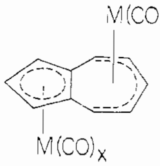
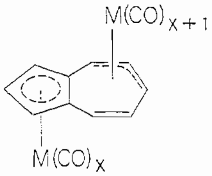
will depend on the relative energies for localization of an electron on the *ortho* and *para* positions. Qualitatively, localization at the *ortho* position would seem to be the more probable, since it conserves a conjugated butadiene system. [Although the stereochemistry of the $[C_{10}H_8Mo(CO)_3CH_3]_2$ molecule is established as involving *ortho–ortho* coupling, no definitive information is yet available on $[C_{10}H_8V(CO)_4]_2$[4] or $[C_{10}H_8Mn(CO)_3]_2$.[3]] (b) The five available carbon atoms in the seven-membered ring may combine with a further metal carbonyl residue, to form a *trans* product such as VI[34] or VII. [A *cis* product is unlikely since it would require the metal atoms to be within bonding distance.]

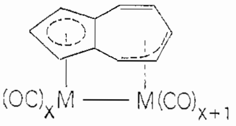


VI

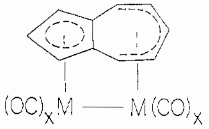


VII

(iii) If the metal atom in the pseudo-π-cyclopentadienyl complex (III–V) has only a 17-electron configuration, a metal–metal bond will be formed and a second metal carbonyl residue will be linked to the seven-membered ring *via* a π-allyl (VIII) or π-pentadienyl (IX) linkage. The reason why azulenediiron (I) contains a π-allyl–metal linkage whereas azulenedimolybdenum hexacarbonyl (II) has a π-pentadienyl–metal bond is not fully understood. It may be due to the 3d orbitals of the iron atom being too small to overlap effectively with all five atoms in the prospective π-pentadienyl system, or to the intrinsic stability of the $Fe(CO)_3$ system *per se*. It is hoped that current experiments involving the isoelectronic azulene–ruthenium–carbonyl system may clarify this problem.



VIII



IX

Acknowledgments.—This work has been generously supported by the Advanced Research Projects Agency (Grant No. SD-88).

(34) We have recently prepared a complex which mass spectrometric analysis indicates to be $C_{10}H_8Mn_2(CO)_6$. We expect this to have structure VI. Note Added in Proof.—This has now been confirmed (P. H. Bird and M. R. Churchill, *Chem. Commun.*, in press).

Contribution from the Noyes Chemical Laboratory and Materials Research Laboratory,
University of Illinois, Urbana, Illinois 61801

Crystal Structure of a Binuclear Vanadyl(IV) Anion. Tetrasodium Divanadyl(IV) *d*-Tartrate *l*-Tartrate Dodecahydrate[1]

By ROBERT E. TAPSCOTT, R. LINN BELFORD, and IAIN C. PAUL

Received June 26, 1967

The crystal structure of the sodium salt of divanadyl(IV) *d*-tartrate *l*-tartrate dodecahydrate ($Na_4[VO\text{-}dl\text{-}C_4H_2O_6]_2\cdot 12H_2O$) has been determined by Fourier methods, and the positional and anisotropic thermal parameters of the atoms were refined by least-squares methods on three-dimensional photographic data. The crystals are orthorhombic, space group Pbca, with $a = 19.85$, $b = 10.76$, and $c = 12.28$ A. The measured density is 1.85 g/cm^3 while that calculated for eight formula units of $Na_2[VOC_4H_2O_6]\cdot 6H_2O$ is 1.858 g/cm^3. The tetranegative dimeric anions contain two VO^{2+} ions bridged by a *d*-tartrate and an *l*-tartrate group which have lost all of the carboxyl and hydroxyl hydrogen atoms to give tetranegative tartrate ions. The vanadium atoms are situated in a normal square-pyramidal coordination site in contrast to the distorted trigonal-bipyramidal coordination found in $(NH_4)_4[VO\text{-}d\text{-}C_4H_2O_6]_2\cdot 2H_2O$. The vanadium–vanadium distance is 4.082 A. The final R factor is 0.10 for 2629 nonzero reflections.

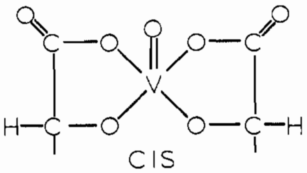
Introduction

Recently, we reported[2] the characterization and comparison of the two different complexes of vanadyl(IV) obtained with *d*-tartaric and racemic tartaric acids. Arguing purely from aqueous solution evidence and molecular models, we postulated structures for these two isomers consisting of two vanadyl(IV) ions bridged by two tartrate anions which have lost the protons from

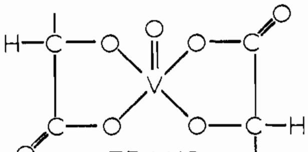
(1) Supported by Advanced Research Projects Agency Contract SD-131, through the Materials Research Laboratory at the University of Illinois, and U. S. Public Health Service Grant No. GM 12470-03 and a predoctoral fellowship awarded to R. E. T., through the Institute of General Medical Sciences.

(2) R. E. Tapscott and R. L. Belford, *Inorg. Chem.*, **6**, 735 (1967).

both carboxyl and both hydroxyl groups—the vanadyl(IV) *d*-tartrate anion having two *d*-tartrate bridges and the vanadyl(IV) *dl*-tartrate anion having one *d*-tartrate and one *l*-tartrate bridge. These proposed structures required the *dd* isomer to exhibit a *trans* configuration about the vanadium atom but the *dl* isomer to have a *cis* configuration



CIS



TRANS

The structure of the *dd* isomer has been determined using X-ray diffraction techniques[3] and confirms the essential features of our postulated model for this complex. For comparison and to obtain data necessary to interpret spectroscopic work now in progress on the solid state of these compounds, we have determined the crystal structure of the sodium salt of vanadyl(IV) *dl*-tartrate.

Experimental Section

Preparation of Compound.—Tetrasodium divanadyl(IV) *d*-tartrate *l*-tartrate dodecahydrate, hereafter referred to as $\mathrm{Na_4[VO\text{-}}dl\text{-}\mathrm{tart]_2\cdot 12H_2O}$,[4] was prepared as previously described[2] and crystals were grown by evaporation of an aqueous solution.

