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.

Acknowledgment. This work was supported by grants from the Minority Biomedical Sciences Program (NIH-DRR No. 506 RR08139), the Petroleum Research Fund, administered by the American Chemical Society, the Research Allocations Committee of the University of New Mexico, and the National Science Foundation for purchase of the Syntex (Nicolet) R3 Computing System used in carrying out the plotting calculations. We wish to thank Dr. Eileen Duesler for her aid in obtaining computer-assisted plots.

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.

Contribution from the Department of Chemistry,
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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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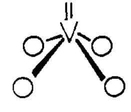
Received April 21, 1981

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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[1] To whom correspondence should be addressed.

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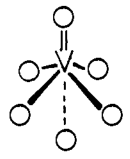
distances are significantly longer in the methyl-substituted derivative.



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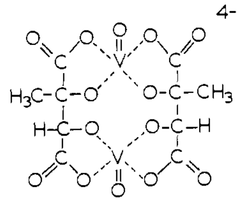
In order to determine whether the binuclear vanadyl(IV) (±)-monomethyltartrate(4−) ("mmt") complex in the solid state also exhibits the shortened V–V distance predicted from ESR studies and the accompanying coordination geometry variations found for the (±)-dimethyltartrate(4−) derivative, a crystal structure determination has been carried out on tetrasodium [μ-(+)-*threo*-monomethyltartrato(4−)]-[μ-(−)-*threo*-monomethyltartrato(4-)]-bis(oxovanadate(IV)) tetradecahydrate, $Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]\cdot 14H_2O$. This complex is also of interest owing to the possibility of two isomers—one having proximal-methyl groups (**3**) and the other having distal-methyl groups (**4**).



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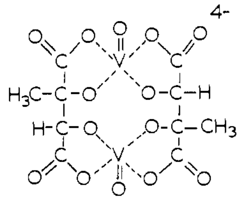

4

Experimental Section

Crystal Preparation. $Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]$ was prepared as previously reported,[3] and crystals of the tetradecahydrate were grown by slow cooling of a warm solution in 60% aqueous ethanol. A thin brown plate was selected and sealed in a thin-walled capillary tube to prevent dehydration.

Crystallographic Data. The determination of Bravais lattice and cell dimensions and the collection of intensity data were carried out with use of a Syntex (Nicolet) P3/F diffractometer system equipped with a graphite-crystal monochromator.

The lattice parameters were determined with use of 25 independently centered reflections, $14° \leq 2\theta$ (Mo Kα) $\leq 27°$. After least-squares refinement of the angle settings, for the determination of the unit cell dimensions, the crystal system and axis lengths were checked with use of axial photographs. The crystal and diffractometer data are listed in Table I.

Data collection was carried out at room temperature with Mo Kα radiation using the θ–2θ scan technique. A hemisphere of data was collected, $h,\pm k,\pm l$ out to $2\theta = 55°$. The intensities of 2 standard reflections, measured every 50 reflections, showed no significant decay during the data collection period. Neutral-atom scattering factors from Cromer and Mann[6] were used for all nonhydrogen atoms, and those from Stewart et al.[7] were used for hydrogen atoms. The net intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied.[8] Extinction corrections were unnecessary.

Solution and Refinement of the Structure. The structure determination and initial refinement calculations were carried out with use of the XTL series of programs[8] while the final refinement employed the SHELXTL 79 series.[9] All calculations were performed on a Syntex (Nicolet) R3 crystallographic computing unit. Phases provided by MULTAN[10] were used to solve the structure. The E map with the highest combined figure of merit yielded the positions of all nonhydrogen atoms except oxygen atoms of the lattice water molecules. A subsequent difference map gave the positions of six full-weighted water oxygen atoms and a water oxygen atom that was initially put in as a single half-weighted atom. Isotropic refinement was continued, ending in a difference map, which revealed the locations of all hydrogen atoms on the monomethyltartrate(4−) ligand and nearly all of the hydrogen atoms of the water molecules, plus two large peaks near the half-weighted water molecule. After various site occupancy models were tried, the best representation of this water molecule was a two-site model with half-weighted positions and a common isotropic thermal factor. Isotropic refinement of this model converged at $R(F) = 0.096$, where $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$.

