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Preparation, Characterization, and Stereochemistry of Binuclear Vanadyl(IV) Monomethyl- and Dimethyltartrate(4–) Complexes and the Crystal Structure of Tetrasodium [μ-(+)-Dimethyltartrato(4–)]-[μ-(–)-dimethyltartrato(4–)]-bis(oxovanadate(IV)) Dodecahydrate[1]

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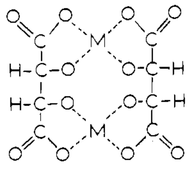
The syntheses and characterizations (by ESR, IR, and electronic spectroscopies) of the sodium salts of the DL and DD (or LL) binuclear complexes of vanadyl(IV) with dimethyltartrate(4–), "dmt", and with monomethyltartrate(4–), "mmt", are described. $Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]$ exists in two crystal forms—a blue dodecahydrate and a pink hexahydrate. An X-ray diffraction study of the former shows that the V–V distance (3.429 (3) Å) of the binuclear anion is decreased relative to that of the unsubstituted tartrate(4–), "tart", complex, as predicted from earlier ESR studies, and that this decrease is due in part to a dropping of the vanadium atom into the plane of the four coordinating equatorial oxygen atoms. A sixth oxygen atom is weakly coordinated (2.377 (3) Å) trans to the vanadyl oxygen atom. A purple tetradecahydrate also obtained with racemic dmt contains a mixture of $[(VO)_2((+)\text{-dmt})_2]^{4-}$ and $[(VO)_2((-)\text{-dmt})_2]^{4-}$. The aqueous solution ligand-exchange reaction between the DD and LL complexes of this salt to give the more stable DL isomer is remarkably slow (several hours at room temperature). Stereoselective effects allow the production of mixed-ligand species containing two of the three ligands tart, dmt, and mmt, and potentiometric titrations indicate a decreasing stability of the DL isomer (relative to the DD and LL isomers) as methyl substitution increases.

Introduction

Binuclear tartrate-bridged complexes (**1**) of Sb(III), As(III), Cu(II), V(IV), and Cr(III) have been reported.[3] Of particular interest are the tartrate(4–)-bridged complexes of vanadyl(IV), which are known in three isomeric forms—DD, LL, and DL—depending on the enantiomeric forms of the bridging ligands.[4] Besides exhibiting a large stereoselectivity, which favors formation of the DL isomer,[5] these exchange-coupled species exhibit unusually well-defined triplet-state ESR spectra in aqueous solution at room temperature.[4] Moreover, the vanadyl(IV) tartrate(4–) complexes are the only discrete, exchange-coupled, binuclear vanadyl(IV) complexes known to have a spin-triplet ground state.[6,7]



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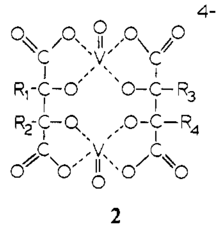
Recently, magnetic susceptibility[7] and low-temperature ESR[8] studies have been reported for binuclear vanadyl(IV) complexes containing methyl-substituted tartrate(4–) bridges (**2**). In addition, studies of the stereoselective effects observed for these methyl-substituted systems have been used to assign absolute configurations to resolved *threo*-monomethyltartaric acid, HOOCC(CH_3)(OH)CH(OH)COOH ("H_4mmt"), and dimethyltartaric acid, HOOCC(CH_3)(OH)C(CH_3)(OH)COOH ("H_4dmt").[9] In this paper, we report the previously undescribed syntheses and characterizations of these binuclear methyl-substituted tartrate complexes, spectral studies of the isomeric and crystal forms, and the structure of the blue dodecahydrate crystal form of the DL isomer of the bis(dimethyltartrato(4–)) complex, which is shown to exhibit the shortened V–V distance predicted from earlier ESR studies.[8]



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R_1, R_2, R_3, R_4 = H and/or CH_3

Experimental Section

Ligands. The various isomers of tartaric acid, $C_4H_6O_6$, were used as obtained commercially. Dimethyltartaric acid, $C_6H_{10}O_6$, and monomethyltartaric acid, $C_5H_8O_6$, were prepared and the isomers separated by literature methods.[10-13] Satisfactory elemental analyses were obtained for all ligands prepared, and melting points and molar rotations were in good agreement with reported values.[12]

Tartrate(4–) Complexes. Tetrasodium (μ-(+)-tartrato(4–)]-[μ-(–)-tartrato(4–)]-bis(oxovanadate(IV)) dodecahydrate, $Na_4[(VO)_2((+)\text{-tart})((-)\text{-tart})]\cdot 12H_2O$, and the sodium and ammonium salts of the corresponding active complex, $Na_4[(VO)_2((+)\text{-tart})_2]\cdot 6H_2O$ and $(NH_4)_4[(VO)_2((+)\text{-tart})_2]\cdot 2H_2O$, were prepared by literature methods.[4] Satisfactory elemental analyses were obtained.

(±)-Dimethyltartrate(4–) Complex Salts. Tetrasodium [μ-(+)-dimethyltartrato(4–)]-[μ(–)-dimethyltartrato(4–)]-bis(oxovanadate(IV)) dodecahydrate, $Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]\cdot 12H_2O$, was prepared by the following reactions (in which the lower pH species is assumed binuclear as is found for the tartrates[14]) and procedure.

$$2VOSO_4(aq) + 2Ba(OH)_2(s) + 2C_6H_{10}O_6(aq) \rightarrow (VO)_2(C_6H_8O_6)_2(aq) + 2BaSO_4(s) + 4H_2O$$

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$$(VO)_2(C_6H_8O_6)_2(aq) + 4NaOH(aq) \rightarrow Na_4[(VO)_2(C_6H_6O_6)_2](aq) + 4H_2O$$

To a solution of vanadyl(IV) sulfate (4 mmol, 0.989 g based on an equivalent mass of 247 determined by EDTA titration) and (±)-dimethyltartaric acid (4 mmol, 0.713 g) in 4 mL of H_2O was added finely ground $Ba(OH)_2 \cdot 8H_2O$ (4 mmol, 1.262 g), and the mixture was heated on a steam bath with stirring until a smooth homogeneous slurry was obtained. $BaSO_4$ was removed by filtration and washed, and the washings were combined with the filtrate to give ~7.5 mL of solution. The vanadyl(IV) dimethyltartrate(2–) solution was brought to pH ~9 by addition of 11 M NaOH solution to give the binuclear tetranegative complex. Addition of 95% ethanol with gentle stirring and heating followed by cooling gave 1.049 g (66% yield) of blue crystalline material, which was washed consecutively with 50% ethanol, 95% ethanol, and acetone and was dried with suction. This blue solid consisted of diamond-shaped plates, which were strongly dichroic under polarized light (light violet with polarization along one axis of the diamond and blue to blue-green with polarization along the other axis). Anal. Calcd for $Na_4[(VO)_2(C_6H_6O_6)_2] \cdot 12H_2O$: C, 18.24; H, 4.59; V, 12.93; H_2O, 27.3. Found: C, 18.36; H, 4.51; V, 12.75; H_2O, 28.2.

The blue dodecahydrate lost water spontaneously under ambient conditions to give a violet-pink material, which analyzed as ~3.5-water complex and which could be rehydrated to give the blue dodecahydrate as a powder.

Dissolution of the blue dodecahydrate in water to give a relatively dilute solution followed by addition of a large excess of 95% ethanol with strong heating gave a pink solid consisting of a mixture of diamond-shaped plates, which were strongly dichroic under polarized light (purple-blue and red), and hexagons. Both crystal types (which could be reconverted to the blue dodecahydrate by dissolution and reprecipitation with ethanol) appeared to be different habits of the same crystal type. Rapid precipitation of the pink compound produced dendrites. Anal. Calcd for $Na_4[(VO)_2(C_6H_6O_6)_2] \cdot 6H_2O$: C, 21.13; H, 3.55; V, 14.94; H_2O, 15.8. Found: C, 21.10; H, 3.69; V, 15.24; H_2O, 15.4.

From the dilute filtrate remaining after removal of the blue or pink forms of the dimethyltartrate complex, purple plates or dendrites were slowly deposited upon cooling overnight in a refrigerator. The diamond-shaped plates (interfacial angles of ~99 and ~81°) were dichroic under polarized light (dark violet with the electric vector along the longer axis of the diamond, light violet with the electric vector along the shorter axis). Anal. Calcd for $Na_4[(VO)_2(C_6H_6O_6)_2] \cdot 14H_2O$: C, 17.44; H, 4.88; V, 12.3; H_2O, 30.5. Found: C, 17.58; H, 4.86; V, 12.8; H_2O, 30.0.