Crystallographic Data.—The crystals belong to the orthorhombic system. Using a sodium chloride crystal as a reference (a = 5.6387 A)[5] and Mo Kα radiation (λ 0.7107 A), the cell parameters were $a = 19.85 \pm 0.06$, $b = 10.76 \pm 0.03$, and $c = 12.28 \pm 0.03$ A as determined from precession photographs at 25°. The standard deviations reported are the sum of the average standard deviations in the measurements of the cell dimensions of NaCl and of $\mathrm{Na_4[VO\text{-}}dl\text{-}\mathrm{tart]_2\cdot 12H_2O}$. The volume of the unit cell is 2623×10^{-24} cm^3. If it contains eight formula units of $\mathrm{Na_2[VOC_4H_2O_6]\cdot 6H_2O}$ (formula weight, 367.09), the calculated density is 1.858 g/cm^3; the value measured by flotation in a mixture of carbon tetrachloride and iodomethane is 1.85 g/cm^3. We had previously reported[2] the empirical formula to be $\mathrm{Na_2[VOC_4H_2O_6]\cdot 5.5H_2O}$ on the basis of microanalytical data, but the density measurement and subsequent structural work indicated six water molecules per vanadium atom.[6] $F(000)$ is 1496. Sytematic absences, as detected from precession (0*kl*, 1*kl*, *h*0*l*, and *h*1*l*) and Weissenberg (*hk*0 and *hk*1) photographs, 0*kl* when k is $2n + 1$, *h*0*l* when l is $2n + 1$, and *hk*0 when h is $2n + 1$ determine the space group as Pbca (D_{2h}^{15}, No. 61). The linear absorption coefficient, μ (Mo Kα), is 9.4 cm^{-1}.

Morphology of Crystals.—The lustrous brown crystals grow easily as large diamond-shaped plates lying on the (100) face. In addition to the well-developed {100} faces, the crystals exhibit all of the {111} faces. The crystals belong to the holohedral class, point group mmm (D_{2h}), with extinction directions along the diagonals of the diamond. The plates exhibit strong dichroism when viewed perpendicular to the (100) face; the color is dark brown when the light is polarized along c and light brown when along b. Figure 1 shows a drawing of the crystal habit for reference to the present work and to the crystal spectra to be reported later.

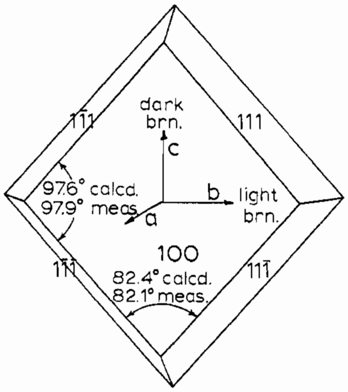


Figure 1.—Crystal habit of $\mathrm{Na_4[VO\text{-}}dl\text{-}\mathrm{tart]_2\cdot 12H_2O}$. The measured angles have an estimated accuracy of ±0.5°.

Collection of X-Ray Data.—To obtain a roughly equidimensional specimen for the intensity measurements, we cut a single, large plate to give a crystal with dimensions $0.47 \times 0.48 \times 0.70$ mm. The crystal was mounted along the c axis and intensities were recorded on multiple films using an equiinclination Weissenberg camera with zirconium-filtered Mo Kα radiation (λ 0.7107 A). Sixteen levels of data were taken (*hk*0–*hk*15) and 2629 independent nonzero reflections were estimated visually by comparison with calibrated film strips. Lorentz and polarization factors were applied, but no correction was made for absorption. Initially, the various levels of data were placed on a common scale according to the exposure time.

Structure Determination.—The space group Pbca has eight general positions and the cell data require one vanadium atom per asymmetric unit. The position of the vanadium atom was readily obtained from the three-dimensional Patterson synthesis.[7] The first Fourier synthesis, with signs from the calculated contribution of the vanadium atom to the structure factors, showed peaks which we considered to be the four coordinating oxygen atoms on the tartrate chain and the two sodium ions. A second Fourier synthesis, based on the further information provided by these atoms, indicated the positions of the remaining atoms, other than hydrogen. At this point, the crystallographic R factor, $R \equiv \Sigma||F_o| - |F_c||/\Sigma|F_o|$, was 0.41. Several cycles of full-matrix least-squares refinement[8] using isotropic temperature coefficients reduced R to 0.11. All reflections were given unit weight and the quantity minimized was $\Sigma w||F_o| - |F_c||^2$. The interlevel scale factors were adjusted to the calculated structure factors prior to the anisotropic refinement but were not adjusted thereafter. Introduction of anisotropic temperature factors reduced R to 0.10 after six cycles of least-squares refinement. Limited computer capacity made it impossible to carry out full-matrix refinement on all 20 atoms (other than hydrogen) when

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(3) J. G. Forrest and C. K. Prout, *J. Chem. Soc., Sect. A*, 1312 (1967).

(4) As in our previous paper,[2] we are using the nomenclature "tart" to indicate a tetranegative tartrate group which has lost all carboxyl and hydroxyl hydrogens, as distinguished from the normal dinegative ion, which has lost only the hydrogens from the carboxylic groups.

(5) J. D. H. Donnay, G. Donnay, E. G. Cox, O. Kennard, and M. V. King, "Crystal Data, Determinative Tables," 2nd ed, Monograph No. 5, American Crystallographic Association, 1963, p 883.

(6) The material analyzed previously[2] was dried for 10 days over $\mathrm{CaCl_2}$ under vacuum, evidently converting at least part of the compound to a lower hydrate. Drying for 10–12 hr over $\mathrm{CaCl_2}$ gives material analyzing as the dodecahydrate. *Anal.* Calcd for $\mathrm{Na_4[VOC_4H_2O_6]_2\cdot 12H_2O}$: C, 13.09; H, 3.85; V, 13.88; $\mathrm{H_2O}$, 29.45. Found: C, 13.66; H, 3.89; V, 13.92; $\mathrm{H_2O}$ (by weight loss at 90° under vacuum with $\mathrm{N_2}$ purge), 29.18. Crystals stored over $\mathrm{CaCl_2}$ eventually exhibit cracking and analysis for a lower hydrate, but those stored under normal atmospheric conditions appear to be indefinitely stable. The crystal used in this work was air dried only.

(7) All calculations were carried out on the IBM 7094 computer at the University of Illinois.

(8) P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, "I.U.C. World List of Crystallographic Programs," International Union of Crystallography, 1962, No. 384.

the thermal motion was treated anisotropically. We divided the atoms into two groups and refined those groups alternately. One group contained all of the atoms of the anionic complex and the other group consisted of the sodium ions and oxygen atoms of the water molecules of crystallization; the vanadium, the vanadyl oxygen, and the two noncoordinating carboxyl oxygen atoms were common to both groups. In the final two cycles of refinement, the parameter shifts were not greater than 10% of the estimated standard deviations.