Table I. Summary of Crystal and Intensity Collection Data for $C_{10}H_{36}O_{28}Na_4V_2$

fw	798.3
a, Å	9.082 (2)
b, Å	9.352 (2)
c, Å	9.682 (2)
α, deg	87.02 (2)
β, deg	79.98 (2)
γ, deg	70.50 (2)
V, Å^3	763.3 (6)
Z	1
ρ, calcd, g cm^{-3}	1.74
space group	$P\bar{1}$
cryst dimens, mm	0.4 × 0.6 × 0.1
cryst shape	plate with major faces {011}
radiation	Mo Kα (λ = 0.710 69 Å)
abs coeff, μ(Mo Kα), cm^{-1}	8.2
scan speed, deg min^{-1}	variable, 3.0-15.0
scan range	1.0° below 2θ (Kα_1)-1.0° above 2θ (Kα_2)
bkgd counting time	1.0 × scan time
2θ limits, deg	2.0-55.0
reflcns collected	3438 total
unique reflcns	3418
unique data used	2366 with $F_o{}^2 > 3\sigma(F_o{}^2)$
$R(F)$	0.066
$R_w(F)$	0.059
F_{000}	410

Idealized hydrogen atom positions were then included. The methyl group was treated as a rigid body with idealized C–C–H and H–C–H angles of 109.5° and H–C bond lengths of 0.96 Å. The torsional conformation of the methyl group was fixed by the location of one hydrogen atom from the difference map. The riding model was used for the methine hydrogen atom, whose length was set at 0.96 Å, and for the water molecule hydrogen atoms, where the H–O–H angle was set at 105° and the O–H distance at 1.00 Å.[11] No hydrogen atoms were placed on the disordered water molecules O(14A) and O(14B) or on O(8), whose hydrogen atoms are indicated to be disordered (vide infra).

Several cycles of anisotropic refinement (except O(14A) and O(14B), which were refined isotropically) using a block-cascade algorithm yielded, at convergence, $R(F) = 0.066$ and $R_w(F) = 0.059$, where $R_w{}^2(F) = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$. All least-squares refinements were based on the minimization of $\sum w(|F_o| - |F_c|)^2$ using counterweights[12] where $w^{-1} = \sigma^2(F_o) + cF_o{}^2$ with c being refined as a parameter whose final value was 0.000 69. A final difference map yielded several interesting peaks (<0.7 e Å^{-3} around O(8), O(14A), O(14B), and C(3)), which are discussed later in this paper. The final fractional coordinates and thermal parameters of the refined atoms are listed on Table II. The idealized hydrogen atom positions and a listing of the observed and calculated structure factors are available.[13]

Results and Discussion

Structure of the Complex Anion. The tetranegative complex lies about a center of symmetry with the methyl groups distal

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(13) Supplementary material.

Table II. Final Positional and Thermal Parameters for $Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]\cdot 14H_2O$

