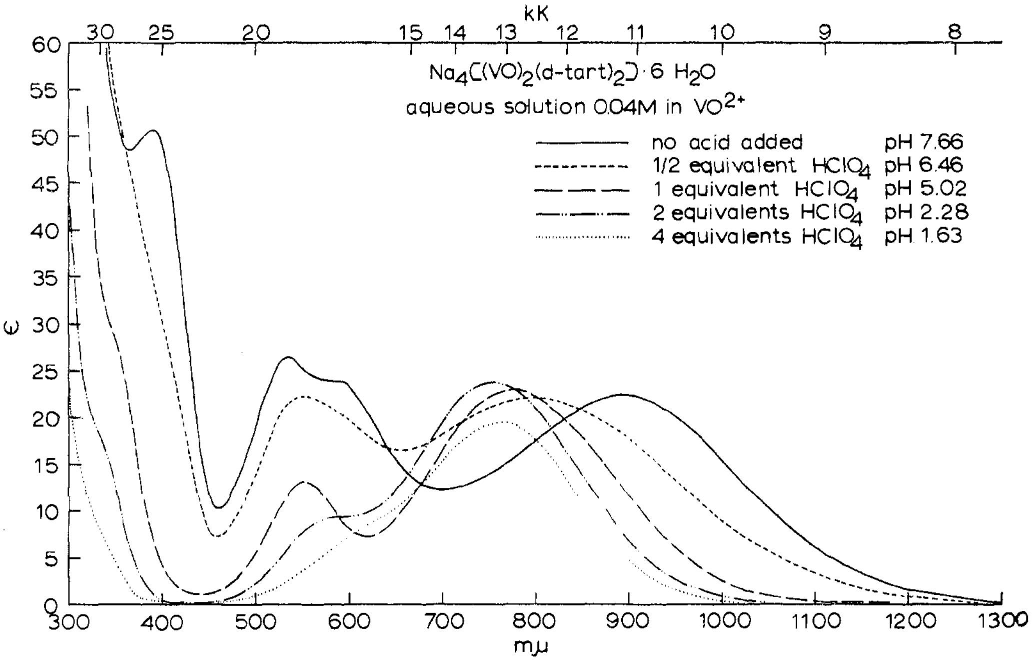

Figure 2.—pH dependence of absorption spectra of vanadyl(IV) *d*-tartrate solution. See text for procedure. Decadic molar extinction coefficient (ε) *vs.* wavelength. Extinction coefficient is based on total vanadium concentration.