At this point a three-dimensional difference map was calculated to assess the correctness of the structure. Some of the largest peaks could be attributed to hydrogen atoms although it was impossible to locate all of the hydrogen positions from this map. The hydrogen atoms were included in the calculation by estimating their positions from the most reasonable hydrogen-bonding scheme and from the assumption of a tetrahedral geometry about the central carbon atoms in the tartrate chain.[9] Four additional cycles of anisotropic refinement were then carried out, after introduction of the 14 hydrogen atoms with an isotropic temperature coefficient (B_θ) of 4.0, alternating groups of atoms as described previously. No attempt was made to refine the hydrogen atom parameters. Introduction of the hydrogen atoms caused no other atomic parameter to change by an amount greater than its estimated standard deviation. The final shift in any parameter was, at most, 12% of its estimated standard deviation when this series of refinements was terminated. The final R factor, excluding unobserved reflections, was 0.10. Tables I and II show the positional and thermal parameters used in the final structure factor calculation and the rms amplitudes of vibration. Table III contains the final list of observed and calculated structure amplitudes. The calculated values of the unobserved reflections, with the exception of a few low-order terms which were obscured by the beam stop, were insufficiently large to indicate that they should have been observed.[10] Scattering factor curves for neutral V, O, C, and H and for Na^+ were taken from the "International Tables for X-Ray Crystallography."[11] No correction was made for anomalous dispersion since this is a nonpolar space group; furthermore, the corrections are small (for V, with Mo Kα, $\Delta f' = 0.3$ and $\Delta f'' = 0.7$).[12]

The final temperature coefficients of all of the atoms refined are much lower than might be expected but may not be unreasonable for crystals with a large amount of ionic and hydrogen bonding. The temperature factors may be artificially small as a calculation shows that a maximum deviation of ±13% may occur in some structure amplitudes due to absorption. The rms amplitudes of vibration, though small, appear to be qualitatively reasonable. The vibrations of all of the oxygen atoms of the dimeric anion are primarily normal to the bonds. We agree, however, with one referee's comment that the anisotropic thermal parameters are suspect, not only owing to absorption effects, but also because of the difficulty in obtaining a uniform set of data from one set of Weissenberg photographs.

TABLE I

FINAL ATOMIC PARAMETERS, WITH ESTIMATED STANDARD DEVIATIONS (×10⁵), IN FRACTIONS OF THE UNIT CELL EDGE AND ORIGIN AS IN INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY

	x	y	z
V	.09607(6)	.06233(12)	.02276(10)
O(7)	.15082(34)	.17252(59)	.03791(56)
C(1)	.12637(36)	−.13532(67)	−.11743(56)
C(2)	.07747(40)	−.05157(75)	−.17870(59)
C(3)	−.00713(39)	.11453(68)	.17515(57)
C(4)	.04232(39)	.02607(70)	.23186(62)
O(1)	.14368(32)	−.23638(57)	−.15468(49)
O(2)	.03618(31)	.00119(68)	.32881(51)
O(3)	.14284(28)	−.09527(52)	−.02009(51)
O(4)	.08847(31)	−.01572(57)	.16944(48)
O(5)	.07376(31)	.06601(56)	−.12901(45)
O(6)	.01162(28)	.13030(56)	.06531(46)
Na(1)	.35093(19)	.29576(33)	.15594(29)
Na(2)	.37490(19)	.42594(36)	.44937(30)
W(1)	.08672(41)	.41274(69)	.07027(70)
W(2)	.29037(33)	.12572(65)	.08471(62)
W(3)	.44901(31)	.19284(58)	.06642(56)
W(4)	.25278(38)	.41743(71)	.20490(70)
W(5)	.14942(43)	.26387(73)	.27173(65)
W(6)	.20665(41)	.06930(77)	.38273(76)
H(1)	.0947	−.0408	−.2668
H(2)	−.0087	.2083	.2187
H(3)	.0975	.3226	.0698
H(4)	.0429	.4184	.1088
H(5)	.2447	.1528	.0622
H(6)	.2825	.0502	.1295
H(7)	.4824	.1339	.0971
H(8)	.4762	.2511	.0215
H(9)	.2157	.3638	.2319
H(10)	.2655	.4690	.2688
H(11)	.1412	.2483	.1932
H(12)	.1163	.3293	.2917
H(13)	.2529	.0892	.4084
H(14)	.1917	.1461	.3444

Although introduction of anistropic thermal parameters did not, in this case, change any bond parameters significantly, a bond length change was noted in another vanadyl(IV) structure determination upon going from an isotropic to an anisotropic refinement[13a] and we wished to check this possibility in the present instance. On the basis of a significance test,[13b] the anisotropic model offers a significantly better fit to the diffraction data than the isotropic one. This test does not, however, assess the systematic errors mentioned in the text.

Results and Discussion

Table IV gives the interatomic distances and bond angles along with their standard deviations. The distances and angles reported for uncoordinated *d*-tartaric acid are also given for comparison. Figure 2 is a drawing of the dimeric anion giving our atom designations and the values of the bond angles; the "primed" and "unprimed" atoms are related by a center of inversion. A stereoscopic drawing of the anion with the bond distances is presented in Figure 3.[14] While our calculation of the standard deviations has neglected some off-diagonal elements (see discussion of final least-squares refinement) and may, therefore, be somewhat optimistic, the excellent agreement among chemically equivalent distances and angles and with other accurate structure determinations gives us confidence that the error, so introduced, is small.

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(9) H(1) and H(2) are the hydrogen atoms on the tartrate chain. To place each one we set the H–C–O and the two H–C–C angles equal and took each carbon–hydrogen bond length to be 1.14 A as determined in *d*-tartaric acid by neutron diffraction: Y. Okaya, N. R. Stemple, and M. I. Kay, *Acta Cryst.*, **21**, 237 (1966). To place the remaining 12 hydrogen atoms we proposed a hydrogen-bonding scheme (see Table VII) and made the following assumptions. If atom A is an oxygen atom of a water molecule acting as the donor of hydrogen atoms H_b and H_c to atoms B and C, we constrained the hydrogen atoms to lie in the ABC plane and the H_b–A–B angle to equal the H_c–A–C angle. A standard water molecule bond angle of 105° and bond length of 0.99 A ("International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 272) were used in the calculations.