The use of excess $Ba(OH)_2$ in the preparation of the racemic vanadyl(IV) dimethyltartrate(4–) complexes gave a purple barium-containing solid, which exhibited a large temperature dependence of water solubility. Anal. Calcd for $Ba_2[(VO)_2(C_6H_6O_6)_2] \cdot 12H_2O$: C, 14.81; H, 3.73. Found: C, 14.56; H, 3.52.

(+)- and (–)-Dimethyltartrate(4–) Complexes. These compounds, as the sodium salts, were prepared from resolved dimethyltartaric acid with use of a procedure analogous to that used to prepare complexes of the racemic ligand. Slow cooling of solutions of the complex salts in ethanol/water mixtures gave elongated purple hexagonal prisms. Anal. Calcd for $Na_4[(VO)_2(C_6H_6O_6)_2] \cdot 12H_2O$: C, 18.24; H, 4.59; V, 12.9; H_2O, 27.4. Found: C, 18.53; H, 4.81; V, 12.3; H_2O, 27.6.

(±)-*threo*-Monomethyltartrate(4–) Complex Salts. The tetrasodium salt, which was prepared by the method employed for the dimethyltartrates, was obtained as two different hydrates, which, except for analyses and powder ESR spectra (vide infra), had nearly identical properties. Slow cooling of warmed ethanol/water solutions of the salt produced a tetradecahydrate (confirmed by a crystal structure determination[15]) consisting of elongated plates, which were light brown when viewed perpendicular to the largest face and violet-brown when viewed from the side. Anal. Calcd for $Na_4[(VO)_2(C_5H_4O_6)_2] \cdot 14H_2O$: C, 15.05; H, 4.56. Found: C, 15.12; H, 4.56.

The tetradecahydrate was relatively stable toward dehydration under ambient conditions; however, a brown decahydrate was consistently produced by rapid precipitation of microcrystalline (needles and plates) material by addition of 95% ethanol to warm solutions of the tetrasodium salt and rapid cooling. Anal. Calcd for $Na_4[(VO)_2(C_5H_4O_6)_2] \cdot 10H_2O$: C, 16.54; H, 3.89; V, 14.03; H_2O, 24.2. Found: C, 16.56; H, 3.88; V, 14.00; H_2O, 24.8.

When growing the brown tetradecahydrate crystals, we occasionally found them mixed with highly irregular violet crystals, which, when mechanically separated, analyzed well as a dodecahydrate and gave an IR spectrum identical with those of the other forms. These crystals were difficult to obtain free of other forms, and the powder ESR spectrum was that expected for a mixture of the deca- and tetradecahydrates. We were unable to obtain crystals that were not twinned for a complete X-ray study; however, preliminary work on one twinned crystal indicated a triclinic cell of slightly larger volume than that determined for the tetradecahydrate.[15]

(+)- and (–)-*threo*-Monomethyltartrate(4–) Complexes. These complexes, prepared by the method described earlier, were difficult to isolate as solid sodium salts owing to their extreme water solubility. Solid glasses, analyzing as octahydrates, could be obtained, however, by allowing solutions of the tetrasodium salts to evaporate under ambient conditions. Anal. Calcd for $Na_4[(VO)_2(C_5H_4O_6)_2] \cdot 8H_2O$: C, 17.41; H, 3.51. Found: C, 17.90; H, 3.40.

Physical Measurements. Electronic spectra between 1300 and 300 nm were determined on both solids and solutions on a Cary 14RI spectrophotometer. Nujol mulls of the solid complex salts were run against Nujol mulls of sodium chloride as references (to help compensate for light scattering). Aqueous solutions were prepared under anaerobic conditions by dissolution of the solids ($[VO^{2+}] = 0.02–0.1$ M) or by addition of NaOH solution to 1:1 mixtures of ligand and vanadyl(IV) perchlorate solutions to give a vanadyl(IV) concentration of 0.02 M and a pH of 8–9.

X-Band ESR spectra of both powders and aqueous solutions were obtained with either a Varian V-4500 or a Bruker ER-200D spectrometer, both equipped with a 12-in. magnet. Aqueous solutions ($[VO^{2+}] = 0.025–0.2$ M) were prepared anaerobically either by dissolution of the tetrasodium salt or by preparation of the complex from ligand/vanadyl(IV) perchlorate solution and NaOH solution.

Infrared spectral band positions (± 3 cm^{-1}) were taken from spectra collected on a Perkin-Elmer 621 grating spectrometer using KBr pellets.

Potentiometric titrations were carried out on aqueous solutions containing 1:1 mixtures of ligand and vanadyl(IV) perchlorate (initial $[VO^{2+}] = 0.01$ M) at 25.0 ± 0.5 °C under anaerobic conditions with 0.185 M NaOH titrant. Hydrogen ion activities were determined with use of an Orion 801 digital pH meter calibrated with NBS standard buffers. Free acid in the vanadyl(IV) perchlorate solution was determined by titration in the presence of sodium oxalate.[4]

X-ray Diffraction Study of $Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})] \cdot 12H_2O$. Crystals of the blue dodecahydrate form of sodium vanadyl(IV) (±)-dimethyltartrate(4–) were obtained by evaporation of an aqueous solution. A blue triangular prismatic specimen was selected, mounted on the tip of a glass fiber, and coated with a thin film of epoxy cement to prevent dehydration.

Preliminary Weissenberg and precession photographs showed systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, corresponding to space group $P2_1/n$, a nonstandard setting of No. 14, $P2_1/c$. The crystal was then transferred to a Datex-automated Picker four-circle diffractometer, and following optical and X-ray alignment, 20 reflections, $7° \leq 2\theta(\text{Mo } K\alpha) \leq 36°$, were centered. Least-squares refinement of the angle settings yielded the unit cell dimensions given in Table I.

Data collection using zirconium-filtered Mo $K\alpha$ radiation and employing a θ–2θ scan technique with collection of a full hemisphere of data out to $2\theta = 55°$ was carried out at room temperature. Three standard reflections, which were measured every fifty reflections, showed no appreciable change during the data collection period. The net intensities were corrected for Lorentz and polarization effects. No absorption or extinction corrections were applied. The $T_{max}:T_{min}$ ratio is 1.1.

Solution and Structure Refinement.[16] The structure was solved

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(16) The computer programs used include: MULTAN, multiple-solution tangent-formula program (Declerq, J. P.; Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A*, **1973**, *A29*, 231); XRAY 76 (Stewart, J. M., Ed., Technical Report TR-446; University of Maryland Computer Science Center: College Park, Md., 1976); SHELXTL 79 plotting programs (Sheldrick, G. M. "Nicolet SHELXTL Operations Manual"; Nicolet XRD Corp.: Cupertino, Calif., 1979). All computations except for plotting were carried out on the IBM 360/67 computer at the University of New Mexico.

Table I. Summary of Crystal Data for $C_{12}H_{36}O_{26}Na_4V_2$

fw	786.18
a, Å	11.632 (4)
b, Å	11.95 (1)
c, Å	10.975 (4)
β, deg	98.04 (3)
V, Å^3	1511.2 (9)
Z	2
ρ, g cm^{-3}	1.737 (calcd), 1.72 (obsd)
space group	$P2_1/n$
cryst dimens, mm	0.72 × 0.50 × 0.60 × 0.22
cryst shape	prism with bounding planes $(\bar{1}\bar{2}\bar{1})$, (101), (010), $(10\bar{1})$, $(\bar{1}01)$
radiation	Mo Kα (λ = 0.710 69 Å)
abs coeff, μ(Mo Kα), cm^{-1}	8.17
takeoff angle, deg	3.0
scan speed, deg min^{-1}	2.0
2θ scan range	1.0° below Kα_1-1.0° above Kα_2
bkgd counting time, s	40
2θ limits, deg	3.0–55.0
reflcns collected	7851 total
unique reflcns	3531
unique data used	2476 with $F_o^2 \geqslant 3\sigma(F_o^2)$
$R(F)$	0.045
$R_w(F)$	0.073
F_{000}	812

by MULTAN using 499 *E*'s with $1.2 < |E| < 4.1$. The three origin-defining reflections and five additional reflections were automatically selected as the starting set by the program. An *E* map calculated from the fifth best phase set yielded the positions of the two independent sodium atoms, the vanadium atom, and the five coordinated oxygen atoms. All nonhydrogen atoms were located on subsequent Fourier maps. Isotropic least-squares refinement of this model converged after four cycles to $R(F) = 0.087$ and $R_w(F) = 0.122$ where $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w^2(F) = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$, with $w^{-1} = \sigma^2(F_o) + C^2F_o^2$.[17] The factor *C* was estimated at 0.0137.