atom	x	y	z	U_{11} or U, Å^2	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	0.0229 (1)	0.3268 (1)	0.1378 (1)	17.1 (4)	22.3 (4)	20.9 (4)	−5.8 (3)	−5.4 (3)	0.7 (3)
Na(1)	0.4415 (2)	0.1952 (2)	0.0517 (2)	28 (1)	28 (1)	42 (1)	−6 (1)	−11 (1)	−2 (1)
Na(2)	0.5081 (3)	0.3499 (3)	0.3977 (3)	36 (1)	43 (1)	97 (2)	3 (1)	−32 (1)	−27 (1)
O(1)	0.2707 (4)	0.5105 (4)	0.3317 (4)	27 (2)	33 (2)	52 (2)	−15 (2)	−24 (2)	−10 (2)
O(2)	0.2313 (4)	0.1172 (4)	−0.2283 (4)	33 (2)	35 (2)	31 (2)	8 (2)	−9 (2)	−11 (2)
O(3)	0.2043 (4)	0.3508 (4)	0.2124 (3)	18 (2)	23 (2)	30 (2)	−3 (1)	−10 (1)	−2 (1)
O(4)	0.1885 (4)	0.2063 (4)	−0.0120 (3)	22 (2)	31 (2)	27 (2)	1 (2)	−7 (1)	−4 (1)
O(5)	−0.0872 (4)	0.5166 (4)	0.2306 (4)	18 (2)	25 (2)	39 (2)	−4 (1)	−7 (1)	−7 (1)
O(6)	−0.0959 (4)	0.3773 (4)	−0.0130 (3)	21 (2)	46 (2)	24 (2)	6 (2)	−8 (1)	−11 (2)
O(7)	−0.0353 (4)	0.2043 (4)	0.2355 (4)	44 (2)	29 (2)	41 (2)	−18 (2)	−5 (2)	2 (2)
O(8)	0.4078 (4)	0.4334 (4)	−0.0563 (4)	28 (2)	36 (2)	38 (2)	−12 (2)	−8 (2)	4 (2)
O(9)	0.7582 (4)	0.2478 (4)	0.4907 (4)	39 (2)	39 (2)	39 (2)	−11 (2)	−4 (2)	−6 (2)
O(10)	0.4618 (4)	−0.0458 (4)	0.1594 (4)	30 (2)	45 (2)	40 (2)	−7 (2)	−5 (2)	4 (2)
O(11)	0.2118 (5)	0.0295 (5)	0.3860 (5)	50 (3)	60 (3)	67 (3)	−12 (2)	−12 (2)	27 (2)
O(12)	0.6443 (5)	0.2048 (5)	0.1812 (5)	35 (2)	51 (2)	70 (3)	−11 (2)	−21 (2)	−14 (2)
O(13)	0.3953 (4)	0.4310 (5)	0.6512 (4)	23 (2)	77 (3)	32 (2)	−6 (2)	1 (2)	−3 (2)
O(14A)[b]	0.3703 (10)	0.1607 (10)	0.4945 (9)	45 (2)					
O(14B)[b]	0.4413 (10)	0.1535 (10)	0.4805 (9)	45 (2)					
C(1)	0.1749 (5)	0.4806 (5)	0.2723 (5)	24 (2)	27 (3)	25 (2)	−8 (2)	−5 (2)	−2 (2)
C(2)	0.0124 (5)	0.5941 (5)	0.2597 (5)	21 (2)	21 (2)	23 (2)	−4 (2)	−7 (2)	−1 (2)
C(3)	−0.0265 (5)	0.2940 (5)	−0.1394 (5)	18 (2)	29 (3)	23 (2)	−4 (2)	−7 (2)	−4 (2)
C(4)	0.1450 (6)	0.1965 (5)	−0.1299 (5)	29 (2)	17 (2)	24 (2)	−2 (2)	−8 (2)	0 (2)
C(5)	−0.1160 (7)	0.1883 (6)	−0.1666 (6)	41 (3)	43 (3)	48 (3)	−17 (3)	−13 (3)	4 (3)

[a] The form of the anisotropic thermal factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. The thermal parameters are $\times 10^3$. [b] Isotropically refined with the U's tied to a common variable. These atoms are half-weighted.

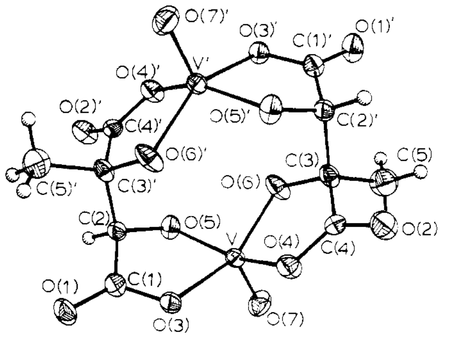

Figure 1. View of the $[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]^{4-}$ anion. Primed atoms are generated by $-x$, $1 - y$, $-z$. Thermal ellipsoids are shown at the 50% probability level (except the hydrogen atoms).

to each other (Figure 1). Evidence for the presence of some proximal-methyl isomers comes from our observation of a peak of about 0.5 e Å^{-3} on the final difference map. This peak, which is along the C(2)–methine hydrogen vector and is located 1.6 Å from C(2), if considered a carbon atom, amounts to between 5% and 10% of the proximal-methyl structure. This difference peak could also result from a twofold disorder about the center of symmetry. Such a disorder would essentially interchange the methyl group and hydrogen atom on carbon atoms C(2) and C(3). No attempt was made to incorporate either model into the refinement because of the uncertainty of these interpretations and the fact that a proximal-methyl form must be disordered with respect to the center of symmetry.

