

Electronic and Molecular Structure of DL Vanadyl(IV) Tartrate(4-) and Methyl-substituted Tartrate(4-) Binuclear Complexes

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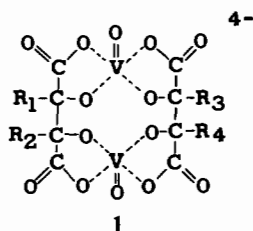
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Abstract

Several Fenske–Hall type molecular orbital calculations have been carried out in order to elucidate electronic and structural changes that occur upon methyl substitution of the DL isomer of binuclear vanadyl(IV) tartrate(4-). In addition, in order to confirm those structural changes that accompany methyl substitution, as observed in a recent crystal structure determination on tetrasodium [μ (+)-dimethyltartrato(4-)]- [μ (-)-dimethyltartrato(4-)]-bis(oxovanadate(IV)) dodecahydrate, an X-ray structure determination on a second crystal form, a hexahydrate, has been completed. The salt $\text{Na}_4[(\text{VO})_2((+)\text{-dmt})(-)\text{-dmt}] \cdot 6\text{H}_2\text{O}$, 'dmt' = dimethyltartrate(4-), $\text{O}=\text{C}(\text{CH}_3)(\text{O})\text{C}(\text{CH}_3)(\text{O})\text{COO}^{4-}$, crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.624(2)$, $b = 11.621(2)$, $c = 11.719(3)$ Å, $\beta = 124.07(2)^\circ$, $Z = 2$. The structure was refined to $R = 0.041$, $R_w = 0.041$ for 2248 independent, observed reflections. Like the blue dodecahydrate studied earlier, the pink hexahydrate exhibits a decreased V–V distance, a dropping of the vanadium atom toward the plane of the four equatorial oxygen ligands, an increased vanadium to tartrate hydroxyl oxygen atom distance (all relative to the nonmethyl-substituted complex), and sixth-site coordination by an ionized tartrate hydroxyl oxygen atom in the other half of the binuclear complex. The complex present in the hexahydrate salt is even more severely distorted from the idealized D_{2h} geometry than is the dodecahydrate structure (though a crystallographic center of symmetry is maintained in both). The molecular orbital calculations confirm an energy level ordering for the HOMO and the lowest four LUMOs of $a'(d_{x^2-y^2})$, $a'(d_{xz})$, $a''(d_{yz})$, $a''(d_{xy})$, and $a'(d_{z^2})$ in C_4 localized symmetry with the $a'(d_{xz})$, $a''(d_{yz})$ pair having nearly the same energy.

Introduction

There have been a number of investigations on the electronic and molecular structure and reactivity of α -hydroxycarboxylate compounds of V(IV). Of particular interest have been the spectral and structural differences between the isomers of the binuclear complexes of vanadyl(IV) tartrate(4-) (which can exist as the DL isomer with bridging tartrate groups of opposite enantiomeric form or as DD and LL isomers with both bridging groups in a complex having the same enantiomeric form) and the effects of methyl substitution in these complexes (1). In this paper we address the latter area of interest for the DL isomers only.



Recently two crystal forms of the tetrasodium salt of the tetranegative anionic complex, μ (+)-dimethyltartrato(4-)- μ (-)-dimethyltartrato(4-)-bis(oxovanadate(IV)), $[(\text{VO})_2((+)\text{-dmt})(-)\text{-dmt}]^{4-}$, a blue dodecahydrate and a pink hexahydrate, were reported [1]. A crystal structure of the former [1] shows a shortened (relative to the nonmethyl-substituted tartrate(4-) complex) V–V distance as predicted from earlier EPR studies [2]. This decrease in the internuclear distance is due to a dropping of the vanadium ion toward the plane of the four basal oxygen atoms (*i.e.*, those ligands which compose the base of the square-pyramidal coordination polyhedron formed by the five nearest donor atoms), and to a horizontal movement of the vanadium atom (opening up the hydroxyl oxygen–vanadium–hydroxyl oxygen bond angle). These changes are seen in a comparison of the structure of the (\pm)-dimethyltartrate(4-) species [1] with that of the (\pm)-tartrate(4-) complex [3, 4]. Another feature of the dimethyltartrate(4-) structure is a weak but significant sixth-site coordination opposite the

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TABLE I. Crystal and Intensity Collection Data for $\text{Na}_4[(\text{VO})_2((+)\text{-dmt})(-\text{-dmt})] \cdot 6\text{H}_2\text{O}$.