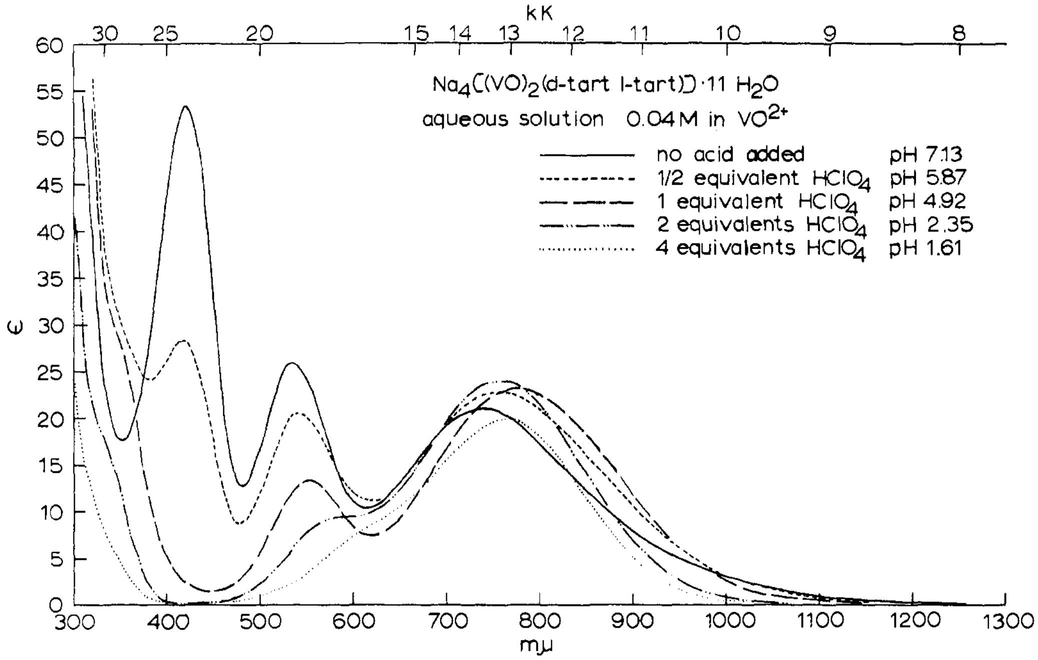

Figure 3.—pH dependence of absorption spectra of vanadyl(IV) *dl*-tartrate solution. See text for procedure. Decadic molar extinction coefficient (ε) *vs.* wavelength. Extinction coefficient is based on total vanadium concentration.

expected owing to splitting by the $^7/_2$ nuclear spin of vanadium. When the pH is raised, however, the spectra become more complicated and a 15-peak spectrum finally results upon formation of the *dl*-tartrate anionic complex (Figure 6). This is the spectrum expected from an electron interacting with two equivalent nuclei of spin $^7/_2$. For such a system, the areas of the peaks should be in the order 1:2:3:4:5:6:7:8:7:6:5:4:3:2:1, and the peak heights obtained upon integrating the esr first-derivative curves do, indeed, qualitatively follow this order. The actual relative magnitudes cannot be evaluated, however, because of the indeterminate areas as a result of overlap.

The spectrum of the *d*-tartrate complex (Figure 7) also shows more than eight bands, although, in this system, there appear to be interfering species. Kuska, *et al.*,[14] described some features of the esr spectra of the vanadyl(IV) *d*-tartrate system. It should be noted that in the case of vanadyl(IV) *dl*-tartrate anion, two overlapping eight-band spectra will not give the observed 15-peak spectrum, which we attribute to exchange between two metal nuclei of a dimer.