Both a decahydrate and a tetradecahydrate form of the sodium salt of the vanadyl(IV) (±)-monomethyltartrate(4−) complex have been obtained;[3] however, that their IR spectra are nearly identical[3] indicates that both hydrates contain as the same principal isomer the distal-methyl form. Since there is no apparent reason for a preference of one isomer over the other, it seems likely that approximately equimolar amounts of the proximal-methyl and distal-methyl isomers are present in equilibrium solutions (as found for the antimony(III) and arsenic(III) monomethyltartrate(4−) binuclear complexes[14]).

Table III. Interatomic Distances (Å) and Angles (Deg) for $Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]\cdot 14H_2O$ with Estimated Standard Deviations in Parentheses[a]

V–V'	4.047 (3)	C(2)–C(3)'	1.544 (7)
V–O(7)	1.613 (4)	C(3)–C(5)	1.532 (9)
V–O(3)	1.991 (4)	C(1)–O(1)	1.232 (7)
V–O(4)	1.979 (3)	C(4)–O(2)	1.224 (5)
V–O(6)	1.912 (4)	C(1)–O(3)	1.298 (6)
V–O(5)	1.904 (3)	C(4)–O(4)	1.289 (6)
C(1)–C(2)	1.523 (6)	C(2)–O(5)	1.404 (7)
C(3)–C(4)	1.535 (6)	C(3)–O(6)	1.414 (5)

O(7)–V–O(3)	107.1 (2)	O(1)–C(1)–O(3)	123.1 (4)
O(7)–V–O(4)	105.3 (2)	O(2)–C(4)–O(4)	123.8 (4)
O(7)–V–O(5)	105.1 (2)	O(1)–C(1)–C(2)	123.0 (4)
O(7)–V–O(6)	108.1 (2)	O(2)–C(4)–C(3)	121.5 (5)
O(3)–V–O(4)	84.4 (1)	O(3)–C(1)–C(2)	113.9 (5)
O(3)–V–O(5)	82.2 (1)	O(4)–C(4)–C(3)	114.7 (4)
O(5)–V–O(6)	93.5 (1)	C(4)–C(3)–O(6)	109.2 (4)
O(4)–V–O(6)	81.7 (1)	C(1)–C(2)–O(5)	109.6 (4)
O(3)–V–O(6)	144.5 (2)	O(6)–C(3)–C(2)'	108.7 (4)
O(4)–V–O(5)	149.2 (2)	O(5)–C(2)–C(3)'	108.6 (4)
V–O(3)–C(1)	114.8 (3)	C(4)–C(3)–C(2)'	105.0 (4)
V–O(4)–C(4)	116.6 (3)	C(1)–C(2)–C(3)'	110.5 (4)
V–O(5)–C(2)	114.0 (2)	O(6)–C(3)–C(5)	111.9 (4)
V–O(6)–C(3)	116.8 (3)	C(4)–C(3)–C(5)	108.1 (4)
O(7)–V–V'	155.3 (2)	C(5)–C(3)–C(2)'	113.8 (4)

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

If this is the case, the two isomers apparently interconvert during crystallization with preferential deposition of the distal-methyl form. Kinetic studies[15] and observations of reactions[3] show that ligand exchange between the binuclear complexes occurs rapidly for the vanadyl(IV) tartrate(4−) system but slowly for the vanadyl(IV) dimethyltartrate(4−) complexes. That the solids obtained from the vanadyl(IV) (±)-monomethyltartrate(4−) system seem to contain only distal-methyl isomers is weak evidence that relatively rapid ligand exchange and/or molecular rearrangement occur for the (±)-monomethyltartrate(4−) complex salts.

Table III gives bond lengths and bond angles for the anionic complex shown in Figure 1. Least-squares planes are reported

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Table IV. Least-Squares Planes[a] and Deviations of Selected Atoms[b] for $Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]\cdot 14H_2O$

atom	dev, Å	atom	dev, Å
Plane A: $4.1970x + 7.4205y - 4.7126z = 2.4197$			
O(3)	0.0406	O(6)	0.0392
O(4)	−0.0409	V*	−0.5484
O(5)	−0.0390	O(7)*	−2.1613
Plane B: $3.8563x + 6.8653y + 6.8899z = 5.8821$			
C(1)	−0.0319	C(3)′	0.0276
C(2)	0.0350	C(4)′	−0.0307
Plane C: $4.2024x + 6.8336y + 6.8621z = 4.7305$			
O(3)	−0.0169	O(4)′	−0.0166
O(5)	0.0157	O(6)′	0.0178