Formula	$\text{C}_{12}\text{H}_{24}\text{O}_{20}\text{Na}_4\text{V}_2$
Formula weight	682.15
Space group	$P2_1/c$ (No. 14)
Systematic absences	$h0l, l = 2n + 1, 0k0, k = 2n + 1$
a , Å	10.624(2)
b , Å	11.621(2)
c , Å	11.719(3)
β , deg	124.07(2)
V , Å ³	1198.5(8)
Z	2
ρ (calcd), g cm ⁻³	1.89
Crystal dimen, mm	0.35 × 0.35 × 0.10
Radiation	Mo $K\alpha$ ($\lambda = 0.71069$ Å)
Monochromator	graphite
μ (Mo $K\alpha$), cm ⁻¹	10.0
Scan speed, deg min ⁻¹	variable, 2.5 to 29.0
Scan range, deg	1.0 below $2\theta(K\alpha_1)$ to 1.25 above $2\theta(K\alpha_2)$
2θ limits, deg	1.0–55.0
Bkgd counting time	0.5 × scan time
Standards monitored	2 stds every 94 rflns
Collected reflections	3064 ($+h, +k, \pm l$)
Unique reflections	2779
m , unique data used	2248 with $F^2 > 2.5\sigma(F^2)$
n , no. of variables refined	221
$\text{ERF} = [\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$ w^{-1}	1.08 $\sigma^2(F_o) + (gF_o)^2, g = 0.03$
x , extinction parameter in $F = F_o[1 - (xF_o)^2/\sin\theta]$	2.4×10^{-4}
$R(F) = \sum F_o - F_c / \sum F_o $	0.041
$R_w(F) = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.041

vanadyl oxygen atom by a hydroxyl oxygen atom from the other half of the dimer (2).



There are also observed significant spectral differences between the (\pm)-dimethyltartrate(4-) species and the (\pm)-tartrate(4-) complex [1]. The nature of the electronic transitions, and the energy level ordering giving rise to these transitions, in vanadyl(IV) systems with oxygen donor atoms, have been the subjects of much discussion [5–8].

In this paper the X-ray crystal structure of the pink hexahydrate form of $[(\text{VO})_2((+)\text{-dmt})(-\text{-dmt})]^{4-}$ is reported. This was accomplished in order to determine whether the structural variations observed for the dimethyltartrate(4-) complex in the blue

dodecahydrate appear to be general, and to obtain additional information in hopes of elucidating the origins of the structural and spectral variations. We also report the results of molecular orbital calculations on models of the vanadyl(IV) (\pm)-tartrate(4-) system. These were carried out to help obtain a correct assignment of electronic transitions, and in hopes of further elucidating the source of the observed structural variations.

Experimental

X-ray

Crystals of the hexahydrate were grown by slow cooling of a hot solution of the sodium salt in an ethanol/water mixture as described elsewhere [1]. A diamond-shaped plate was selected and mounted in a sealed glass capillary. The crystal and reflection collection data are given in Table I. Lorentz, polari-

TABLE II. Atomic Coordinates and Thermal Parameters for $\text{Na}_4[(\text{VO})_2((+)\text{-dmt})(-)\text{-dmt})] \cdot 6\text{H}_2\text{O}$.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{iso} or U^{a}
V	0.53543(5)	0.11062(4)	0.41996(4)	0.0154(2)
Na(1)	0.38274(14)	0.18506(11)	0.58468(13)	0.0293(6)
Na(2)	0.40376(14)	0.07985(10)	0.84735(12)	0.0283(6)
O(1)	0.9849(2)	0.1343(2)	0.6693(2)	0.0346(10)
O(2)	0.2497(2)	-0.0273(2)	0.0749(2)	0.0311(10)
O(3)	0.7530(2)	0.1064(2)	0.4817(2)	0.0203(8)
O(4)	0.4758(2)	-0.0105(2)	0.2731(2)	0.0184(8)
O(5)	0.6225(2)	0.1801(2)	0.6006(2)	0.0177(8)
O(6)	0.3624(2)	0.0446(2)	0.4138(2)	0.0165(8)
O(7)	0.4698(2)	0.2228(2)	0.3209(2)	0.0254(9)
O(W1)	0.1995(3)	0.0978(2)	0.6108(3)	0.0320(11)
O(W2)	0.2561(3)	0.3369(2)	0.4306(2)	0.0311(10)
O(W3)	0.6327(3)	0.0914(2)	1.0761(3)	0.0313(12)
C(1)	0.8475(3)	0.1256(3)	0.6121(3)	0.0216(12)
C(2)	0.7705(3)	0.1331(2)	0.6916(3)	0.0190(11)
C(3)	0.2547(3)	-0.0048(2)	0.2826(3)	0.0184(11)
C(4)	0.3288(3)	-0.0150(2)	0.2009(3)	0.0196(12)
C(5)	0.8627(3)	0.2072(3)	0.8202(3)	0.0245(13)
C(6)	0.1119(3)	0.0687(3)	0.2059(3)	0.0250(12)
H(5A)	0.805(4)	0.222(3)	0.851(3)	0.033(9)
H(5B)	0.955(4)	0.173(3)	0.891(4)	0.039(10)
H(5C)	0.903(4)	0.282(4)	0.805(4)	0.052(11)
H(6A)	0.030(4)	0.039(3)	0.120(4)	0.043(10)
H(6B)	0.065(4)	0.077(3)	0.256(3)	0.027(9)
H(6C)	0.144(4)	0.146(3)	0.194(4)	0.045(11)
H(1A)	0.116(4)	0.113(3)	0.586(4)	0.047(11)
H(1B)	0.192(5)	0.034(4)	0.583(5)	0.058(14)
H(2A)	0.174(4)	0.330(3)	0.365(4)	0.047(11)
H(2B)	0.250(5)	0.390(3)	0.467(4)	0.051(12)
H(3A)	0.634(5)	0.161(4)	1.093(4)	0.061(13)
H(3B)	0.686(5)	0.081(4)	1.044(5)	0.065(13)