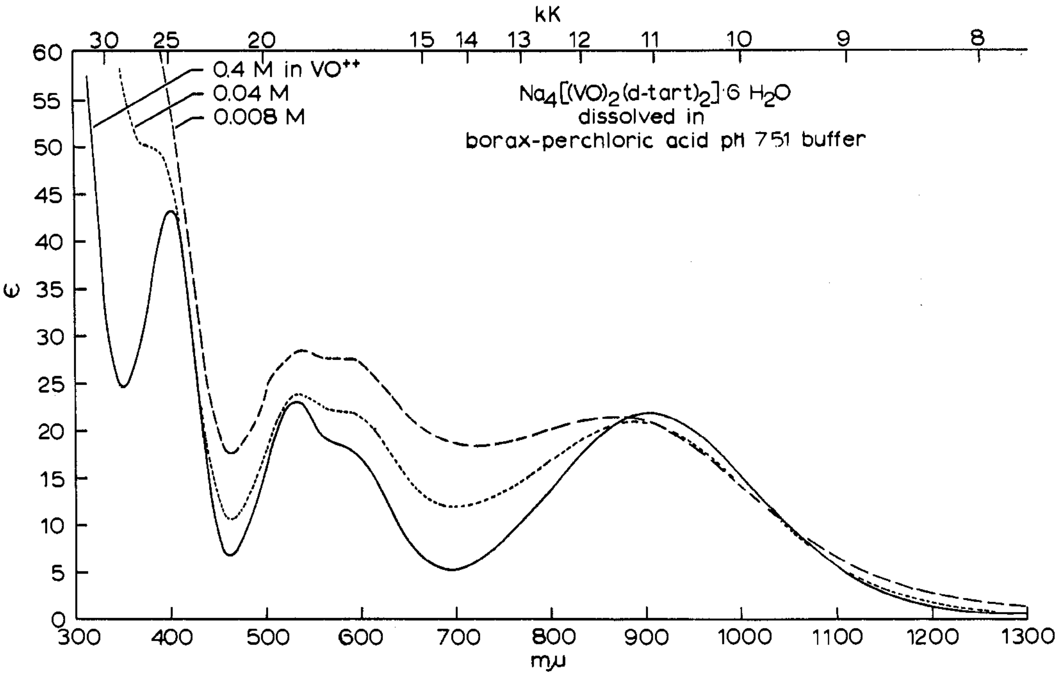

Figure 4.—Variation with concentration of absorption spectra of the sodium salt of vanadyl(IV) *d*-tartrate in aqueous solution.

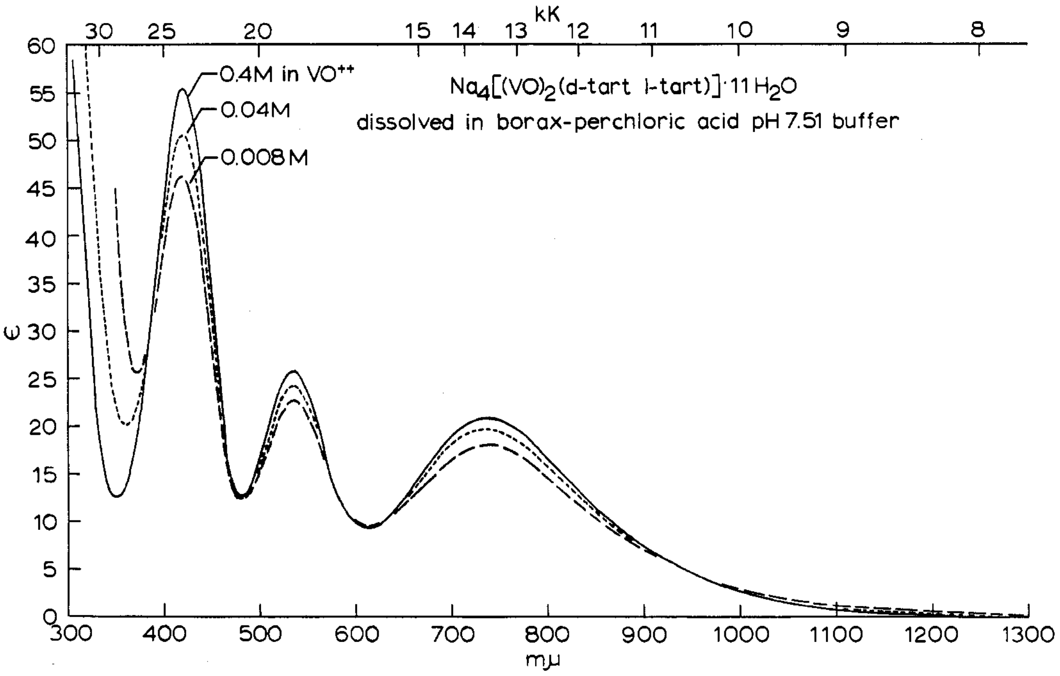

Figure 5.—Variation with concentration of absorption spectra of the sodium salt of vanadyl(IV) *dl*-tartrate in aqueous solution.

Kuska, *et al.*, report a g value of 1.974 for the *d*-tartrate complex at pH 7.2 and a splitting constant A of 88.5. This agrees with the A value which we calculate from the left side of Figure 7 by measuring twice the splitting between adjacent bands. For the vanadyl(IV) *dl*-tartrate anion we obtain a g value of 1.98 and a hyperfine splitting constant A of 80 gauss, derived from the experimental 40-gauss spacing.