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

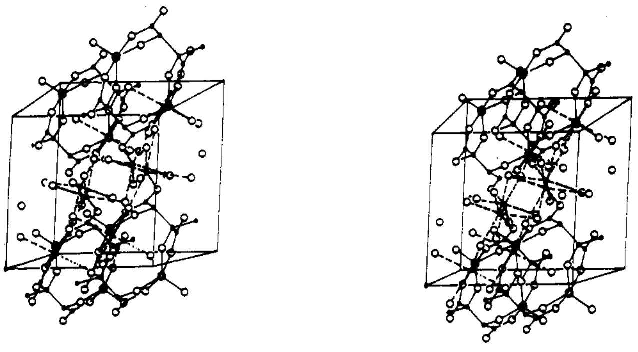

Figure 2. Stereoview of the unit cell of $Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]\cdot 14H_2O$. The view is into the *ac* plane. A dot marks the origin of the right-handed coordinate system. Oxygen atoms are denoted by open circles and vanadium atoms by crosshatching. Other atom types are designated by filled circles. Hydrogen atoms are not shown. Dotted lines show the sodium coordination.

in Table IV. A comparison of selected geometrical parameters for the vanadyl(IV) (±)-monomethyltartrate(4−) complex with those that have been determined for the (±)-tartrate(4−)[4,5] and (±)-dimethyltartrate(4−)[3] complexes is presented in Table V. We note that this comparison is made particularly easy since the same atom designations have been maintained in all of the structure determinations cited in this table.

There are several geometrical features shared by the $[(VO)_2((\pm)\text{-ligand})((-)\text{-ligand})]^{4-}$ complexes whose structures have been determined to date (Table V). All of the complexes have nearly perfectly staggered bridging ligands (O(5)–C(2)–C(3)′–O(6)′ torsion angle ≈ 60°). All have only a center of symmetry in the solid though the idealized maximum symmetry is C_{2h}.[4] Moreover, all of these complexes show similar distortions with the binuclear anion squashed to one side so that the V–O(6)′ distance is shorter than the V–O(5)′ distance (though this distortion is much more pronounced in the (±)-dimethyltartrate(4−) structure). Molecular models show that such a distortion will lead to a distinct nonplanarity for the five-membered chelate ring containing the hydroxyl oxygen atom (O(5) for all of these structures) furthest from the vanadium in the other half of the complex. This nonplanarity is shown in the nonzero value of the O(3)–C(1)–C(2)–O(5) torsion angle.

The coordination geometry found in the (±)-monomethyltartrate(4−) binculear complex is very similar to that found in the (±)-tartrate(4−) derivative (Table V).[4,5] There is no sixth-site coordination or dropping of the vanadium atom into the basal plane of coordinating oxygen atoms—characteristics of the (±)-dimethyltartrate(4−) structure.[3] That the geometrical parameters involving the methyl-substituted portion of the monomethyltartrate(4−) bridging ligand are not significantly different from those involving the nonmethyl-substituted half indicates that the anomalies in the coordination geometry of the (±)-dimethyltartrate(4−) structure are not the result of some electronic effect owing to the presence of methyl groups.

The V–V′ distance in the (±)-monomethyltartrate(4−) structure is similar to those that have been determined for the (±)-tartrate(4−) derivative. The shortening found for the totally methyl-substituted compound and predicted for the monomethyltartrate from ESR studies[2] is not observed. This