^a U_{iso} (for non-hydrogen atoms) is defined as one-third the trace of the anisotropic thermal parameter matrix in an orthogonalized coordinate system. U (for hydrogen atoms) is in the form $\exp[-8\pi^2 U^2 \sin^2 \theta / \lambda^2]$.

zation, and empirical absorption corrections were applied. The positions of the vanadium atoms and of one sodium atom were obtained by MULTAN, a direct method program [9]; heavy atom techniques were employed to obtain the positions for the other atoms*. The positions of all hydrogen atoms were obtained from a difference map calculated following anisotropic refinement of the non-hydrogen atoms. Positional parameters for all atoms, isotropic thermal parameters for hydrogen atoms, and anisotropic thermal parameters for non-hydrogen atoms were refined by least-squares methods. The weighting parameter g and the extinction parameter x (Table I) were varied in the last 17 cycles of block least squares. A final difference map showed two residual peaks with densities of 0.77 and 0.64 $\text{e}\text{\AA}^{-3}$. These peaks were within 1 \AA of the vanadium atom posi-

tion. The remaining residual peaks had densities of 0.42 $\text{e}\text{\AA}^{-3}$ or less. Scattering factors and dispersion corrections for neutral atoms were applied. The final atomic coordinates and thermal parameters (U_{iso} or U) are given in Table II.**

MO Calculations

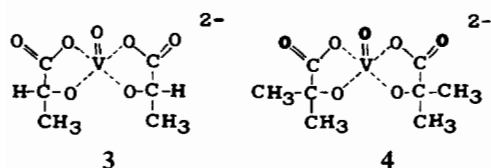
The computational method used was an approximate Hartree-Fock-Roothan SCF-LCAO molecular orbital calculation developed by Fenske and Hall [11] and modified by Campana and Ortega for the University of New Mexico's IBM-360 computer system. The method is parameter-free and self-consistent depending only on the atomic coordinates and choice of wave functions as input data. The calculations were iterated until the absolute value of

*All calculations and plots were carried out using the SHELXTL 79 package (Ref. 10(a)). SHELXTL uses anomalous dispersion and scattering factor data found in Ref. 10(b).

**Tables of structure factors, anisotropic thermal parameters, interatomic distances and angles involving hydrogen atoms, and sodium ion and water coordination distances are available from the Editor on request.

the difference in the Mulliken population in each valence orbital was less than 0.001. The vanadium atomic functions were those of Richardson [12] for V(IV) with 4s and 4p exponents of 1.25 and 1.60 respectively. The carbon and oxygen functions were double ζ functions of Clementi [13] reduced to single ζ functions. An exponent of 1.16 was used for hydrogen atom 1s functions.

The actual molecules used for the MO calculations were (+)-2-hydroxypropanoato(2-)-(-)-2-hydroxypropanoato(2-)oxovanadate(IV) (3) and the methyl-substituted complex (4). This was done in order to simulate one half of each binuclear complex. Calculations on the entire molecule would have been excessively time consuming. The bond lengths and bond angles were obtained from the X-ray structure determination of tetraethylammonium vanadyl(IV) (\pm)-tartrate(4-) octahydrate [4]. The coordinates were idealized so that C_s symmetry was preserved, the mirror plane being the zx plane. The sixth-site coordination by a hydroxyl oxygen was simulated for some calculations by placing an OH^- functionality at the



distance from the vanadium atom determined by X-ray analysis [1].

Eight calculations were accomplished. Calculations were done on half complexes of vanadyl(IV) (\pm)-tartrate(4-) (3), vanadyl(IV) (\pm)-dimethyltartrate(4-) without sixth-site coordination (4), and vanadyl(IV) (\pm)-dimethyltartrate(4-) with sixth-site coordination (4). All these calculations were done both with the vanadium to basal oxygen plane distance found for the unsubstituted vanadyl(IV) (\pm)-tartrate(4-) complex (0.510 Å) [4] and with the distance found for the dimethyltartrate(4-) complex (0.350 Å) [1] (referred to as 'vanadium-up' and 'vanadium-dropped' respectively). In addition,

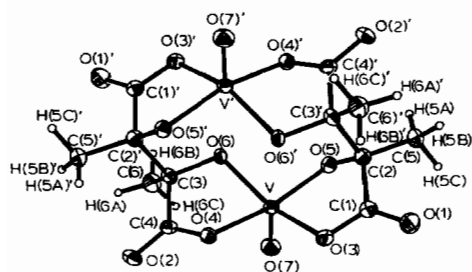


Fig. 1. View of the $[(\text{VO})_2((+)\text{-dmt})(-)\text{-dmt}]^{4-}$ anionic complex with atom designations. Primed atoms are generated by $1-x, -y, 1-z$. Thermal ellipsoids are shown at the 50% probability level (except for hydrogen atoms which are drawn as arbitrarily dimensioned spheres).