At this point, anomalous dispersion corrections[18] were applied to the sodium and vanadium scattering factors, all atoms not bonded to hydrogen were assigned anisotropic thermal parameters, and the refinement was continued. After two cycles of least-squares refinement, a difference Fourier map revealed the locations of the eighteen independent hydrogen atoms, whose coordinates were then idealized. The H–O–H angles and O–H distances for the water molecules were set at 105° and 1.00 Å, respectively. The methyl groups were idealized to tetrahedra with C–H distances of 1.00 Å. Isotropic thermal parameters of 5.0 Å^2 were assigned to the hydrogen atoms. No attempt was made to refine any hydrogen atom parameters.

Anisotropic full-matrix least-squares refinement of all nonhydrogen atoms gave $R_1(F) = 0.045$ at convergence. During the final cycle of refinement, no parameter shifted by more than 0.7σ. The final data:parameter ratio was 14.6:1 with 199 variables refined. The largest peak in the final difference map was less than 0.2 e Å^{-3}. Neutral-atomic scattering factors for all nonhydrogen atoms were taken from Cromer and Mann[19] while that for hydrogen was taken from Stewart et al.[20]

Table II gives atomic positions and thermal parameters with estimated standard deviations for the nonhydrogen atoms as determined in the final least-squares refinement. Idealized hydrogen positions and a listing of the observed and calculated structure factors are available.[21]

Results and Discussion

Potentiometric Titrations. pH titration curves for 1:1 mixtures of tartrate with vanadyl(IV) ion have been reported previously[4,22] but are reproduced here for easy reference (Figure 1). In these curves, a lower pH buffer region corresponding to addition of 3 equiv of base (per mole of VO^{2+}) over and above that required to neutralize the free acid in the vanadyl(IV) perchlorate is followed by a higher pH plateau for the addition of a fourth equivalent of base. Pettit and Swash[22] have shown that the principal reaction in this higher pH plateau region is deprotonation of a dinegative binuclear complex to give tetranegative complexes—presumably those found in crystal structure determinations.[23-25] It is only in this higher pH plateau region, corresponding to the addition of a fourth equivalent of base, that there are easily discernible differences between the titration curves obtained with optically active and racemic tartaric acids. These differences arise owing to stereoselective formation of primarily the DL isomer in the racemic system.

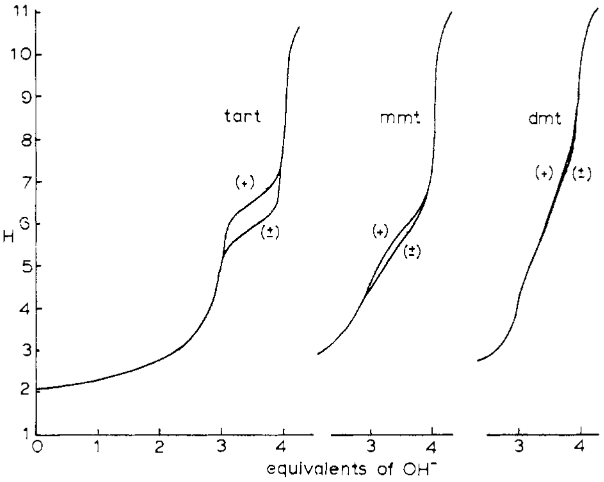

Figure 1. Titration curves for 1:1 mixtures of VO^{2+} (initial [VO^{2+}] = 0.01 M) and ligand with 0.185 M NaOH in aqueous solution. The abscissas give the equivalents of base added per mole of VO^{2+} over and above that required to neutralize the free acid in the VO^{2+} solution.

The titration curves for 1:1 mixtures of vanadyl(IV) with methyl-substituted tartaric acids are similar to those obtained with unsubstituted tartrates though the buffer region that occurs upon addition of the fourth equivalent of base rises more steeply. Again differences between optically active and racemic systems are observed primarily in these higher pH plateaus, which are shown in Figure 1. Assuming that these plateaus correspond to successive deprotonations of binuclear complexes as found for the tartrates,[22] we have calculated p*K* values for these deprotonation steps shown by eq 1 and 2. The

$$H_2(VO)_2(\text{ligand})_2^{2-} \overset{K_1}{\rightleftharpoons} H(VO)_2(\text{ligand})_2^{3-} + H^+ \quad (1)$$

$$H(VO)_2(\text{ligand})_2^{3-} \overset{K_2}{\rightleftharpoons} (VO)_2(\text{ligand})_2^{4-} + H^+ \quad (2)$$

p*K* values were determined by solving simultaneous equations involving data from only two titration curve points (near 3.25 and 3.75 equiv of base added). A more elaborate fit of the titration data is not justified since no attempt was made to hold ionic strength constant and the possible presence of mononuclear species (known to be present to a small extent in the tartrate system)[22] has been ignored. We note, however, that nonideality corrections should be nearly identical for these very similar systems and, therefore, though the interpretation of the absolute values obtained may be debatable, the relative values are much more meaningful. The results are given in Table III. The mixed-ligand results, obtained for mixtures

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Table II. Positional Parameters and Thermal Factors for Nonhydrogen Atoms in $Na_4[(VO)_2((+)\text{-}C_6H_6O_6)((-)\text{-}C_6H_6O_6)]\cdot 12H_2O$[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	0.46289 (5)	0.13773 (4)	0.01393 (5)	200 (4)	165 (3)	117 (3)	4 (2)	42 (2)	4 (2)
Na(1)	0.8836 (1)	0.0742 (1)	0.4378 (2)	384 (9)	324 (9)	401 (10)	−22 (7)	4 (7)	4 (7)
Na(2)	0.6994 (1)	0.3591 (1)	0.3325 (2)	248 (7)	345 (8)	268 (8)	−37 (6)	20 (6)	−10 (6)
O(1)	0.1822 (2)	0.0893 (2)	0.1756 (3)	253 (13)	335 (14)	284 (14)	25 (11)	112 (11)	67 (11)
O(2)	0.4478 (3)	0.1198 (2)	−0.3461 (2)	332 (14)	383 (15)	146 (12)	60 (11)	44 (10)	72 (10)
O(3)	0.2974 (2)	0.1530 (2)	0.0464 (2)	211 (12)	245 (12)	175 (12)	56 (9)	59 (9)	26 (9)
O(4)	0.3957 (2)	0.1154 (2)	−0.1605 (2)	193 (11)	356 (14)	130 (11)	45 (9)	38 (9)	−10 (9)
O(5)	0.4865 (2)	0.1172 (2)	0.1932 (2)	225 (11)	199 (11)	139 (11)	−47 (8)	40 (9)	1 (8)
O(6)	0.5893 (2)	0.0515 (2)	−0.0444 (2)	225 (11)	196 (11)	110 (10)	20 (9)	43 (8)	11 (8)
O(7)	0.5061 (3)	0.2665 (2)	0.0084 (2)	372 (14)	215 (12)	232 (13)	−30 (11)	66 (10)	6 (10)
O(8)	0.0548 (3)	−0.0011 (2)	0.3619 (3)	408 (15)	354 (15)	278 (14)	−93 (13)	106 (12)	5 (11)
O(9)	0.8003 (3)	0.0555 (3)	0.1144 (3)	370 (15)	427 (17)	355 (16)	−58 (13)	18 (13)	25 (13)
O(10)	0.9848 (3)	0.1761 (3)	0.0435 (3)	345 (14)	390 (15)	264 (14)	38 (12)	20 (11)	−18 (12)
O(11)	0.7214 (3)	0.1544 (3)	0.3112 (3)	372 (16)	384 (16)	455 (19)	−33 (13)	3 (14)	−33 (13)
O(12)	0.5012 (2)	0.3256 (2)	0.2953 (3)	313 (13)	275 (12)	280 (14)	−41 (11)	69 (11)	−46 (11)
O(13)	0.6995 (2)	0.3957 (2)	0.1136 (3)	313 (14)	338 (14)	307 (15)	0 (11)	2 (11)	−5 (12)
C(1)	0.2791 (3)	0.1028 (3)	0.1445 (3)	240 (16)	205 (14)	171 (15)	22 (13)	57 (12)	−7 (12)
C(2)	0.3901 (3)	0.0551 (3)	0.2226 (3)	219 (15)	233 (15)	137 (14)	7 (12)	71 (12)	−4 (12)
C(3)	0.5922 (3)	0.0651 (3)	−0.1738 (3)	230 (15)	211 (15)	120 (14)	−11 (12)	62 (11)	−33 (12)
C(4)	0.4707 (3)	0.1027 (3)	−0.2349 (3)	239 (16)	202 (14)	171 (15)	4 (12)	46 (12)	31 (12)
C(5)	0.3800 (3)	0.0642 (3)	0.3595 (3)	353 (19)	371 (20)	133 (15)	−11 (15)	99 (14)	−24 (14)
C(6)	0.6844 (3)	0.1509 (3)	−0.1979 (4)	250 (17)	281 (18)	297 (19)	−50 (14)	80 (4)	9 (14)

[a] The form of the thermal factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. The thermal parameters are $\times 10^4$.