Table V. Comparison of Selected Geometrical Parameters for $[(VO)_2((+)\text{-tart})((-)\text{-tart})]^{4-}$, $[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]^{4-}$, and $[(VO)_2((+)\text{-dmt})((-)\text{-dmt})]^{4-}$[a]

	tart		mmt	dmt
	$(C_2H_5)_4N$ salt[b]	Na salt[c]	Na salt[d]	Na salt[e]
	Distances (Å)			
V–V′	3.985 (1)	4.082 (2)	4.047 (3)	3.429 (3)
V–O(3)	2.021 (3)	2.004 (6)	1.991 (4)	2.015 (3)
V–O(4)	2.026 (2)	1.994 (6)	1.979 (3)[f]	1.981 (3)
V–O(5)	1.955 (3)	1.971 (6)	1.904 (3)	1.964 (2)
V–O(6)	1.913 (2)	1.902 (6)	1.912 (4)[f]	1.974 (2)
V–O(7)	1.599 (3)	1.619 (7)	1.613 (4)	1.623 (3)
V–O(5)′	3.885 (3)	3.870 (6)	3.810 (4)	3.897 (3)
V–O(6)′	3.037 (3)	3.168 (6)	3.187 (4)	2.377 (3)
V–basal plane[g]	0.510	0.546	0.548	0.394
	Angles (Deg)			
O(7)–V–O(3)	105.7 (1)	109.8 (3)	107.1 (2)	103.3 (1)
O(7)–V–O(4)	105.6 (1)	104.8 (3)	105.3 (2)[f]	100.0 (1)
O(7)–V–O(5)	105.3 (1)	104.6 (3)	105.1 (2)	98.9 (1)
O(7)–V–O(6)	108.3 (1)	106.2 (3)	108.1 (2)	103.6 (1)
O(3)–V–O(4)	88.5 (1)	85.2 (3)	84.4 (1)	85.7 (1)
O(5)–V–O(6)	94.1 (1)	93.2 (2)	93.5 (1)	104.7 (1)
	Torsion Angles (Deg)			
O(4)–C(4)–C(3)–O(6)	−4.8 (4)	−1.0	1.8 (6)	0.7 (5)
O(3)–C(1)–C(2)–O(5)	20.5 (3)	15.0	20.9 (5)	23.5 (4)
O(5)–C(2)–C(3)′–O(6)′	−60.3 (4)	−61.5	−61.7 (6)	−59.1 (5)

[a] The atom nomenclature is constant for all of the structures. Primed and unprimed atoms are related by inversion centers. [b] Reference 5. [c] Reference 4. [d] This work. [e] Reference 3. [f] Oxygen atom near the methyl group. [g] Distance from the vanadium atom to the least-squares plane of O(3), O(4), O(5), O(6).

Table VI. Sodium and Water Coordination Distances in $Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]\cdot 14H_2O$[a]

Na(1)-O(4)	2.448 (5)	Na(2)-O(1)	2.352 (4)
-O(3)	2.480 (4)	-O(9)	2.461 (5)
-O(8)	2.358 (4)	-O(12)	2.457 (5)
-O(10)	2.397 (5)	-O(13)	2.539 (5)
-O(12)	2.429 (6)	-O(14A)	2.544 (11)
-O(10)[b]	2.398 (4)	-O(14B)	2.192 (10)
		-O(13)[c]	2.480 (6)
O(8)-O(8)[d]	2.777 (11)	O(11)←O(14A)	2.554 (17)
O(8)→O(6)[e]	2.780 (5)	O(11)←O(14B)	2.986 (17)
O(8)←O(13)[f]	2.856 (5)	O(12)→O(7)[h]	3.044 (7)
O(9)←O(11)[g]	2.747 (5)	O(12)→O(2)[i]	2.884 (7)
O(9)→O(1)[c]	2.827 (5)	O(13)→O(5)[j]	2.722 (5)
O(9)→O(7)[h]	2.787 (5)	O(14A)-O(14A)[g]	3.15 (3)
O(10)→O(11)	2.797 (5)	O(14A)→O(2)[f]	2.832 (15)
O(10)→O(2)[i]	2.832 (5)	O(14B)-O(14B)[g]	2.74 (3)
		O(14B)→O(2)	3.189 (15)

[a] The arrows indicate hydrogen atom donor-acceptor relationships between hydrogen bonded oxygen atoms. [b] $1-x, -y, -z$. [c] $1-x, 1-y, 1-z$. [d] $1-x, 1-y, -z$. [e] $-x, 1-y, -z$. [f] $x, y, 1+z$. [g] $1-x, y, z$. [h] $1+x, y, z$. [i] $1-x, -y, -z$. [j] $x, 1-y, 1-z$.

is most likely due to variations between the structures in the 77 K glass, in which the ESR studies were conducted, and in the crystal. That this is the case is indicated by our calculation of a zero-field splitting parameter D for the crystalline material of -0.0279 cm^{-1} from the V–V′ distance of 4.047 Å, the measured isotropic g value (solution) of 1.964, and the angle between the V═O and V—V′ vectors (θ) of 24.70° (assumed equal to the angle between the interelectron vector R and the magnetic quantization axis) using equations in ref 3. This value is in excellent agreement with the value of $|D| \approx 0.028$ cm^{-1} estimated from the powder ESR spectrum of the tetradecahydrate.[3] Thus, not only is the D value different for the crystal and the glass, but the crystal value can be calculated from the geometrical parameters determined in the crystal structure.