TABLE III. Interatomic Distances (Å) and Angles (Deg) Determined for the Anionic Complex in $\text{Na}_4[(\text{VO})_2((+)\text{-dmt})(-)\text{-dmt}]\cdot 6\text{H}_2\text{O}$ with e.s.d.s in Parentheses.^a

V-V'	3.504(1)	C(1)-C(2)	1.550(5)
V-O(7)	1.620(3)	C(3)-C(4)	1.547(6)
V-O(3)	1.999(2)	C(2)-C(3)'	1.574(5)
V-O(4)	2.030(3)	C(1)-O(1)	1.222(4)
V-O(6)	1.956(2)	C(4)-O(2)	1.231(4)
V-O(5)	1.949(3)	C(1)-O(3)	1.294(4)
V-O(6)'	2.420(3)	C(4)-O(4)	1.295(4)
C(2)-C(5)	1.522(5)	C(2)-O(5)	1.425(4)
C(3)-C(6)	1.520(5)	C(3)-O(6)	1.426(4)
O(7)-V-O(3)	103.0(1)	O(1)-C(1)-O(3)	124.1(4)
O(7)-V-O(4)	98.4(1)	O(2)-C(4)-O(4)	123.5(4)
O(7)-V-O(5)	101.4(1)	O(1)-C(1)-C(2)	122.4(3)
O(7)-V-O(6)	105.7(1)	O(2)-C(4)-C(3)	120.6(3)
O(3)-V-O(4)	92.2(1)	O(3)-C(1)-C(2)	113.5(3)
O(5)-V-O(6)	93.8(1)	O(4)-C(4)-C(3)	116.0(3)
O(3)-V-O(5)	82.4(1)	O(6)-C(3)-C(4)	108.6(3)
O(4)-V-O(6)	81.8(1)	O(5)-C(2)-C(1)	107.8(3)
O(3)-V-O(6)	151.2(1)	O(6)-C(3)-C(2)'	107.1(2)
O(4)-V-O(5)	160.3(1)	O(5)-C(2)-C(3)'	105.8(2)
O(6)'-V-O(3)	77.5(1)	O(6)-C(3)-C(6)	110.1(3)
O(6)'-V-O(4)	87.3(1)	O(5)-C(2)-C(5)	110.6(3)
O(6)'-V-O(5)	73.1(1)	C(1)-C(2)-C(3)'	105.5(3)
O(6)'-V-O(6)	74.1(1)	C(4)-C(3)-C(2)'	104.3(3)
O(6)'-V-O(7)	174.3(1)	C(1)-C(2)-C(5)	111.3(3)
V-O(3)-C(1)	113.4(3)	C(4)-C(3)-C(6)	111.3(3)
V-O(4)-C(4)	105.7(2)	C(6)-C(3)-C(2)'	115.1(3)
V-O(5)-C(2)	107.9(2)	C(5)-C(2)-C(3)'	115.4(3)
V-O(6)-C(3)	111.5(2)	O(7)-V-V'	147.0(1)

^aPrimed atoms are generated by $1-x, -y, 1-z$.

two calculations were carried out on the free ligands where the $(\text{VO})^{2+}$ was removed from structures (3) and (4).

Results and Discussion

Structure of $\text{Na}_4[(\text{VO})_2((+)\text{-dmt})(-)\text{-dmt}]\cdot 6\text{H}_2\text{O}$

As found in all structures of tartrate(4-)-bridged and substituted-tartrate(4-)-bridged vanadyl(IV) complexes with oppositely enantiomeric bridging ligands (*i.e.*, DL isomers) determined to date [1, 3, 4, 14], the tetranegative complex anion $[(\text{VO})_2((+)\text{-dmt})(-)\text{-dmt}]^{4-}$ (Fig. 1) has a crystallographic center of symmetry. Interatomic distances and angles are given in Table III, and Table IV provides a selected list of specific structural parameters which can be used to compare the anionic complexes of the two hydrates (see Table V of Ref. 14 for analogous data from other tartrate(4-)-bridged vanadyl(IV) complexes). Like the blue dodecahydrate complex, the anion in the present structure contains a V-V' distance (3.504(1) Å) which is significantly shorter than the corresponding distances found in the tar-