(10) The following reflections were obscured by the beam stop: *h* = 0, *kl* = *20, 21, 22, 23, 25, 26, 27*; *h* = 1, *kl* = *11, 21, 02, 12, 22, 13, 23, 04, 14, 15, 06, 16, 26, 17, 27, 08, 18, 19, 010, 110, 111, 012, 12, 014, 115*; *h* = 2, *kl* = *00, 10, 11, 21, 02, 12, 22, 13, 04, 14, 15, 06, 16, 17, 27, 08, 18, 19, 010, 110, 111, 012, 112, 113, 014, 115*; *h* = 3, *kl* = *02, 12, 13, 04, 15, 06, 16, 17, 08, 18, 010, 014*; *h* = 4, *kl* = *02, 04*.

(11) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 201–205.

(12) C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

(13) (a) P. K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.*, **43**, 1323 (1965); (b) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965). From the weighted R_2 factors of 0.132 and 0.124 for the isotropic and anisotropic refinements, respectively, the anisotropic refinement offers a significant improvement at the 99.995% confidence level.

(14) This figure and Figures 5 and 6 were constructed on a Calcomp plotter by the ORTEP computer program: C. K. Johnson, Oak Ridge National Laboratory Report ORNL-3794, Oak Ridge, Tenn., 1965.

TABLE II

Final Anisotropic Temperature Parameters ($\times 10^4$)[a]

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	$B(A^2)$[b]
V	2.2(.2)	9.1(.7)	7.6(.6)	3.1(.9)	1.3(.7)	1.0(1.4)	.42(.02)
O(7)	9(2)	24(5)	28(5)	−10(5)	−7(4)	−13(6)	1.39(.11)
C(1)	2(1)	15(5)	5(4)	6(4)	1(3)	6(6)	.43(.09)
C(2)	7(2)	18(6)	7(4)	−1(5)	−1(4)	−3(7)	.72(.10)
C(3)	6(2)	13(5)	2(4)	10(4)	−1(3)	−4(6)	.62(.10)
C(4)	5(2)	12(5)	11(4)	13(4)	−1(4)	1(7)	.60(.10)
O(1)	8(1)	21(4)	14(4)	9(4)	2(3)	13(6)	1.02(.09)
O(2)	5(1)	52(6)	12(4)	−14(5)	3(3)	14(7)	1.28(.10)
O(3)	5(1)	22(4)	16(3)	11(3)	10(3)	4(6)	.89(.08)
O(4)	6(1)	27(5)	12(3)	−18(4)	−1(3)	−2(6)	.96(.09)
O(5)	11(1)	8(4)	11(3)	−5(4)	−10(3)	−10(6)	.87(.08)
O(6)	4(1)	23(4)	11(3)	16(4)	5(3)	22(6)	.73(.08)
Na(1)	8(1)	18(3)	18(2)	−5(2)	−1(2)	8(4)	1.06(.06)
Na(2)	7(1)	26(3)	24(2)	4(3)	4(2)	5(4)	1.29(.06)
W(1)	14(2)	36(6)	47(6)	2(6)	13(5)	−4(8)	2.25(.15)
W(2)	4(2)	30(6)	41(5)	−10(5)	10(4)	6(8)	1.59(.12)
W(3)	4(1)	18(5)	34(4)	−8(4)	−1(3)	22(7)	1.14(.10)
W(4)	9(2)	37(7)	53(6)	10(5)	0(5)	17(9)	2.11(.13)
W(5)	21(2)	39(6)	31(5)	8(7)	8(6)	−11(8)	2.34(.14)
W(6)	14(2)	28(6)	65(7)	−9(6)	5(6)	6(10)	2.41(.14)

Root-Mean-Square Amplitudes of Vibration (.01A)

	Minimum	*Intermediate*	*Maximum*	*Direction Cosine*[c]			
V	5	7	8	.81	−.56	−.16	Min
O(7)	8	14	16	−.57	−.72	−.40	Min
C(1)	5	6	10	−.43	−.87	−.26	Max
C(2)	7	10	12	.10	.19	.98	Min
C(3)	4	7	13	.82	.56	−.10	Max
C(4)	3	9	12	.65	−.76	.08	Min
O(1)	8	11	14	.74	.59	.33	Max
O(2)	7	11	18	−.28	.95	.16	Max
O(3)	5	11	14	−.79	.41	.45	Min
O(4)	6	10	15	−.64	.77	.00	Max
O(5)	3	10	15	−.28	−.76	−.58	Min
O(6)	2	7	15	.49	.75	.45	Max
Na(1)	9	12	13	−.25	−.88	.41	Min
Na(2)	11	12	14	−.46	−.44	−.77	Max
W(1)	14	16	20	.53	−.03	.84	Max
W(2)	7	14	18	.88	.41	−.23	Min
W(3)	6	11	17	.09	−.38	−.92	Max
W(4)	12	16	21	.07	.28	.96	Max
W(5)	13	16	21	−.96	−.18	−.20	Max
W(6)	12	17	22	.33	.94	−.08	Min

[a] Anisotropic thermal parameters are expressed in the form exp $-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$. The estimated standard deviations are given in parentheses.

[b] The B values given in the last column are those obtained in the final isotropic refinement before refining anisotropically. These isotropic B values agree closely with those estimated from the anisotropic thermal parameters by averaging $4a^2 \times b_{11}$, $4b^2 \times b_{22}$, and $4c^2 \times b_{33}$.

[c] The direction of the most nearly unique axis of the thermal ellipsoid is given. The last column indicates whether this is for the minimum (Min) or the maximum (Max) amplitude of vibration. The direction cosines listed refer to the x, y, and z axes in that order.

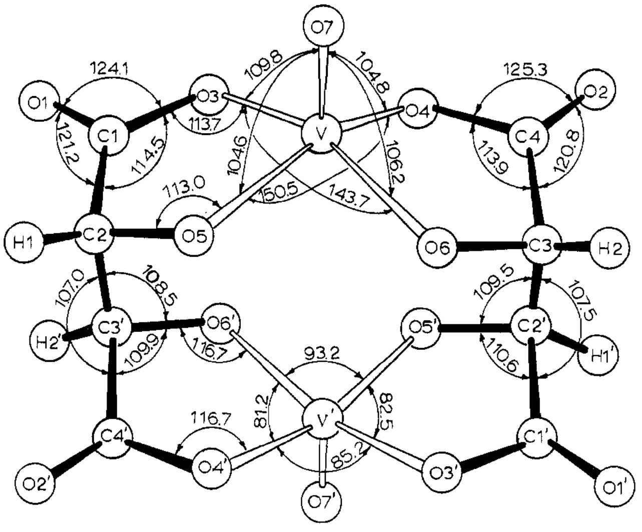

Figure 2.—$[VO\text{-}dl\text{-tart}]_2^{4-}$ anion with atom designations and bond angles. See Table IV for standard deviations.