Table III. pK Values for Deprotonation of $H_2(VO)_2(\text{ligand})_2^{2-}$

ligand	pK_1	pK_2	pK_2 − pK_1
(±)-tart	7.09	4.69	−2.40
(+)-tart	7.01	5.99	−1.03
(±)-mmt	5.19	5.98	0.80
(+)-mmt	5.44	6.31	0.88
(±)-dmt	5.21	6.94	1.73
(+)-dmt	5.24	7.19	1.95
(+)-tart/(+)-mmt	5.61	5.96	0.35
(+)-tart/(+)-dmt	5.71	6.60	0.89
(+)-mmt/(−)-dmt	5.24	6.47	1.23

Table IV. pK_3 Values for the Reaction $^1/_2$DD + $^1/_2$LL ⇄ DL for the Complexes $(VO)_2(\text{ligand})_2^{4-}$

system	no. of methyl groups/ DL complex	pK_3	system	no. of methyl groups/ DL complex	pK_3
tart	0	−1.22	tart/dmt	2	−0.40
tart/mmt	1	−0.80	mmt/dmt	3	−0.38
mmt	2	−0.58	dmt	4	−0.28

of ligands with opposite absolute configurations, though determined for systems known to give primarily a single DL isomer at higher pH,[9] must be viewed with caution since several binuclear isomers may be present at lower pH and the pK values may be composite.

Our results that pK_1 > pK_2 for the unsubstituted vanadyl(IV) tartrates are in agreement with equilibrium studies showing that the species $H(VO)_2(\text{tart})_2^{3-}$ is present to only a small extent in any pH region.[22] That the second deprotonation in the plateau region of interest occurs more readily than the first is probably due to a molecular rearrangement, which takes place during the deprotonation. ESR studies indicate structural changes as a result of pH variations even though the complexes remain binuclear.[14] In the presence of only statistical factors, $K_1/K_2 = 4$ for a diprotic acid with equivalent sites available for deprotonation.[26] Electrostatic interactions are expected to cause the ratio to be even larger ($K_1/K_2 > 4$, pK_2 − pK_1 > 0.6). For most of the methyl-substituted complexes, the pK_2 − pK_1 values are in the range expected though this does not rule out the presence of molecular rearrangements during deprotonation for these systems also. Any structural changes should be less effective in causing a reversal of pK values for the methyl-substituted systems since the resultant tetranegative binuclear complexes are expected to be destabilized by gauche methyl–methyl or methyl–hydrogen interactions.

Aqueous solution electronic spectra of active and racemic species formed after addition of 3 equiv of OH^- (i.e., for $H_2(VO)_2(\text{ligand})_2^{2-}$) are nearly identical. Moreover, except in the region where the fourth equivalent of base is added, pH titration curves of the active and racemic systems show only minor differences. Finally, there are known to be essentially no differences between the stability constants of species formed below the third equivalence point in active and racemic vanadyl(IV) tartrate solutions.[22] From these observations, we may assume that the systems containing the lower pH species $H_2(VO)_2(\text{ligand})_2^{2-}$ have free energies that are nearly independent of the ligand isomer composition and that we can use the pK values given in Table III to determine the equilibrium constant K_3 for interconversion of active and racemic tetranegative binuclear complexes (eq 3).

$$^1/_2(VO)_2(\text{D-ligand})_2^{4-} + {^1/_2}(VO)_2(\text{L-ligand})_2^{4-} \overset{K_3}{\rightleftharpoons} (VO)_2(\text{D-ligand})(\text{L-ligand})^{4-} \quad (3)$$

It is easily shown that when the free energies of the lower pH species are independent of isomer composition

$$pK_3 = (pK_1 + pK_2)_{DL} - {^1/_2}(pK_1 + pK_2)_{DD} - {^1/_2}(pK_1 + pK_2)_{LL} \quad (4)$$

For the non-mixed-ligand systems, the last two terms are, of course, identical.

The trend in the pK_3 values calculated (Table IV) is somewhat unexpected since there appears to be a decreasing stabilization of the DL isomer relative to the DD and LL complexes with increasing methyl substitution. Elementary considerations would predict the opposite trend since the destabilization of DD and LL isomers is believed to be due to a larger gauche steric interaction for these species between substituents on the central carbon atom of the bridging ligands.[5,22,27] Such

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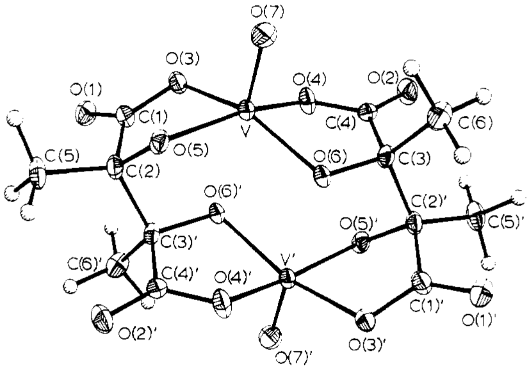

Figure 2. View of the $[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]^{4-}$ anion complex. Primed atoms are generated by $1 - x, -y, -z$. Thermal ellipsoids are shown at the 50% probability level (except hydrogen atoms drawn as arbitrary spheres).

interactions should increase with increasing methyl substitution. We acknowledge that several approximations and assumptions have been made in the derivation of the equilibrium constants given in Table IV; however, we must point out that nonideality corrections, which should be nearly identical for isomeric systems, are expected to cancel in the calculation of pK_3 values. Moreover, our pK_3 value of −1.22 for the tartrate system is in excellent agreement with the value of −1.20 obtained in a more sophisticated study.[22]

As found for *meso*-tartaric acid,[22] pH titration curves for 1:1 mixtures of vanadyl(IV) with (±)-*erythro*-monomethyltartaric acid and with *meso*-dimethyltartaric acid fail to show a break at 4 equiv of base added. The meso isomers do not form binuclear vanadyl(IV) complexes with quadridentate bridging ligands owing to unfavorable conformational requirements.[22,27,28]

Solid Products. The formation of three crystalline forms of sodium vanadyl(IV) (±)-dimethyltartrate(4−) (a blue dodecahydrate, a pink hexahydrate, and a purple tetradecahydrate) and at least two crystal forms of the (±)-monomethyltartrate(4−) complex salt (deca- and tetradecahydrates), the easy dehydration of most of the solids obtained, and the ease of contamination of active complex salts owing to incomplete ligand resolution make the preparation of pure solid complex salts having reproducible analyses and properties difficult. However, with patient work, careful resolutions, and (usually) slow crystallizations, homogeneous materials can be obtained.

Crystal form can usually be controlled by varying crystal growth conditions. Thus, in the racemic dimethyltartrate system, the pink hexahydrate sodium salt is obtained from hot dilute solution containing a large amount of ethanol, the blue dodecahydrate is obtained by cooling more concentrated solutions containing smaller amounts of ethanol or by evaporation of aqueous solutions, and the purple tetradecahydrate is obtained by slow deposition from cold, dilute filtrates remaining after removal of either the blue or pink forms. The blue and pink modifications interconvert readily by dissolution and reprecipitation, but the purple modification does not convert easily to the other forms. The various forms of the (±)-dimethyltartrate(4−) complex salts exhibit definite IR and visible spectral differences, but the crystal morphologies and color and elemental analyses are more useful for identification owing to the breadth of the visible bands and to the lack of strong, characteristic IR peaks. All of the solids characterized gave consistent results for several preparations and analyses.

Similarly, the tetradecahydrate of the (±)-monomethyltartrate(4−) complex salt is a consistent product of slow crystal growth from slowly cooled solutions in ethanol/water mixtures while the decahydrate is a consistent product of rapid deposition by addition of ethanol to warm aqueous solutions followed by rapid cooling. Though the two crystal forms are both brown and have nearly indistinguishable IR and electronic (mull) spectra, they are easily differentiated by their ESR spectral bandwidths (vide infra). The two materials interconvert readily upon recrystallization.