Magnetic Susceptibility.—After correction for diamagnetism, the magnetic moments obtained were 1.72 BM for $Na_4[(VO)_2(d\text{-tart})(l\text{-tart})]\cdot 11H_2O$ and 1.75 BM for $Na_4[(VO)_2(d\text{-tart})_2]\cdot 7H_2O$. These are normal magnetic moments and thus indicate that the splitting between triplet and singlet states in the coupled system (evidenced by the esr spectra) is small in comparison with kT (T = 300°K); probably the splitting is not greater than 50 cm^{-1}. Temperature-dependent susceptibility measurements on these salts are in progress to establish the magnitude of the splitting.

Conclusions and Speculations

Based upon our observations, the following conclusions can be made.

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(14) H. A. Kuska, T. Krigas, and M. T. Rogers, 152nd National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

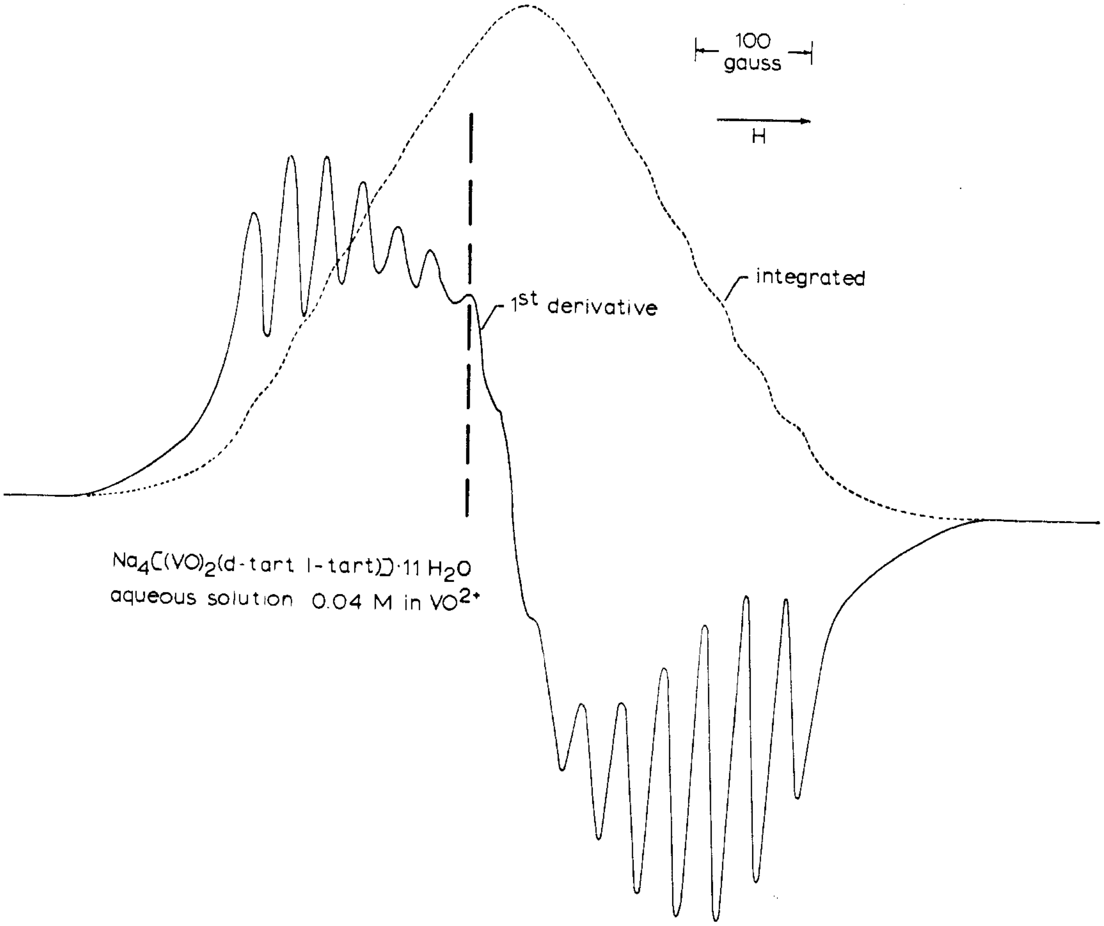

Figure 6.—Electron spin resonance spectrum of sodium vanadyl(IV) *dl*-tartrate, 0.04 *M* in H_2O. Vertical dashed line locates DPPH resonance.