Structure of Vanadyl(IV) *dl*-Tartrate Anion.—This crystal structure determination confirms the previously postulated structure[2] for the vanadyl(IV) *dl*-tartrate anion. The dimeric tetranegative anions are centrosymmetric, consisting of two vanadyl(IV) ions bridged by two tetranegative tartrate groups which have lost the protons from the two hydroxyl oxygen atoms as well as the two carboxyl oxygen atoms. If all chemically equivalent bond lengths and angles were equal, the anion would possess symmetry C_{2h}, the twofold axis bisecting the C(2) to C(3′) and the C(3) to C(2′) bonds. The coordination geometry of the vanadium atoms is approximately square pyramidal. Each vanadium atom coordinates two hydroxyl oxygen atoms and two carboxyl oxygen atoms of the tartrate group in a *cis* configuration with average V–O bond lengths of 1.91 and 2.00 A, respectively. The vanadyl oxygen completes the fivefold coordination with a V–O bond length of 1.619 A. The oxygen coordination pyramid is shown in Figure 4. Comparison with a similar figure given by Hon, Belford, and Pfluger[13a] for vanadyl(IV) bisbenzoylacetonate shows that while the general features of the coordination geometry about the vanadium atoms are similar in the two compounds, the distances between the coordinating oxygen atoms in the six-membered chelate rings in vanadyl(IV) bisbenzoylacetonate are longer than the distances between the oxygen atoms on two different chelate rings whereas in $Na_4[VO\text{-}dl\text{-tart}]_2 \cdot 12H_2O$, where the chelate rings are five-membered, the reverse is true.

The best planes through various groups of atoms are given in Table V. The carbon atoms of the tartrate chain (C(1), C(2), C(3′), and C(4′)) are approximately planar, as are the coordinating oxygen atoms on this chain (O(3), O(4′), O(5), and O(6′)). These planes are approximately parallel to the V–V vector. The angle between the plane of the four carbon atoms and the plane of the four oxygen atoms is 1.7°; the angles between the V–V vector and these two planes are 4.8 and 4.4°, respectively.

The angle between the planes of the V, O(3), and O(5) atoms and of the V, O(4), and O(6) atoms is 136.1°, which one can compare with the values 135.6 and 134.7° in vanadyl(IV) bisbenzoylacetonate and vanadyl(IV) bisacetylacetonate.[15] The vanadium atom lies 0.546 A above the best plane of the four coordinating tartrate oxygen atoms (O(3), O(4), O(5), and O(6)) compared with 0.538 A found in the bisbenzoylacetonate

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(15) The value given for vanadyl(IV) bisacetylacetonate was calculated by P. K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.*, **43**, 1323 (1965), from the coordinates reported by R. P. Dodge, D. H. Templeton, and A. Zalkin, *ibid.*, **35**, 55 (1961), and reported along with the angle found in vanadyl(IV) bisbenzoylacetonate.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS (×1.48)[a]