Table V. Interatomic Distances (Å) and Angles (Deg) of the Anionic Complex in $Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]\cdot 12H_2O$ with Estimated Standard Deviations in Parentheses[a]

V–V'	3.429 (3)	C(1)–C(2)	1.555 (5)
V–O(7)	1.623 (3)	C(3)–C(4)	1.543 (5)
V–O(3)	2.015 (3)	C(2)–C(3)'	1.558 (5)
V–O(4)	1.981 (3)	C(1)–O(1)	1.233 (5)
V–O(6)	1.974 (3)	C(4)–O(2)	1.229 (4)
V–O(5)	1.964 (2)	C(1)–O(3)	1.277 (4)
V–O(6)'	2.377 (3)	C(4)–O(4)	1.285 (5)
C(2)–C(5)	1.526 (5)	C(2)–O(5)	1.418 (4)
C(3)–C(6)	1.534 (5)	C(3)–O(6)	1.435 (4)
O(7)–V–O(3)	103.3 (1)	O(1)–C(1)–O(3)	124.2 (3)
O(7)–V–O(4)	100.0 (1)	O(2)–C(4)–O(4)	122.6 (3)
O(7)–V–O(5)	98.9 (1)	O(1)–C(1)–C(2)	121.4 (3)
O(7)–V–O(6)	103.6 (1)	O(2)–C(4)–C(3)	122.5 (3)
O(3)–V–O(4)	85.7 (1)	O(3)–C(1)–C(2)	114.5 (3)
O(5)–V–O(6)	104.7 (1)	O(4)–C(4)–C(3)	114.8 (3)
O(3)–V–O(5)	80.6 (1)	O(6)–C(3)–C(4)	108.4 (3)
O(4)–V–O(6)	80.1 (1)	O(5)–C(2)–C(1)	107.7 (3)
O(3)–V–O(6)	151.4 (1)	O(6)–C(3)–C(2)'	105.0 (2)
O(4)–V–O(5)	158.7 (1)	O(5)–C(2)–C(3)'	104.9 (3)
O(6)'–V–O(3)	78.0 (2)	O(6)–C(3)–C(6)	111.1 (3)
O(6)'–V–O(4)	86.2 (2)	O(5)–C(2)–C(5)	111.0 (3)
O(6)'–V–O(5)	75.1 (2)	C(1)–C(2)–C(3)'	106.8 (2)
O(6)'–V–O(6)	76.4 (2)	C(4)–C(3)–C(2)'	106.0 (2)
O(6)'–V–O(7)	173.7 (2)	C(1)–C(2)–C(5)	110.1 (3)
V–O(3)–C(1)	112.5 (2)	C(4)–C(3)–C(6)	110.5 (3)
V–O(4)–C(4)	114.8 (2)	C(6)–C(3)–C(2)'	115.3 (3)
V–O(5)–C(2)	106.8 (2)	C(5)–C(2)–C(3)'	115.9 (3)
V–O(6)–C(3)	112.5 (2)		

[a] Primed atoms are generated by $1 - x, -y, -z$.

Crystal Structure of $Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]\cdot 12H_2O$. Interatomic distances and angles for the centrosymmetric binuclear complex (Figure 2) found in the blue dodecahydrate modification of sodium vanadyl(IV) dimethyltartrate(4−) are given in Table V. As found in the binuclear vanadyl(IV) (±)-tartrate salts,[24,25] the five nearest neighbors to the vanadium atom form an approximately square-pyramidal coordination polyhedron with the vanadyl oxygen atom lying at the apex; however, the dimethyltartrate(4−) structure in addition shows occupation of a sixth site, opposite the vanadyl oxygen atom, by a hydroxyl oxygen atom, O(6)', at a distance of 2.377 (3) Å. Vanadium to sixth site oxygen atom (other than oxide(2−) ions) distances of 2.18[29] to 2.51 Å[30] with an average distance of ~2.3 Å have been observed by X-ray techniques in tetragonally distorted octahedral vanadyl(IV) complexes.

The intramolecular V–V distance of 3.429 (3) Å determined for $Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]\cdot 12H_2O$ is significantly shorter than the 4.082 (2) and 3.985 (1)-Å distances reported for the vanadyl(IV) (±)-tartrate(4−) complex anion.[24,25] This decrease in the V–V distance is attributable to two changes in the coordination geometry relative to the (±)-tartrate(4−) complex. First, there has been a vertical movement of the vanadyl group into the plane of the four equatorial oxygen atoms. The distance of the vanadium atom to the best plane of the four equatorial ligators (plane A, Table VI) is 0.394 Å in the (±)-dimethyltartrate(4−) species as compared to

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Table VI. Least-Squares Planes with Deviations of Selected Atoms for $Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]\cdot 12H_2O$[a]

atom	dev, Å	atom	dev, Å
Plane A: $3.6529x + 11.3343y - 1.0219z = 2.8445$			
O(3)	−0.071	O(6)	−0.062
O(4)	0.071	V*	0.394
O(5)	0.062	O(7)*	2.015
Plane B: $-6.7844x - 4.4871y + 8.7235z = 5.7655$			
C(4)	0.066	C(2)′	−0.066
C(3)	−0.066	C(1)′	0.066
Plane C: $-7.0669x - 4.4446y + 8.5601z = -4.7238$			
O(4)	0.043	O(5)′	−0.038
O(6)	−0.051	O(3)′	0.046

[a] Atoms marked with an asterisk were excluded in the calculation of the plane. The equations are expressed in direct space. Primed atoms are generated by $1 - x, -y, -z$.

Table VII. Selected Torsion Angles for $[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]^{4-}$

atoms[a]	angle, deg
O(3)–C(1)–C(2)–O(5)	23.5 (4)
O(4)–C(4)–C(3)–O(6)	0.7 (5)
C(5)–C(2)–C(3)′–C(6)′	56.3 (5)
O(5)–C(2)–C(3)′–O(6)′	−59.1 (5)

[a] Primed atoms are generated by $1 - x, -y, -z$.

values of 0.546 and 0.510 Å determined for the (±)-tartrate(4−) complex.[24,25] Such a vertical movement had been proposed earlier as a possible explanation for the decreased V–V distances predicted from ESR studies for the methyl-substituted tartrate complexes.[8] A second coordination geometry change, which also contributes to the decreased V–V distance, is a horizontal movement of the vanadium atom to open up the O(5)–V–O(6) angle to 104.7 (1)°. This can be compared with values of 93.2 (2) and 94.1 (1)° found for the anion present in (±)-tartrate(4−) complex salts.[24,25]

The average vanadium to equatorial hydroxyl oxygen bond length of 1.97 Å (±0.01 Å average deviation) found for the dimethyltartrate(4−) complex is significantly longer than the average value of 1.92 (±0.01) Å observed for the unsubstituted DL complex.[24,25] On the other hand, the carboxyl oxygen to vanadium bond lengths for the (±)-dimethyltartrate and (±)-tartrate structures are not significantly different. Though one might expect π bonding to be increased by the dropping of the vanadium atom into the plane of the four equatorial oxygen atoms, it may be that this is offset by a decrease, which would primarily affect the hydroxyl oxygen atoms, owing to the increase in the O(5)–V–O(6) angle. It is interesting that a structure determination on $Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]\cdot 14H_2O$ shows a coordination geometry with the vanadium atom even further out of the equatorial plane than found for the (±)-tartrate complex[24,25] and having very short vanadium to hydroxyl oxygen distances.[15]

Table VII gives selected torsion angles for the bis(dimethyltartrato(4−)) complex anion. The bridging ligands are well staggered. Characteristic of all DL binuclear tartrate-bridged and substituted-tartrate-bridged structures determined to date[15,24,25] are the significantly different torsion angles found for the two crystallographically independent α-hydroxycarboxylate groups (23.5 (4) and 0.7 (5)° in the present case).