TABLE IV. Comparison of Selected Geometrical Parameters for $\text{Na}_4[(\text{VO})_2((+)\text{-dmt})((-)\text{-dmt})] \cdot x\text{H}_2\text{O}$, $x = 12$ and $x = 6$.^a

	$\cdot 12\text{H}_2\text{O}^b$	$\cdot 6\text{H}_2\text{O}$
Distances (Å)		
V–V'	3.429(3)	3.504(1)
V–O(3)	2.015(3)	1.999(2)
V–O(4)	1.981(3)	2.030(3)
V–O(5)	1.964(2)	1.949(3)
V–O(6)	1.974(2)	1.956(2)
V–O(5)'	3.897(3)	3.719(3)
V–O(6)'	2.377(3)	2.420(3)
V–basal plane ^c	0.392(1)	0.416(1)
Angles (Deg)		
O(3)–V–O(4)	85.7(1)	92.2(1)
O(5)–V–O(6)	104.7(1)	93.8(1)
Torsion Angles (Deg)		
O(4)–C(4)–C(3)–O(6)	0.7(5)	18.9(3)
O(3)–C(1)–C(2)–O(5)	23.5(4)	–32.1(3)
O(5)–C(2)–C(3)'–O(6)'	–59.1(5)	48.0(3)
C(5)–C(2)–C(3)'–C(6)'	56.3(5)	–66.5(4)

^aThe atom nomenclature is the same for both structures. Primed and unprimed atoms are related by an inversion center.
^bReference 1. ^cDistance of the vanadium atom from the least-squares plane of O(3), O(4), O(5), O(6).

trate(4–) (4.082(1) Å [3], 3.985(1) Å [4]) and monomethyltartrate(4–) (4.047(3) Å [14]) compounds. This appears to be due primarily to a dropping of the vanadium atom toward the basal plane of the four most closely coordinated tartrate oxygen atoms. The vanadium to basal plane distance of 0.416 Å is about 0.1 Å shorter than that found for binuclear complexes containing tartrate(4–) and monomethyltartrate(4–) ligands [14]. In addition, as found also for the anion of the blue dodecahydrate, the complex of the pink hexahydrate is severely 'squashed' to one side so that the V–O(6)' distance of 2.420(3) Å is significantly shorter than the V–O(5)' distance of 3.719(3) Å giving a weak sixth-site coordination by O(6)'.

That these similarities exist for the anions of the two crystal forms indicates that generic features of the vanadyl(IV) dimethyltartrate(4–) complex may indeed include sixth-site coordination, a shortened V–V distance (as indicated by earlier EPR studies in glasses [2]), a 'squashed' structure, and a dropping of the vanadium atom toward the basal plane, and that these features are not due to crystal packing effects. Moreover, the similarity in band positions in electronic spectra of solutions and solids containing the DL complex of dimethyltartrate(4–) [1] indicate that these features persist in solution. The crystal structure results give no indication of how methyl group substitution might cause these geometrical features. Moreover, molecular models indicate no steric interactions which are likely to lead

to the observed geometries. On the other hand, from the result of a crystal structure determination on the vanadyl(IV) monomethyltartrate(4–) complex, it has been concluded that electronic effects owing solely to the presence of methyl groups are also unlikely to be the cause of the geometrical features observed for the dimethyltartrate(4–) complex [14]. One reason for carrying out molecular orbital calculations was the hope that the results obtained would help solve this dilemma.

Though the anions of the dodecahydrate and hexahydrate have several geometrical features in common, there are a number of important differences (Table IV), the most obvious being the severe distortion of the chelate rings in the present structures. This distortion can be seen in Fig. 2 and also in the values of 18.9(3)°, and –32.1(3)° for the O–C–C–O α -hydroxycarboxylate group dihedral angles. Though all of the DL isomer vanadyl(IV) tartrate(4–) and substituted-tartrate(4–) complex structures determined to date exhibit distinctly different dihedral angles for the two α -hydroxycarboxylate chelate rings coordinated to a particular vanadium atom [14], none show the large nonplanarities seen here (α -hydroxycarboxylate groups are usually nearly planar [15]). As seen in the other structures and as predicted from molecular models [14], the α -hydroxycarboxylate group containing the hydroxyl oxygen atom furthest from the vanadium atom in the other half of the complex (O(5)') is the most nonplanar. Both of the crystallographically non-

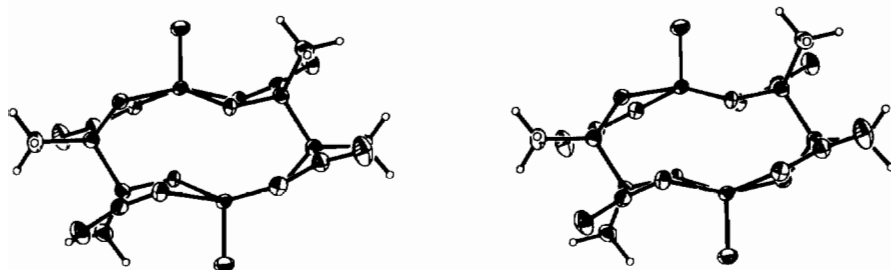
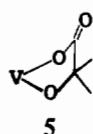