*** L= 0 ***			
0	4	151	-132
0	6	508	-603
0	8	391	-369
0	14	211	203
2	3	310	-311
2	4	190	165
2	5	255	-236
2	6	199	165
2	7	175	-145
2	11	326	315
4	1	191	-170
4	2	162	135
4	3	472	-509
4	4	295	-276
4	5	246	-224
4	6	378	390
4	7	130	109
4	8	364	380
4	10	139	119
4	12	110	-94
4	13	135	138
6	0	313	-284
6	1	74	-76
6	2	794	-996
6	3	291	-234
6	5	200	-180
6	6	276	282
6	7	106	95
6	8	373	414
6	10	182	184
6	14	124	-151
8	1	340	313
8	2	192	-166
8	3	320	328
8	4	267	-248
8	5	405	440
8	6	245	-235
8	9	386	-402
8	11	165	-179
8	13	183	-155
10	0	134	-78
10	1	308	279
10	2	507	634
10	3	307	336
10	4	304	-330
10	5	173	132
10	6	183	-153
10	7	163	-148
10	9	173	-152
10	10	219	-230
10	11	157	-128
12	0	149	114
12	1	318	-327
12	2	139	102
12	3	222	-221
12	5	220	-212
12	6	179	-147
12	8	161	-145
12	9	146	148
12	13	177	174
14	0	274	310
14	1	275	-288
14	2	332	-322
14	3	340	-221
14	4	134	-122
14	6	94	-107
14	9	108	106
14	11	192	216
16	0	353	-350
16	4	242	-230
16	5	112	108
18	0	324	-298
18	2	124	-126
18	3	293	348
18	5	271	289
18	11	219	-231
20	0	272	357
20	3	85	77
20	8	119	-136
22	0	188	190
22	2	127	123
22	3	231	-212
24	2	151	178
24	3	152	-156
24	5	172	-152
26	6	130	144
28	5	155	159
*** L= 1 ***			
0	6	209	205
0	8	173	-191
0	10	74	-107
1	4	86	-50
1	5	134	-111
1	6	77	-72
1	7	108	-97
1	8	133	-129
1	9	132	-133
1	10	131	144
1	11	140	-177
1	12	96	120
2	3	226	-222
2	5	245	-230
2	11	79	-110
3	2	344	-319
3	3	161	156
3	4	405	-420
3	5	355	-374
3	6	401	-398
3	7	101	99
3	10	298	323
3	12	206	228
4	2	189	-190
4	3	242	-235
4	4	112	101
4	5	130	-143
4	6	103	-85
4	7	259	-280
4	9	125	-151
4	10	86	-86
5	1	508	-503
5	2	200	-166
5	3	299	-266
5	4	194	180
5	7	200	192
5	9	180	218
5	11	113	116
6	1	110	-121
6	2	299	-250
6	3	238	-220
6	4	239	-239
6	6	186	183
6	7	129	-128
6	13	136	-65
7	1	180	152
7	2	81	84
7	3	560	-629
7	4	463	458
7	6	247	250
7	7	157	147
7	9	241	254
7	10	175	-186
7	12	183	-202
8	1	158	-137
8	6	191	168
9	2	125	122
9	4	142	159
9	6	89	89
10	1	221	-197
10	2	250	-245
10	3	172	-153
10	7	145	129
10	8	135	153
11	1	417	406
11	2	228	-221
11	3	236	219
11	4	200	-193
11	7	180	-161
11	9	202	-214
12	1	112	-116
12	2	154	158
12	3	123	-117
13	1	348	336
13	2	149	-131
13	3	95	-89
13	4	221	-221
13	6	95	-105
13	7	134	-129
14	5	110	-110
14	6	135	150
15	1	227	-209
15	3	113	-117
15	6	113	130
15	7	217	227
15	8	151	-161
15	9	178	211
16	1	124	117
16	4	167	162
17	1	192	-176
17	2	123	139
17	7	220	242
18	1	189	162
21	1	243	267
21	5	110	-119
21	7	160	-178
*** L= 2 ***			
0	4	543	-667
0	6	282	-279
0	8	368	-417
0	10	115	-113
0	12	70	57
0	14	124	118
0	16	119	153
0	18	78	62
1	3	342	-359
1	4	93	80
1	6	235	-220
1	7	205	193
1	9	74	-88
1	10	145	-145
1	11	105	98
1	12	68	79
2	3	263	-219
2	4	120	-103
2	5	170	-158
2	6	229	-222
2	7	278	-269
2	8	195	-166
2	9	65	50
2	10	64	-44
2	11	151	131
2	13	131	151
2	14	63	75
2	16	72	60
3	3	119	-99
3	4	137	-122
3	5	122	98
3	6	139	-115
3	8	113	113
3	10	103	-90
3	11	152	-155
4	1	141	-122
4	2	508	-667
4	3	455	-455
4	4	280	269
4	5	287	-266
4	6	293	299
4	7	114	115
4	8	327	341
4	11	143	140
4	12	124	-128
4	13	104	112
4	14	74	-72
5	1	218	218
5	2	145	103
5	3	303	300
5	4	152	150
5	5	185	169
5	6	192	179
5	8	147	-135
5	9	106	-101
5	10	75	61
5	11	146	-145
5	12	54	-53
5	13	77	-75
6	1	108	98
6	2	77	59
6	3	105	-87
6	4	170	-167
6	6	260	245
6	7	234	228
6	8	197	173
6	10	95	99
6	14	79	-93
6	16	87	-120
7	1	335	-346
7	2	290	329
7	3	354	-357
7	4	173	157
7	7	133	122
7	9	105	-105
7	11	62	60
7	12	70	88
7	17	70	-90
8	1	158	141
8	2	280	270
8	3	401	430
8	4	81	-66
8	5	498	526
8	7	65	63
8	9	83	-79
8	10	71	-61
8	11	170	-153
8	13	62	-68
9	1	218	-227
9	2	165	164
9	3	59	-68
9	4	71	70
9	8	236	239
9	9	78	93
9	12	65	70
9	13	80	84
10	1	137	126
10	2	230	221
10	3	282	285
10	4	145	121
10	5	203	190
10	6	313	-301
10	8	157	-122
10	10	193	-172
10	14	133	140
10	16	92	108
11	1	151	-124
11	3	63	-60
11	6	47	55
11	8	95	-93
11	9	110	107
11	10	135	134
11	13	84	100
12	1	172	-146
12	2	90	91
12	3	331	-311
12	5	214	-204
12	6	48	57
12	10	91	-95
12	11	98	92
12	13	78	89
13	2	246	-224
13	5	95	79
13	6	181	194
13	7	83	79
13	9	55	-46
13	10	113	111
13	12	78	-95
13	13	63	-54
13	14	77	-88
14	1	305	-296
14	2	100	81
14	3	379	-391
14	4	138	-127
14	5	223	-201
14	6	122	118
14	7	139	-130
14	8	129	134
14	9	97	99
14	10	121	134
14	11	80	91
14	13	83	102
15	3	70	70
15	4	81	72
15	5	94	82
15	6	121	-123
15	9	79	-78
15	11	70	-65
16	1	65	-63
16	2	144	-129
16	3	62	62
16	4	134	140
16	6	149	146
16	7	128	-109
16	8	206	192
16	9	65	-53
16	10	120	133
16	11	73	-85
17	1	73	-64
17	5	54	58
17	6	87	-82
17	8	99	-109
17	11	90	-96
18	1	76	72
18	3	168	165
18	4	93	91
18	5	189	190
18	7	128	112
18	9	148	-155
18	11	192	-200
18	13	101	-123
19	1	116	117
19	2	78	69
19	8	121	-140
20	2	103	96
20	5	127	115
20	8	144	-164
20	10	76	-75
20	11	76	-87
20	13	72	-82
21	3	93	-93
21	11	69	72
22	1	117	-108
22	2	71	66
22	3	144	-149
22	6	146	-156
22	8	146	-171
22	11	70	82
22	13	64	93
23	2	99	-95
23	8	115	125
24	2	93	-111
24	3	123	-142
24	5	118	-128
24	11	62	97
24	13	86	109
25	2	67	-74
26	2	122	-126
26	6	98	83
26	8	99	99
27	3	63	39
28	3	97	98
28	5	150	165
30	8	79	-90
32	8	90	-130
*** L= 3 ***			
0	4	216	248
0	6	123	111
0	10	71	-51
0	12	96	85
0	14	89	102
1	3	161	159
1	4	112	-99
1	5	167	-153
1	6	322	-336
1	9	159	-161
1	10	93	94
1	12	121	120
1	13	85	67
1	14	89	74
2	2	245	258
2	3	82	-79
2	4	297	308
2	5	44	-37
2	7	216	213
2	9	161	157
2	11	50	30
2	13	85	-84
2	14	83	74
3	2	226	-252
3	4	138	-142
3	5	315	320
3	6	310	-316
3	8	103	-93
3	9	152	167
3	11	81	-61
3	12	129	135
3	13	56	44
3	14	113	124
4	1	155	176
4	2	273	-287
4	3	46	-35
4	4	185	-183
4	5	194	169
4	6	79	85
4	7	129	-138
4	8	109	110
4	10	67	60
4	11	97	98
5	1	117	111
5	2	43	23
5	3	73	65
5	4	276	-315
5	5	148	159
5	6	156	162
5	7	168	174
5	8	42	-30
5	9	121	123
5	11	77	52
5	12	62	-43
6	1	265	296
6	2	131	-141
6	4	54	46
6	5	108	99
6	6	122	121
6	7	123	-150
6	9	78	-50
6	10	62	-49