Table VIII. Sodium Ion and Water Molecule Oxygen Atom Coordination Distances[a] (Å) and Angles (Deg) for $Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]\cdot 12H_2O$

Na(1)–O(7)^b	2.440 (4)	O(8)→O(1)	2.897 (4)
Na(1)–O(8)^c	2.436 (4)	O(8)→O(12)^g	2.717 (4)
Na(1)–O(8)^d	2.382 (4)	O(9)→O(6)	2.805 (4)
Na(1)–O(13)^e	2.376 (4)	O(9)→O(10)	2.785 (5)
Na(1)–O(11)	2.382 (4)	O(9)←O(11)	2.731 (5)
Na(2)–O(3)^b	2.466 (4)	O(10)←O(12)^h	2.757 (4)
Na(2)–O(4)^b	2.295 (4)	O(10)→O(2)^b	2.784 (5)
Na(2)–O(9)^f	2.419 (4)	O(10)→O(1)^c	2.742 (4)
Na(2)–O(11)	2.475 (4)	O(11)→O(5)	2.890 (4)
Na(2)–O(12)	2.319 (4)	O(12)→O(5)	2.727 (4)
Na(2)–O(13)	2.442 (4)	O(13)→O(7)	2.839 (4)
		O(13)→O(2)^b	2.866 (4)
O(7)^b–Na(1)–O(8)^c	85.9 (1)	Na(2)^d–O(9)–O(6)	96.0 (1)
–O(8)^d	84.6 (1)	–O(10)	126.4 (1)
–O(11)	104.5 (1)	–O(11)	102.6 (1)
–O(13)^e	167.4 (2)	O(6)–O(9)–O(10)	118.5 (2)
O(8)^c–Na(1)–O(8)^d	91.4 (2)	–O(11)	97.9 (2)
–O(11)	124.6 (1)	O(10)–O(9)–O(11)	110.7 (2)
–O(13)^e	85.0 (1)	O(1)^c–O(10)–O(2)^b	105.7 (2)
O(8)^d–Na(1)–O(11)	142.9 (1)	–O(9)	106.1 (2)
–O(13)^e	87.1 (1)	–O(12)^h	110.5 (2)
O(11)–Na(1)–O(13)^e	87.7 (1)	O(2)^b–O(10)–O(9)	99.2 (2)
O(3)^b–Na(2)–O(4)^b	69.5 (1)	–O(12)^h	118.2 (2)
–O(9)^f	80.9 (1)	O(9)–O(10)–O(12)^h	115.8 (2)
–O(11)	89.5 (1)	Na(1)–O(11)–Na(2)	115.3 (1)
–O(12)	118.2 (1)	–O(5)	145.2 (1)
–O(13)	152.0 (1)	–O(9)	87.7 (1)
O(4)^b–Na(2)–O(9)^f	84.0 (1)	Na(2)–O(11)–O(5)	95.2 (1)
–O(11)	91.1 (1)	–O(9)	123.6 (1)
–O(12)	171.5 (1)	O(5)–O(11)–O(9)	88.9 (2)
–O(13)	82.6 (1)	Na(2)–O(12)–O(5)	103.5 (1)
O(9)^f–Na(2)–O(11)	170.3 (1)	–O(8)^j	97.1 (1)
–O(12)	100.3 (1)	–O(10)^k	91.8 (1)
–O(13)	93.6 (1)	O(5)–O(12)–O(8)^j	116.1 (2)
O(11)–Na(2)–O(12)	85.8 (1)	–O(10)^k	113.0 (2)
–O(13)	94.0 (1)	O(8)^j–O(12)–O(10)^k	126.1 (2)
O(12)–Na(2)–O(13)	89.7 (1)	Na(1)^f–O(13)–Na(2)	109.8 (1)
Na(1)^d–O(8)–Na(1)^i	88.6 (2)	–O(2)^b	117.5 (1)
–O(1)	132.1 (1)	–O(7)	96.8 (1)
–O(12)^g	111.3 (1)	Na(2)–O(13)–O(2)	88.6 (1)
Na(1)^i–O(8)–O(1)	128.8 (1)	–O(7)	101.1 (1)
–O(12)^g	108.7 (1)	O(2)–O(13)–O(7)	138.8 (2)
O(1)–O(8)–O(12)^g	97.7 (2)		

[a] Hydrogen donor–acceptor relationships are designated by "→". [b] $x + 1/2, 1/2 - y, z + 1/2$. [c] $x + 1, y, z$. [d] $1 - x, -y, 1 - z$. [e] $3/2 - x, y - 1/2, 1/2 - z$. [f] $x - 3/2, y + 1/2, z - 1/2$. [g] $1/2 - x, y - 1/2, 1/2 - z$. [h] $x + 1/2, 1/2 - y, z - 1/2$. [i] $x - 1, y, z$. [j] $1/2 - x, y + 1/2, 1/2 - z$. [k] $x, 1/2 - y, z + 1/2$.

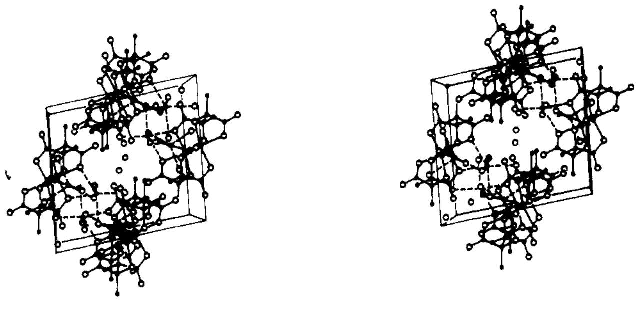


Figure 3. Stereoview of the unit cell of $Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]\cdot 12H_2O$. The view is into the *ab* plane. A black dot marks the origin of the right-handed coordinate system. Oxygen atoms are denoted by open circles and vanadium atoms by crosshatching. All other atoms are designated by filled circles. Dotted lines show the sodium coordination. Hydrogen atoms have been omitted.

The oxygen atoms of the tetranegative complex, the water molecules, and the sodium ions form a complex system of hydrogen, ion–ion, and ion–dipole bonds. Table VIII lists coordination distances and angles for the sodium ions and water molecules and indicates hydrogen atom donor–acceptor relationships in hydrogen bonding of the latter. Irregular fivefold and sixfold coordination polyhedra are found for Na(1) and Na(2), respectively. The water molecule oxygen atoms are all in pseudotetrahedral environments. A packing diagram is shown in Figure 3.

ESR Spectra. The room-temperature aqueous solution ESR spectra determined for the vanadyl(IV) monomethyl-

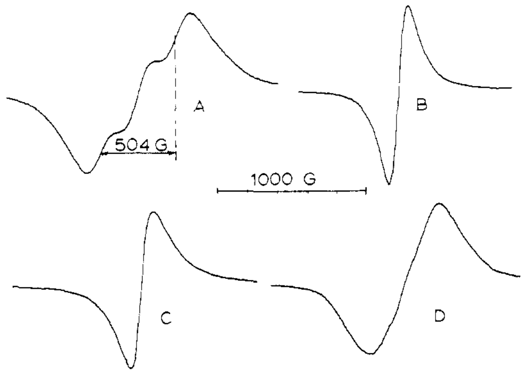


Figure 4. ESR powder spectra (9 GHz) of (A) $Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]\cdot12H_2O$ (blue form), (B) $Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]\cdot6H_2O$ (pink form), (C) $Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]\cdot10H_2O$, and (D) $Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]\cdot14H_2O$.

tartrate(4–) and dimethyltartrate(4–) complexes resemble those found for the tartrate(4–) derivatives[4] though the hyperfine splittings are more poorly resolved. As expected, spectral resolution decreases with increasing zero-field splitting. The zero-field splitting parameter D increases with methyl substitution.[8] Thus, the ESR spectrum of the (±)-dimethyltartrate(4–) derivative shows no hyperfine structure while that of the (±)-monomethyltartrate(4–) complex is a relatively well-resolved 15-line triplet-state spectrum. Owing to line width variations, which give an asymmetry to the ESR spectra (apparently owing to anisotropic nuclear hyperfine interactions,[31] the high-field sides are better resolved), and to the generally poor spectral resolutions, hyperfine splitting constants are not reported here though they appear similar to those of the vanadyl(IV) tartrates.[4] The isotropic g values are in the range 1.96–1.99 and exhibit no apparent trend with methyl substitution.

In the characterization of these methyl-substituted tartrate(4–) complexes, the ESR powder spectra prove to be more informative than the solution spectra. The powder spectrum of the blue dodecahydrate modification of the vanadyl(IV) (±)-dimethyltartrate(4–) salt, shown in Figure 4, exhibits some structure that is probably due to overlapping parallel and perpendicular components, the former split by $2D$ and the latter by D, in a pseudoaxial system.[8] That the minimum intermolecular V–V distance for $Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]\cdot12H_2O$ (7.887 Å) is greater than that for $Na_4[(VO)_2((+)\text{-tart})((-)\text{-tart})]\cdot12H_2O$ (7.351 Å)[24] and $Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]\cdot14H_2O$ (7.765 Å),[15] whose ESR powder spectra show little structure, may account for the observed fine structure in the (±)-dimethyltartrate(4–) complex salt. On the other hand, $[N(C_2H_5)_4]_4[(VO)_2((+)\text{-tart})((-)\text{-tart})]\cdot8H_2O$, where the minimum intermolecular V–V distance is 8.906 Å, exhibits a well-resolved triplet-state ESR powder spectrum characteristic of a magnetically dilute system.[25] If the inflection points (Figure 4) of the $Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]\cdot12H_2O$ ESR powder spectrum are due to perpendicular components split by D, the separation of 504 G allows a calculation of 0.0468 cm^{-1} for $|D|$. Previous work[8,32] has shown that simple magnetic dipole calculations account for the D values of the vanadyl(IV) tartrates so that

$$D_{\text{calcd}}\ (\text{cm}^{-1}) = \frac{0.325}{R^3} g^2(1 - 3\cos^2\theta)\ \text{Å}^3 \qquad (5)$$

where R is the interelectron distance (taken as the intramolecular V–V distance) and θ is the angle between the R vector and the magnetic field. If the magnetic field is quantized along the V–V direction, $\theta = 0°$ and $D_{\text{calcd}} = -0.063$ cm^{-1}. If the field is quantized along the vanadyl direction, $\theta = 34.5°$ (from the crystal data) and $D_{\text{calcd}} = -0.033$ cm^{-1}. These two values, which were calculated with use of our measured isotropic g value of 1.973 and the observed V–V′ distance of 3.429 Å, bracket the D value (assumed negative) of –0.0468 cm^{-1}, determined experimentally with the assumption of axial symmetry (an assumption that is admittedly questionable).