Fig. 2. Stereoview of the anionic complex present in $\text{Na}_4[(\text{VO})_2((+)\text{-dmt})((-)\text{-dmt})] \cdot 6\text{H}_2\text{O}$. Thermal ellipsoids of the non-hydrogen atoms are shown at the 50% probability level.

equivalent chelate rings have asymmetric envelope conformations (5) with the chelate ring containing O(5)' (that which is most distinctly nonplanar) bent away from the vanadyl oxygen atom and that containing O(6)' bent toward the vanadyl oxygen. Asymmetric envelope conformers are common for α -hydroxycarboxylate chelates [15].



The vanadium atom of the hexahydrate structure is 0.02 Å further from the basal plane and 0.04 Å further from the weakly coordinating O(6)' atom than is the vanadium atom of the dodecahydrate salt. This increase in the sixth-site coordination distance is accompanied by a decrease in the average vanadium to basal hydroxyl oxygen bond lengths. A comparison of the present structure with others [14] indicates that variations in the average vanadium to basal hydroxyl oxygen atom bond length are probably due to the presence and degree of bonding in the sixth-site. As this bonding becomes stronger (shorter V–O(6)' distances), the coordination to the basal hydroxyl oxygen atoms becomes weaker (longer V–O(5) and V–O(6) distances). This interpretation is supported by visible spectra studies and molecular orbital calculations (*vide infra*).

One final difference between the structures of the complex anions in the two hydrate forms is the absence of an opening of the O(5)–V–O(6) angle, which in the hexahydrate salt is nearly that found for the unsubstituted tartrate complexes [14]. This difference explains the slightly shorter V–V' distance for the dodecahydrate where the O(5)–V–O(6) angle has opened [1].

Molecular Orbital Calculations

One of the objectives for the molecular orbital calculations was a determination of the energy level ordering that gives rise to the three electronic transitions observed for (\pm)-tartrate(4⁻) and substituted (\pm)-tartrate(4⁻) complexes of vanadyl(IV) [1]. There

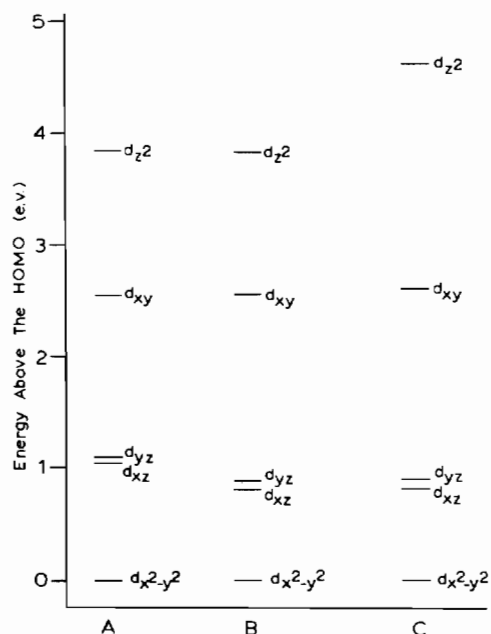


Fig. 3. Energy level ordering obtained from molecular orbital calculations as a function of molecular structure. A, B, and C correspond to model complexes based on $[(\text{VO})_2((+)\text{-tart})((-)\text{-tart})]^{4-}$ vanadium-up, $[(\text{VO})_2((+)\text{-dmt})((-)\text{-dmt})]^{4-}$ vanadium-dropped, and $[(\text{VO})_2((+)\text{-dmt})((-)\text{-dmt})]^{4-}$ vanadium-dropped and with sixth-site coordination, respectively.

has been considerable interest in the ordering and source of electronic transitions in vanadyl(IV) α -hydroxycarboxylates [16, 17]. Figure 3 shows the ordering obtained from the MO calculations reported here. This ordering, which is obtained assuming Koopmans' theorem holds, is constant throughout our six calculations and is essentially the same as those obtained by Ballhausen and Gray [8] and by Vanquickenborne and McGlynn [18] for vanadyl(IV) sulfate pentahydrate. The only differences are a reversal of the $d_{x^2-y^2}$ and d_{xy} orbitals, owing to the coordinate system orientation, and the distinct energies for the orbitals comprised primarily of d_{xz} and d_{yz} in our calculations. Ballhausen and Gray [8]

TABLE V. Energies of Electronic Transitions (μm^{-1}) Calculated from Eigenvalues Found by Molecular Orbital Calculations.