6	14	60	-58
7	2	220	239
7	3	135	134
7	4	402	470
7	5	76	-52
7	6	182	174
7	7	204	223
7	9	65	-44
7	10	112	-112
7	11	115	112
7	12	140	-160
7	14	60	-44
7	15	81	-88
8	1	67	47
8	2	109	-97
8	3	233	265
8	4	73	-60
8	5	55	39
8	6	97	92
8	7	146	-119
8	8	76	-60
8	9	126	-123
8	10	80	-72
9	1	110	110
9	2	52	-46
9	4	349	383
9	5	43	35
9	6	85	73
9	7	251	-264
9	8	131	137
9	9	133	-136
9	10	50	-44
9	11	105	-100
9	12	55	-54
9	14	79	-36
9	15	116	93
10	1	105	-119
10	2	64	-54
10	4	219	-220
10	5	104	111
10	7	155	157
10	8	101	-93
10	10	51	-55
10	11	75	-59
10	12	97	90
10	13	68	-57
10	14	79	91
11	1	77	63
11	2	107	-93
11	3	107	-104
11	4	294	-307
11	6	102	85
11	7	286	-311
11	9	162	-172
11	10	94	81
11	11	138	-147
11	12	93	106
11	13	49	53
11	15	124	128
12	1	185	-182
12	2	52	40
12	4	128	-136
12	5	118	116
12	6	96	-91
12	7	78	64
12	9	64	61
12	15	93	-92
13	1	157	-155
13	2	199	-189
13	3	82	-85
13	4	311	-338
13	5	136	-149
13	6	76	-54
13	7	103	83
13	9	101	-90
13	10	102	86
13	11	56	43
13	12	89	74
14	1	91	-63
14	2	73	-40
14	3	143	144
14	4	103	89
14	5	121	-116
14	6	111	99
14	7	86	-88
14	10	104	-123
14	11	98	109
14	12	68	-51
15	1	260	-284
15	2	90	-70
15	3	101	-92
15	4	97	88
15	5	64	53
15	6	155	-171
15	7	161	169
15	8	58	-57
15	9	152	145
15	10	90	-75
15	11	94	98
15	13	63	-59
15	14	53	69
15	15	110	-129
16	2	108	91
16	4	142	139
16	5	123	-129
16	6	107	91
16	10	108	-100
16	12	100	-111
17	1	191	-212
17	2	77	51
17	3	52	-52
17	4	89	65
17	5	197	202
17	6	131	120
17	7	83	63
17	9	139	155
17	10	128	-127
17	12	72	-74
18	4	48	42
18	7	96	-103
18	9	142	-110
19	1	155	169
19	2	92	100
19	3	97	83
19	4	81	63
19	5	110	-110
19	6	211	247
19	7	116	-108
19	9	159	-161
19	10	77	-87
19	12	111	-120
19	13	66	77
20	2	162	-185
20	4	132	-132
20	6	103	-103
20	8	87	91
20	10	131	144
20	12	65	53
21	1	173	194
21	2	93	-84
21	3	90	87
21	4	61	48
21	5	161	-176
21	7	150	-155
21	8	75	76
21	9	170	-203
22	1	74	-79
22	3	75	55
22	6	57	-61
22	7	67	-79
22	11	75	73
23	1	54	-27
23	2	83	-86
23	4	72	-49
23	6	89	-107
23	7	91	-90
23	12	79	97
24	1	56	-62
24	4	74	68
24	5	89	80
24	6	69	77
25	1	159	-181
25	2	124	-126
25	4	152	-192
25	5	115	128
25	7	114	136
25	9	100	129
26	2	103	123
26	4	99	94
26	5	61	64
27	1	70	-67
27	4	72	56
27	7	135	164
27	9	78	109
28	7	66	-84
29	4	119	161
29	10	92	-102
*** L= 4 ***			
0	2	165	184
0	6	169	-183
0	8	210	-199
0	10	122	-113
0	12	96	93
1	2	182	173
1	3	349	-404
1	5	139	-147
1	6	74	-56
1	8	47	-58
1	9	106	95
1	10	155	145
1	11	140	125
1	15	72	-70
2	3	224	211
2	5	173	-163
2	6	50	-47
2	7	128	-131
2	8	74	-72
2	9	109	-99
2	13	125	127
3	1	275	318
3	2	65	-72
3	3	61	76
3	5	157	135
3	6	193	186
3	7	164	140
3	8	213	213
3	9	219	-216
3	10	94	75
4	1	155	142
4	2	251	-260
4	3	315	-337
4	4	142	131
4	5	176	-181
4	6	196	197
4	7	100	-102
4	8	166	163
4	10	109	86
4	11	52	67
4	12	78	-70
5	0	296	-370
5	1	256	240
5	2	137	-129
5	3	441	454
5	4	130	94
5	5	229	244
5	8	132	126
5	9	129	-116
5	10	128	-123
5	11	74	-67
5	12	78	84
6	0	134	-148
6	1	270	274
6	2	64	-54
6	3	57	-59
6	5	185	179
6	6	117	106
6	8	162	148
6	10	71	62
6	11	148	-143
6	12	69	70
6	13	118	-127
6	14	76	-79
7	0	277	-290
7	1	325	-322
7	5	141	148
7	6	139	-126
7	8	164	-140
7	9	71	75
7	10	104	-120
7	12	69	-53
8	0	241	234
8	1	160	-167
8	2	236	215
8	3	371	390
8	6	186	-181
8	8	159	-155
8	11	108	-106
8	13	94	-97
9	0	199	242
9	1	64	-68
9	2	214	212
9	3	185	-199
9	4	229	-224
9	5	203	-180
9	6	349	-352
9	7	87	-79
9	8	293	-300
9	9	78	67
9	11	96	98
9	13	74	67
9	14	78	87
10	1	51	-49
10	3	69	63
10	4	134	132
10	5	80	81
10	6	83	-78
10	8	214	-196
10	9	79	-71
10	10	93	-88
10	14	101	119
11	0	102	-114
11	1	71	-66
11	2	58	-60
11	3	83	-76
11	4	97	97
11	5	101	-86
11	7	65	-62
11	8	96	-95
11	9	72	-57
11	10	65	-74
12	0	162	155
12	1	124	108
12	3	392	-415
12	4	85	-70
12	5	145	-135
12	6	70	-62
12	9	81	79
12	10	96	-96
12	11	113	120
13	0	191	-180
13	1	162	-150
13	2	185	-184
13	4	140	117
13	6	169	177
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10	6	92	83
10	8	62	60
11	0	89	-88
11	1	78	-71
11	3	120	-120
11	5	90	-94
11	6	94	79
11	9	66	79
11	11	118	130
11	13	127	158
12	1	57	-61
12	3	70	64
12	5	79	83
12	11	73	-66
13	0	87	-83
13	2	61	-63
13	3	89	-77
13	4	56	-66
13	5	58	-16
13	6	82	75
13	7	63	56
13	8	96	106
13	11	74	71
14	0	54	42
15	0	56	-19
15	1	56	60
15	3	126	133
15	5	71	77
15	8	96	96
15	11	76	-68
15	13	92	-95
16	0	79	59
16	2	83	76
16	3	98	-96
17	0	99	98
17	3	137	129
17	5	95	96
17	11	110	-103
18	1	111	-107
18	3	94	-93
18	13	67	95
19	0	64	76
19	2	75	83
19	3	66	-73
19	5	68	-50
19	7	72	-38
19	8	85	-82
21	1	68	-75
21	3	143	-146
21	5	97	-101
21	11	81	82
22	2	70	-51
22	5	85	81
22	7	76	76
23	2	72	-78
23	8	79	106
*** L=15 ***			
0	2	52	-68
0	4	153	-205
0	6	74	-90
0	8	51	29
0	10	95	109
0	12	88	100
0	14	70	-11
1	4	36	45
1	7	96	98
1	15	98	19
2	4	36	-35
2	6	69	-87
2	7	79	78
2	9	104	119
2	11	88	91
2	12	65	52
3	1	49	62
3	4	52	56
4	1	91	-132
4	2	87	96
4	3	34	-33
4	4	154	200
4	5	78	90
4	6	45	51
4	7	80	98
4	8	61	-66
4	9	105	107
4	10	87	-91
5	1	98	124
5	3	50	50
5	4	39	27
5	14	71	32
5	15	84	61
6	2	83	104
6	4	55	64
6	6	64	65
6	7	50	22
6	12	66	-60
6	14	71	-81
7	2	74	-86
7	3	55	66
7	4	42	-48
7	7	59	41
7	8	63	52
7	10	61	66
8	1	107	129
8	3	76	84
8	4	69	-73
8	5	63	-62
8	6	67	-67
8	7	105	-114
8	9	111	-115
8	10	71	69
9	2	55	-53
9	3	70	-81
9	5	55	61
9	8	65	57
10	1	96	95
10	2	73	-68
10	3	63	58
10	4	47	-49
10	5	49	-36
10	6	104	-112
10	7	102	-104
10	9	69	-60
10	10	73	75
10	12	79	93
11	1	62	-78
11	3	94	-101
11	4	56	56
11	6	87	89
12	1	75	-84
12	5	77	75
12	7	70	62
12	8	59	-43
13	2	57	46
13	4	73	68
13	6	82	89
13	10	80	-96
13	12	81	-65
14	1	120	-119
14	3	52	-52
14	6	74	74
14	7	137	147
14	9	87	87
15	1	74	78
15	2	53	-44
15	7	61	-54
15	9	75	-77
16	2	80	93
16	4	89	98
17	1	76	79
17	2	92	-90
17	4	93	-96
17	7	118	-60
17	9	91	-29
18	1	58	46
19	1	60	-63
19	2	85	-93
19	4	88	-83
20	4	86	-92
21	1	111	-121
21	7	69	71
22	4	77	-82
22	6	79	-83
23	4	78	91
23	6	81	80