Table IX. Positions and Extinction Coefficients of Aqueous Solution Spectral Bands for Vanadyl(IV) Complexes

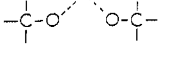
complex	$\bar{\nu}$, µm^{-1} (ϵ, M^{-1} cm^{-1})^a I	II	III
DL Isomers			
$[(VO)_2((+)\text{-tart})((-)\text{-tart})]^{4-\,b}$	1.36 (41)	1.87 (51)	2.38 (106)
$[(VO)_2((+)\text{-mmt})((+)\text{-tart})]^{4-\,c}$	1.19 (31)	1.87 (46)	2.63 (148)
$[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]^{4-\,b}$	1.27 (43)	1.83 (40)	2.47 (78)
$[(VO)_2((+)\text{-dmt})((+)\text{-tart})]^{4-\,c}$	1.19 (38)	1.86 (35)	2.58 (85)
$[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]^{4-\,b}$	1.18 (45)	1.76 (26)	2.73 (96)
DD or LL Isomers			
$[(VO)_2((+)\text{-tart})_2]^{4-\,b}$	1.11 (45)	1.69 (46), 1.88 (55)	2.51 (83)
$[(VO)_2((+)\text{-mmt})_2]^{4-\,c}$	1.11 (39)	1.72 (30), 1.85 (31)	2.60 (75)
$[(VO)_2((+)\text{-dmt})_2]^{4-\,b}$	1.09 (32)	1.74 (27), 1.83 (26)	2.50 (52)

^{a} Based on the binuclear complex concentration. ^{b} Prepared by dissolution of the appropriate sodium salt. ^{c} Prepared by mixing ligand, vanadyl(IV) perchlorate, and NaOH to give pH 8-9.

The powder spectrum of the tetradecahydrate of the monomethyltartrate(4–) complex salt (Figure 4) also exhibits very small inflection points, which are separated by ~300 G, giving an experimental $|D|$ of 0.028 cm^{-1}. This value is in excellent agreement with the value of –0.0279 cm^{-1}, which has been calculated[15] from the geometrical parameters found in the structure of $Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]\cdot14H_2O$.

That the ESR spectral band observed in the powder spectrum of the pink hexahydrate modification of the (±)-dimethyltartrate(4–) complex salt is much narrower than that observed in the powder spectrum of the blue dodecahydrate form (Figure 4) might be taken to imply an increased V–V distance for the former compound; however, an incomplete X-ray crystal structure that has been determined in our laboratory shows only a very small increase in the intramolecular V–V distance (3.504 Å). Of interest also is the great difference in the ESR spectral bandwidths found in powder spectra of the tetradeca- and decahydrate modifications of the (±)-monomethyltartrate(4–) complex salt (Figure 4). Other than in their chemical analyses and ESR spectra, these two forms are essentially indistinguishable.

Electronic Spectra. In the visible region of the spectrum, vanadyl(IV) α-hydroxycarboxylates exhibit spectra having either three or four bands in the region 1000–300 nm. These most likely correspond to transitions that are of primarily d–d origin.[33] It has been proposed that the three-band spectrum is diagnostic of a cis coordination (**3**) by the α-hydroxycarboxylate groups while the four-band spectrum is diagnostic of a trans coordination (**4**) perhaps accompanied by some distortion toward a trigonal-bipyramidal geometry.[33] Our



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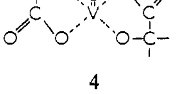

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Table X. Positions of Band Maxima in Visible Spectra of Solid Complex Salts as Nujol Mulls

compd	$\bar{\nu}$, μm^{-1}		
	I	II	III
Tartrate(4–) Complex Salts			
$Na_4[(VO)_2((+)\text{-tart})((-)\text{-tart})]\cdot 12H_2O$	1.33	1.88	2.34
$Na_4[(VO)_2((+)\text{-tart})_2]\cdot 6H_2O$	1.10	1.70, 1.95	2.58
$(NH_4)_4[(VO)_2((+)\text{-tart})_2]\cdot 2H_2O$	1.20	1.70, 1.96	2.55
Monomethyltartrate(4–) Complex Salts			
$Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]\cdot 14H_2O$	1.39	1.90	2.36
$Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]\cdot 10H_2O$	1.40	1.90	2.38
$Na_4[(VO)_2((+)\text{-mmt})_2]\cdot 8H_2O$	1.10	1.65, 1.87	2.43
Dimethyltartrate(4–) Complex Salts			
$Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]\cdot 12H_2O$	1.20	1.75	2.74
$Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]\cdot 6H_2O$	1.26	1.88	2.70
$Na_4[(VO)_2((\pm)\text{-dmt})_2]\cdot 14H_2O$	1.06	1.72, 1.89	2.52
$Na_4[(VO)_2((+)\text{-dmt})_2]\cdot 12H_2O$	1.10	1.72, 1.90	2.45
$Ba_2[(VO)_2((\pm)\text{-dmt})_2]\cdot 12H_2O$	1.13	1.71, 1.91	2.58

aqueous solution spectral results (Table IX) are in agreement with this. The DL complexes, all of which must be cis owing to the steric requirements for bridging,[27] give three-band spectra while the DD and LL complexes, which must be trans, give four-band spectra—the bands arbitrarily designated "II"[34] being distinctly split (though the two components invariably overlap). We also find that the lowest energy band ("I") lies at much lower energy in spectra of the DD and LL complexes than in spectra of DL isomers. We wish to point out the interesting technique of stereoselective control to obtain visible spectra of mixed-ligand complexes in these basically labile systems. Equimolar mixtures of two ligands of opposite absolute configuration[9] are used to obtain the mixed-ligand species (in the more stable DL form only).

Vanadyl(IV) ion electronic spectra are highly sensitive to small changes in the vanadium coordination geometry. We have seen this in the isomeric differences in aqueous solution spectra, and it can also be seen in the solid-state electronic spectra (Table X). Thus, for example, there is a significant shift, apparently owing to packing force distortions, in the lowest energy band of the DD tartrate(4–) complex in the solid state upon going from sodium to ammonium counterions. Similarly, the blue dodecahydrate and pink hexahydrate crystals of sodium vanadyl(IV) (±)-dimethyltartrate(4–), both of which contain binuclear anionic complexes of the same gross geometry, exhibit significant spectral differences. It is surprising, therefore, that the tetradeca- and decahydrate modifications of the sodium salt of the (±)-monomethyltartrate complex, whose ESR spectra are significantly different, have essentially identical visible solid-state spectra.

Visible spectral data obtained for the purple tetradecahydrate sodium salt isolated from the (±)-dimethyltartrate complex system (Table X) provide strong evidence that this material contains DD and LL isomers, apparently obtained owing to a small amount of these complexes being present in equilibrium mixtures. Thus, not only is the energy of spectral band I very low but band II is distinctly split. Moreover, the entire spectrum resembles that of the sodium salt of the (+)-dimethyltartrate(4–) complex. Finally, we find that in aqueous solution, the ESR and visible spectra of the purple tetradecahydrate (±)-dimethyltartrate(4–) complex salt initially are essentially those of aqueous solutions of sodium vanadyl(IV) (+)-dimethyltartrate(4–) but change over a period of several hours to those of the DL isomer (prepared by dissolving either the blue dodecahydrate or the pink hexahydrate salts).