Model Complex based on	Calculated Transition Energies (μm^{-1})		
	I	II	III
$[(\text{VO})_2((+)\text{-tart})(-)\text{-tart}]^{4-}$ vanadium-dropped	0.677	2.089	3.087
$[(\text{VO})_2((+)\text{-tart})(-)\text{-tart}]^{4-}$ vanadium-up	0.862	2.047	3.086
$[(\text{VO})_2((+)\text{-dmt})(-)\text{-dmt}]^{4-}$ vanadium-dropped	0.677	2.055	3.079
$[(\text{VO})_2((+)\text{-dmt})(-)\text{-dmt}]^{4-}$ vanadium-up	0.870	2.039	3.086
$[(\text{VO})_2((+)\text{-dmt})(-)\text{-dmt}]^{4-}$ vanadium-dropped with sixth-site coordination	0.652	2.087	3.691
$[(\text{VO})_2((+)\text{-dmt})(-)\text{-dmt}]^{4-}$ vanadium-up with sixth-site coordination	0.830	2.055	3.579

assumed C_{4v} symmetry, where d_{xz} and d_{yz} belong to an e representation.

For vanadyl(IV) (\pm)-tartrate(4-) complexes two possible orderings have been proposed [16] – the ordering described in Fig. 3, and one in which the d_{xy} and d_{xz} , d_{yz} orbitals have been interchanged. It is possible to relate the transition energies to the shift in the g values from the free electron value of 2.0023 [19]. Using the approximations of Belford [19] and EPR data obtained by McIlwain [2] we have calculated $\Delta g_{\parallel}/\Delta g_{\perp}$ for (\pm)-tartrate(4-) and methyl-substituted (\pm)-tartrate(4-) complexes of vanadyl(IV). The calculations depend on the transition energies and the ratio β^2/γ^2 , where β and γ are molecular orbital coefficients. When these calculations were carried out (using spectral data reported elsewhere [1] and setting $\beta^2/\gamma^2 = 1$, as found in our MO calculations) we obtain for vanadyl(IV) dimethyltartrate(4-) $\Delta g_{\parallel}/\Delta g_{\perp}$ values of 2.7 for the ordering shown in Fig. 3 and 6.0 for the described alternate ordering. This may be compared to a value of 3.0 ± 0.5 obtained from the experimentally determined g values. For vanadyl(IV) tartrate(4-), calculated values of 2.9 and 5.5 were obtained for the ordering described in Fig. 3 and the alternate ordering respectively, compared to an experimental value of 2.0 ± 0.5 . Thus reported EPR data strongly support the energy level ordering indicated by our MO calculations.

The vanadyl(IV) (\pm)-tartrate(4-) and methyl-substituted tartrate(4-) complexes exhibit three bands in the visible region [1]. These have been arbitrarily designated bands I, II, and III from lower to higher energies, and, according to our calculations, correspond to the transitions $a'(d_{x^2-y^2}) \rightarrow \{a'(d_{xz}), a''(d_{yz})\}$, $a'(d_{x^2-y^2}) \rightarrow a''(d_{xy})$, and $a'(d_{x^2-y^2}) \rightarrow a'(d_{z^2})$ respectively. Our calculations show $a'(d_{xz})$ and

$a''(d_{yz})$ to be so close together in energy that the transitions to these levels are not expected to be resolvable. With increasing methyl substitution of the (\pm)-tartrate(4-) complexes, one observes a decrease in the lowest energy transition (band I), and an increase in the highest energy transition (band III), while band II remains relatively unaffected (see Table X, Ref. 1). The results of the MO calculations are consistent with these experimental results and elucidate the source of the spectral changes. The transition energies calculated applying Koopmans' theorem are summarized in Table V. The data contained in Table V indicates that the changes resulting from methyl group substitution in band I, $a'(d_{x^2-y^2}) \rightarrow \{a'(d_{xz}), a''(d_{yz})\}$, are due to the dropping of the vanadium toward the basal plane of the four oxygen atoms, and that the changes in band III, $a'(d_{x^2-y^2}) \rightarrow a'(d_{z^2})$, are due primarily to sixth-site coordination. Thus the calculations indicate that the spectral changes observed are due to structural changes rather than some type of inductive effect accompanying methyl group substitution.

We can calculate, using the two-center overlap populations, the orders of the bonds between coordinating oxygen atoms and the vanadium atom. These can then be related to observed structural changes in the molecule. There is a general decrease in vanadium to coordinating oxygen atom bond order (excluding the sixth-site oxygen atom) upon going from the tartrate(4-) molecule with the vanadium up to the dimethyltartrate(4-) molecule with the vanadium dropped toward the basal plane and with sixth-site coordination. The largest changes are observed for the addition of sixth-site coordination, with the bond order decreases ranging from 15% for bonds involving the tartrate oxygen atoms to 35% for the bond involving the vanadyl oxygen atom (a

table of calculated bond orders is available from the Editor on request). In the case where the vanadyl ion is dropped toward the basal plane of the four equatorial oxygen atoms, one might expect an increase in the overall bond order owing to increased sigma bonding. However the maximum increase observed is only 1%. This further emphasizes the importance of sixth-site coordination to the structure of the compound.