Crystal Packing. Water molecules and oxygen atoms of the tetranegative anion form octahedral coordination polyhedra around the two crystallographically independent sodium ions. Table VI lists the coordination distances for the sodium ions and the hydrogen-bonded water molecule, and Figure 2 shows the contents of the unit cell. As mentioned earlier, O(14) is disordered with a similar coordination about both positions though the Na(2)–O(14B) distance of 2.192 Å is very short. The final difference map indicates hydrogen disorders involving the hydrogen donor–acceptor relationships between O(8) and another atom related by a center of symmetry. A similar disorder may be present with O(14A) and O(14B) where water molecule oxygen atoms also related by a center of symmetry are coordinated. The difference peaks observed about O(8), O(14A), and O(14B) were not well resolved, and the disorder was not probed further.

Acknowledgment. This work was supported by grants from the Minority Biomedical Sciences Program (NIH-DRR No. 506 RR08139), the National Science Foundation (No. CH-780921) for purchase of the Syntex P3/F and R3 diffractometer and computing systems, and the University of New Mexico for the use of the IBM 360/67/65 computers and for a faculty grant through the Research Allocations Committee. Dr. Eileen Duesler aided in the preparation of computer-generated figures.

Registry No. $Na_4[(VO)_2((+)\text{-mmt})((-)\text{-mmt})]\cdot 14H_2O$, 79854-25-4.

Supplementary Material Available: Listings of idealized hydrogen atom positions and observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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Dioxygenase Models. Crystal Structures of [*N*,*N*′-(1,2-Phenylene)bis(salicylideniminato)](catecholato-*O*)iron(III) and μ-(1,4-Benzenediolato-*O*,*O*′)-bis[*N*,*N*′-ethylenebis(salicylideniminato)iron(III)]

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Received July 9, 1981

Two iron phenolate complexes have been synthesized to serve as models for dioxygenase enzyme–substrate and enzyme–inhibitor interactions; their X-ray structures have been determined. Fe(saloph)catH, a monodentate catecholate complex, crystallizes in the triclinic space group $P\bar{1}$ (a = 9.960 (6) Å, b = 8.108 (3) Å, c = 13.849 (8) Å, α = 95.73 (4)°, β = 91.93 (5)°, γ = 72.13 (4)°), while $[Fe(salen)]_2hq$, a bridged hydroquinone complex, crystallizes in the orthorhombic space group *Pbca* (a = 12.917 (3) Å, b 13.100 (4) Å, c = 19.440 (4) Å, $\alpha = \beta = \gamma$ = 90°). The irons in both complexes exhibit properties typical of square-pyramidal geometry—metal atom raised above the basal mean plane (0.55 Å for Fe(saloph)catH and 0.50 Å for $[Fe(salen)]_2hq$) and short apical Fe–O bonds (1.828 (4) Å for Fe(saloph)catH and 1.861 (2) Å for $[Fe(salen)]_2hq$). The average Fe–O and Fe–N bond lengths in the two tetradentate ligands are the same in both structures (1.905 and 2.079 Å, respectively) and are in excellent agreement with those found for similar complexes. Fe(saloph)catH and $[Fe(salen)]_2hq$ represent the first monodentate catecholate and the first bridged hydroquinone structures, respectively, of iron(III).

Introduction

The active-site structure and the reaction mechanism of the catechol-cleaving dioxygenases have been the subject of many investigations in recent years.[1,2] The active sites of these enzymes have been demonstrated to consist of mononuclear high-spin ferric centers[3,4] coordinated to two tyrosinates.[5,6] Other coordinating groups are not known at present, though nitrogen[3] and sulfur[7] donors have been suggested. Catechols

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