IR spectra also indicate that the purple tetradecahydrate salt obtained in the vanadyl(IV) (±)-dimethyltartrate(4–) system contains DD and LL isomers. We have found a moderately strong IR band in the range 398–412 cm^{-1} for a variety of vanadyl(IV) complex salts prepared from resolved tartrate and methyl-substituted tartrates but no such band in any DL complex salt. The purple tetradecahydrate has a moderately strong IR band at 415 cm^{-1}, only very slightly outside the observed range. Furthermore, IR spectral data for a variety of salts in our laboratory show that the vanadyl group IR stretching frequencies of DD and LL complexes are always lower than those of DL isomers with the same ligand and counterion. The V═O stretch of 924 cm^{-1} found for the purple tetradecahydrate salt is lower than those found for the blue dodecahydrate DL (939 cm^{-1}) and pink hexahydrate DL (937 cm^{-1}) complex salts and is the same within experimental error as that found for the sodium salt of the (+)-dimethyltartrate(4–) complex (925 cm^{-1}).

The tetradecahydrate purple sodium salt isolated from the vanadyl(IV) (±)-dimethyltartrate(4–) system must contain both DD and LL isomers within the lattice as otherwise it would be expected to exhibit the same IR spectrum and analysis as determined for the salt isolated with (+)-dimethyltartrate(4–) (which is a dodecahydrate). The ligand-exchange reaction, which evidently takes place when the purple tetradecahydrate compound is dissolved in water to give the more stable DL isomer, is unusually slow when compared with that observed for the tartrate(4–) system where $t_{1/2} < 1$ min.[35] However, we find that a very slow ligand exchange also takes place when enantiomeric complex salts prepared from resolved dimethyltartrate are mixed in aqueous solution in agreement with the observations made with the purple tetradecahydrate where both reactants are present in the same lattice before dissolution. Kinetic studies are now underway on these systems. It is interesting that very slow kinetics (involving metal ion exchange) have been observed for other binuclear dimethyltartrate complexes.[13]

Visible spectral data (Table X) for the barium salt obtained in small amounts as a byproduct in some syntheses employing (±)-dimethyltartrate indicate that this salt also contains DD and/or LL complexes. The electronic spectrum is four-banded, and band I lies at very low energy. Moreover, the IR spectrum of the barium salt exhibits a moderately strong band at 409 cm^{-1} and a V═O stretch at 924 cm^{-1}—both features indicative of active complexes (vide supra).

Presumably a barium salt containing DD and/or LL isomers is obtained from the racemic reaction mixtures because this salt has a lower solubility than that containing DL complexes. Therefore, either barium ion scavenges the active complexes from the equilibrated system or it catalyzes a ligand-exchange reaction, which is normally slow for the dimethyltartrate(4–) complexes. Metal ion catalysis of ligand-exchange reactions in the vanadyl(IV) tartrate(4–) system is known to occur.[35]

Summary and Conclusions

Stereoselective effects, ESR spectra, analyses, and X-ray structure determinations show that the vanadyl(IV) methyl-substituted tartrate(4–) complexes, like the unsubstituted compounds, are binuclear in the solid state and in solution. Potentiometric titration data indicate a decreasing stability of the DL isomer relative to the DD (and LL) with increasing methyl substitution. This may be connected with the increased metal to equatorial hydroxyl oxygen bond length found for the DL dimethyltartrate(4–) complex (but not for the monomethyltartrate[15]).

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(34) The band maxima have been numbered I, II, and III with increasing energy. This does not necessarily imply that each band in a spectrum is due to only one electronic transition or that the same transition gives rise to all bands having the same designation.

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The crystal structure of the blue dodecahydrate form of sodium vanadyl(IV) (±)-dimethyltartrate(4−) shows a binuclear DL structure with the shortened (relative to the tartrate(4−) complex) V–V distance predicted from earlier ESR studies[8] and, moreover, shows that this shortened distance is due in part to a movement of the vanadium atom into the plane of the four equatorial oxygen atoms as proposed earlier.[8] However, we note that the monomethyltartrate structure[15] does not exhibit this shortened distance.

The pink hexahydrate and purple tetradecahydrate forms of sodium vanadyl(IV) (±)-dimethyltartrate also contain binuclear structures. The former form contains DL complexes while the latter contains a mixture of DD and LL molecular anions, which, when dissolved in water, undergo slow ligand exchange to give the more stable DL complexes.

Finally, this work provides empirical information on the use of spectral tools for characterization of vanadyl(IV) α-hydroxycarboxylates. Additional strong evidence is provided, showing that three-band electronic spectra are diagnostic of cis coordinations while four-band electronic spectra are diagnostic of trans structures. Furthermore, we find that the position of the lowest energy d–d band may also be indicative of the coordination geometry. IR spectral results indicate that IR bands in the region of 398–415 cm^{-1} are indicative of DD and LL binuclear vanadyl(IV) tartrates and methyl-substituted tartrates while an absence of a band in this region provides evidence for the DL isomer. The lower V=O stretching frequency for DD and LL complexes may also provide another technique for isomer identification. It will be interesting to determine whether these IR spectral techniques can be extended to determination of cis/trans differences in mononuclear vanadyl(IV) α-hydroxycarboxylates.

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Registry No. $Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]\cdot 12H_2O$, 79813-74-4; $Na_4[(VO)_2((\pm)\text{-dmt})_2]$, 79813-75-5; $Na_4[(VO)_2((+)\text{-dmt})_2]$, 79813-76-6; $Ba_2[(VO)_2((\pm)\text{-dmt})_2]$, 79854-24-3; $Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]$, 79813-77-7; $Na_4[(VO)_2((+)\text{-mmt})_2]$, 79813-78-8; $Na_4[(VO)_2((+)\text{-tart})((-)\text{-tart})]$, 79813-79-9; $Na_4[(VO)_2((+)\text{-tart})_2]$, 24355-12-2; $(NH_4)_4[(VO)_2((+)\text{-tart})_2]$, 79813-80-2; $[(VO)_2((+)\text{-mmt})((+)\text{-tart})]^{4-}$, 79814-93-0; $[(VO)_2((+)\text{-dmt})((+)\text{-tart})]^{4-}$, 79813-81-3.

Supplementary Material Available: Listings of idealized hydrogen positions and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of the Distal-Methyl Isomer of Tetrasodium [μ-(+)-*threo*-Monomethyltartrato(4−)]-[μ-(−)-*threo*-monomethyltartrato(4−)]-bis(oxovanadate(IV)) Tetradecahydrate

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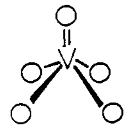
Received April 21, 1981

The crystal structure of $Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]\cdot 14H_2O$, where mmt is *threo*-monomethyltartrate(4−), $C_5H_4O_6^{4-}$, has been solved to determine the coordination geometry about the vanadium atom and the intramolecular V–V distance. The compound crystallizes in the triclinic space group $P\bar{1}$ with one centrosymmetric binuclear unit in a cell of dimensions $a = 9.082$ (2) Å, $b = 9.352$ (2) Å, $c = 9.682$ (2) Å, $\alpha = 87.02$ (2)°, $\beta = 79.98$ (2)°, and $\gamma = 70.50$ (2)°. Full-matrix least-squares refinement of 2366 unique reflections ($2\theta_{max} = 55°$, Mo Kα radiation) with $F_o^2 > 3\sigma(F_o^2)$ gave final discrepancy indices of $R(F) = 0.066$ and $R_w(F) = 0.059$. The square-pyramidal coordination geometry (vanadium atom to basal least-squares plane distance of 0.548 Å), coordination bond lengths (vanadium to hydroxyl oxygen atoms 1.912 (4) and 1.904 (3) Å; vanadium to carboxyl oxygen atoms 1.991 (4) and 1.979 (3) Å), and V–V distance (4.047 (3) Å) differ significantly from those which have been found for the binuclear (±)-dimethyltartrate(4−) complex but closely resemble those reported for the vanadyl(IV) (±)-tartrate(4−) anion. The structure found for the monomethyltartrate(4−) complex in this study differs somewhat from that determined previously by ESR spectroscopy for a glass at 77 K.

Introduction

An ESR study of exchange-coupled binuclear vanadyl(IV) tartrates and their methyl-substituted derivatives in glasses at 77 K indicates a decreasing intramolecular V–V distance with increasing methyl substitution, and it has been suggested that this is due, at least in part, to a dropping of the vanadium atom into the plane of the four basal oxygen atoms in the square-pyramidal coordination polyhedron expected (**1**).[2] In partial agreement with these surmises, a crystal structure of one crystal form of the sodium salt of the (±)-dimethyltartrate(4−) ("dmt") complex[3] shows V–V and vanadium to basal plane distances that are respectively 0.60 and 0.13 Å shorter than the averages found for the (±)-tartrate(4−) ("tart") complex;[4,5] however, unlike that of the latter anion, the coordination geometry is distorted octahedral owing to a weak but significant sixth-site coordination by a hydroxyl oxygen atom from the other half of the binuclear structure (**2**). Moreover, the vanadium–hydroxyl oxygen coordination



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