Data obtained from IR spectra are also consistent with the bond order changes discussed above. We observe a decrease in V=O stretching frequency upon going from the tartrate(4-) ligand (948 cm^{-1} for $\text{Na}_4[(\text{VO})_2((+)\text{-tart})(-\text{-tart})]\cdot 12\text{H}_2\text{O}$) to the dimethyltartrate(4-) ligand (939 cm^{-1} for $\text{Na}_4[(\text{VO})_2((+)\text{-dmt})(-\text{-dmt})]\cdot 12\text{H}_2\text{O}$). The V=O stretching frequency observed for the monomethyltartrate(4-) complex is similar to that observed for the tartrate(4-) complex (947 cm^{-1} for $\text{Na}_4[(\text{VO})_2((+)\text{-mmt})(-\text{-mmt})]\cdot 14\text{H}_2\text{O}$). The decrease in V=O stretching frequency for the dimethyltartrate(4-) complex is apparently due to the sixth-site coordination.

One possible explanation for sixth-site coordination is the following: Increasing alkyl group substitution has been shown to decrease the basicity of hydroxyl groups [20], and calculations carried out on the free ligands support this. We observe a decrease in energy in the MO's which are primarily hydroxyl oxygen $2p_z$ in character from 15.88 and 15.98 eV to 15.47 and 15.56 eV upon methyl group substitution. This decrease in basicity should lead to a loss in coordinating ability of the hydroxyl oxygen atoms of the tartrate ligand. In fact we see a decrease in bond orders calculated from our MO results for nearly all bonds to vanadium when methyl groups are added while keeping the geometry constant. In order to offset this loss in equatorial oxygen ligand ability the vanadium acquires coordination at the sixth-site by a hydroxyl oxygen from the other half of the dimer. In order for this to occur the molecule distorts and the vanadium atom drops toward the basal plane of the four oxygen atoms. It should be pointed out that for the monomethyltartrate(4-) complex, one observes a short V-V distance in the ESR spectra of glasses at 77 K [2], while X-ray analysis yields a V-V distance and coordination geometry similar to those observed in the unsubstituted vanadyl(IV) tartrate(4-) species [14]. Moreover, the solution and solid-state electronic spectra of the monomethyltartrate(4-) complex are much less similar than those for the tartrate(4-) and dimethyltartrate(4-) derivatives [1]. The spectral differences are such that sixth-site coordination and a dropped vanadium atom are indicated to be present to some extent in solution. (There is a decrease in the energy of band I and an increase in the energy of band III on going from

solid to solution [1].) These observations support a more dynamic picture of the monomethyltartrate(4-) bridged complexes with sixth-site coordination only moderately favored.

Summary and Conclusions

Our X-ray results indicate certain inherent structural features in vanadyl(IV) (\pm)-dimethyltartrate(4-) complex. These structural features include a decreased (as compared with nonmethyl-substituted (\pm)-tartrate(4-) complexes) V-V distance, a squashed structure, a dropping of the vanadyl(IV) ion toward the basal plane of the four equatorial oxygen ligands, and a weak sixth-site coordination by a hydroxyl oxygen atom from the other half of the dimer.

The molecular orbital calculations reported here correlate well with the electronic spectral changes observed for the (\pm)-tartrate(4-) complex with methyl substitution. The three-band spectra arise primarily from d-d transitions with the ordering $d_{x^2-y^2} \rightarrow (d_{xz}, d_{yz}), d_{x^2-y^2} \rightarrow d_{xy}$, and $d_{x^2-y^2} \rightarrow d_z^2$ from lower to higher energies. We are unable to comment on the contribution to the spectra from charge transfer mechanisms. This work along with the work of others [5, 6, 8, 18] indicates a common electronic picture for pentacoordinate vanadyl(IV) systems with oxygen donor atoms.

Because certain structural changes are apparently manifested in band-specific spectral changes, one can use the spectra of (\pm)-tartrate(4-)-bridged vanadyl(IV) species to make predictions with regards to the structure of the molecules. Specifically, an increase in the energy of the lowest energy spectral band indicates a vanadium-dropped structure with a decreased V-V distance, and an increase in the energy of the highest energy d-d transition implies sixth-site coordination.

Finally, this work points to the importance of the observed sixth-site coordination to the electronic and molecular structure of vanadyl(IV) (\pm)-dimethyltartrate(4-), the effect of which is manifested in several ways. Sixth-site coordination may be acquired in order to offset the loss in bonding with the other ligands as a result of decreased tartrate basicity upon methyl group substitution. In order for this to occur the molecule must distort and the vanadium must drop toward the basal plane of the four tartrate ligand oxygen atoms. The sixth-site coordination leads to a decrease in the bond orders between the vanadium atom and the basal oxygen atoms. This is manifested in increased vanadium to hydroxyl oxygen atom bond lengths.

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