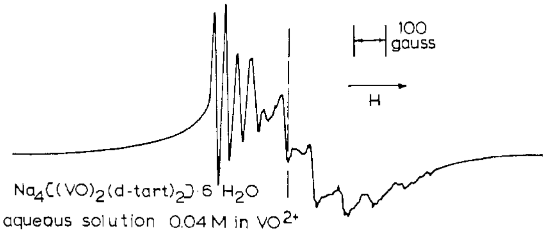

Figure 7.—Electron spin resonance spectrum of sodium vanadyl(IV) *d*-tartrate, 0.04 *M* in H_2O. Vertical dashed line locates DPPH resonance.

(1) When one to three hydrogens are removed from tartaric acid, complexes are formed with vanadyl(IV) which are similar for both the active and racemic systems.

(2) Upon removal of the fourth hydrogen from the tartrate anion, anionic dimeric complexes are formed containing two vanadyl(IV) ions bridged by two tetranegative tartrate ions.

(3) The dimers formed with *d*-tartrate ions and those formed with *dl*-tartrate ions differ in optical and esr spectra and in stability. The racemic dimer is more stable.

(4) Rapid electron exchange between the two vanadium nuclei occurs in the *dl* dimer and probably also in the *dd* dimer, but the exchange splitting is small (less than 50 cm^{-1}).

(5) The same anionic dimers which are the principal species in the concentrated solutions are the anions of the crystalline salts $M_4[(VO)_2(tart)_2]\cdot xH_2O$.

Obviously, given conclusion 5, one can learn much about these systems through an X-ray structural study of the salts. Such studies are in progress in this laboratory on the rubidium salt of the active form[15] and the sodium salt of the racemic form;[16] work on the ammonium salt of the active form was abandoned before completion when we learned that Prout[17] has solved the same structure. His results fully confirm that all of the vanadium atoms are in dimeric units. Moreover, the geometry which he has found is that which we had postulated by construction of molecular models. These proposed geometries for the *dd* and the *dl* dimers are shown in Figures 8 and 9.

It should be noted that there are significant geometric differences in these proposed structures. The *dd* structure contains vanadyl(IV) ions which are directly opposed whereas in the *dl* dimer they are staggered. Also, a *dl* dimer would have a *cis* arrangement about the vanadium, whereas a *trans* arrangement would be found in the *dd* dimer.

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[15] B. Bersted, I. C. Paul, and R. L. Belford, work in progress. See footnote *c* of Table I.

[16] R. E. Tapscott, I. C. Paul, and R. L. Belford, work in progress. The crystal belongs to space group Pbca, eight vanadium atoms per unit cell, with dimensions a = 19.73 A, b = 10.68, A, c = 12.22 A.

[17] C. K. Prout, Oxford University, England, private communication.

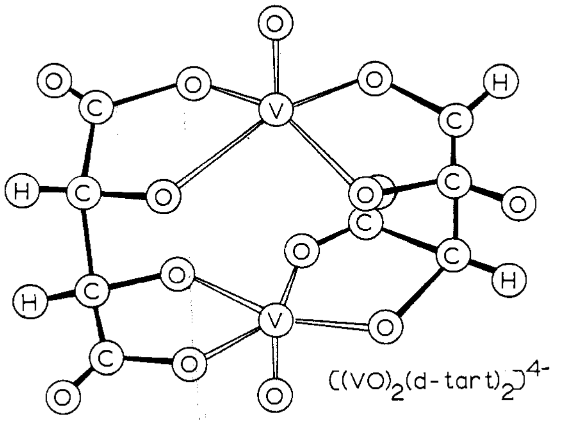

Figure 8.—Proposed structure of the vanadyl *dd* dimeric complex.

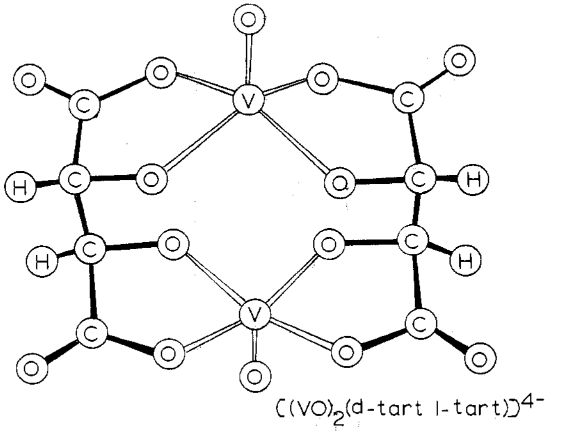

Figure 9.—Proposed structure of the vanadyl *dl* dimeric complex. Note that there is some flexibility in this model and that of Figure 8, on account of torsion about the single bonds.

These proposed structures bring about some interesting speculations. In the only X-ray crystallographic study[18] completed thus far on a vanadyl(IV) compound having *cis–trans* isomerism possible (vanadyl(IV) bisbenzoylacetonate), only the *cis* complex was obtained. It may be that vanadyl(IV) prefers a *cis* configuration and this is the reason for the higher stability of the *dl* dimer. Furthermore, it may be the *cis* and *trans* differences are what we see in comparing spectra of the active and racemic complexes. However, there are also difficulties in this proposition. Vanadyl(IV) lactates and mandelates are reported[4] to have four-band optical spectra very similar to that of the active tartrate. However, the lactate and mandelate would be free to form *cis* complexes with vanadyl(IV), in which case, if the *cis* is more stable, one would expect to see spectra more like those of the *dl*-tartrate than of the *d*-tartrate. Obviously, definitive conclusions on this matter cannot be reached until we know precisely what sort of complexes vanadyl(IV) forms with these and similar α-hydroxycarboxylates.

It is interesting to note that a recent paper[19] has presented temperature dependence of magnetic susceptibility of powders of other vanadyl(IV) complexes with tridentate ligands. These were interpreted on the basis of dimers with singlet–triplet exchange splittings ranging from 90 to 218 cm^{-1}, and a general structure is proposed in which two vanadyl(IV) ions are linked by two common atoms in a coordination plane. The vanadium nuclei in that case would be less than 3 A apart, while according to our models (Figures 8 and 9) the distance would be at least 4 A in the active vanadyl(IV) tartrate dimer and still larger in the racemic dimer.[20] Furthermore, the *xy* orbitals in which we presume the odd electrons to reside would be better oriented for overlap in the compounds studied by Ginsberg, *et al.*, than in the tartrate complexes having the proposed structures. Thus we are not surprised to find the exchange splittings to be much smaller in the tartrates.

Acknowledgment.—The authors wish to thank Mr. Josef Nemeth, who did the formula weight determinations and aided in the analytical work. R. L. B. thanks the National Institute of General Medical Sciences for a Senior Fellowship.

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(18) P. K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.*, **43**, 1323 (1965).

(19) A. P. Ginsberg, E. Koubek, and H. J. Williams, *Inorg. Chem.*, **5**, 1656 (1966). Also see references cited therein concerning previous papers by Zelentsov.

(20) NOTE ADDED IN PROOF.—Since submission of this paper, we have essentially completed the structural study (footnote 16) of the *racemic* sodium salt, finding the structure predicted in Figure 9 with a V–V distance of 4.06 A. J. G. Forrest and C. K. Prout (private communication, see footnote 17) report severe distortion of the coordination arrangement about V in the *active* ammonium salt, leading to a V–V distance of 4.35 A.