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[a] The data are divided into groups having a common value of *l*. The four columns in each group give *h*, *k*, F_o, and F_c in that order.

TABLE IV

Interatomic Distances and Angles for the Vanadyl (IV) *dl*–Tartrate Anion[a]

Environment of Vanadium

Distances (A)

V–V	4.082(.002)	V–O(4)	1.994(.006)
V–O(7)	1.619(.007)	V–O(5)	1.917(.006)
V–O(3)	2.004(.006)	V–O(6)	1.902(.006)

Angles (deg)

O(7)–V–O(3)	109.8(.3)	O(3)–V–O(4)	85.2(.3)
O(7)–V–O(4)	104.8(.3)	O(3)–V–O(5)	82.5(.2)
O(7)–V–O(5)	104.6(.3)	O(5)–V–O(6)	93.2(.2)
O(7)–V–O(6)	106.2(.3)	O(4)–V–O(6)	81.2(.2)
V–O(3)–C(1)	113.7(.3)	O(3)–V–O(6)	143.7(.2)
V–O(4)–C(4)	116.7(.6)	O(4)–V–O(5)	150.5(.2)
V–O(5)–C(2)	113.0(.3)		
V–O(6)–C(3)	116.7(.5)	O(7)–V–V'	152.1(.2)

The Tartrate Group and Comparison with Uncomplexed *d*–Tartaric Acid[b]

Distances (A)

	$Na_4[VOC_4H_2O_6]_2 \cdot 12H_2O$	*d*–Tartaric Acid
C(1)–O(1)	1.229(.009)	1.202, 1.198
C(4)–O(2)	1.227(.010)	
C(1)–O(3)	1.312(.009)	1.315, 1.319
C(4)–O(4)	1.277(.010)	
C(2)–O(5)	1.407(.010)	1.400, 1.408
C(3)–O(6)	1.410(.009)	
C(1)–C(2)	1.523(.011)	1.527, 1.519
C(3)–C(4)	1.534(.011)	
C(2)–C(3')	1.553(.011)	1.542

Angles (deg)

O(1)–C(1)–O(3)	124.1(.6)	125.5, 125.9
O(2)–C(4)–O(4)	125.3(.4)	
O(1)–C(1)–C(2)	121.2(.6)	123.6, 125.2
O(2)–C(4)–C(3)	120.8(.6)	
O(3)–C(1)–C(2)	114.5(.5)	110.9, 108.9
O(4)–C(4)–C(3)	113.9(.5)	
C(4)–C(3)–O(6)	109.9(.7)	111.8, 108.4
C(1)–C(2)–O(5)	110.6(.7)	
O(6)–C(3)–C(2')	108.5(.6)	111.4, 111.1
O(5)–C(2)–C(3')	109.5(.7)	
C(4)–C(3)–C(2')	107.0(.4)	106.8, 110.5
C(1)–C(2)–C(3')	107.5(.4)	

[a] Standard deviations given in parentheses.

[b] Y. Okaya, N. R. Stemple, and M. I. Kay, *Acta Cryst.*, *21*, 237 (1966). Estimated standard deviations on bond lengths of .006 to .007 A are reported.

TABLE V

BEST PLANES DEFINED BY $Ax + By + Cz = D$ WITH DEVIATIONS (DISTANCES TO PLANE)

Atoms	Deviations(A)	A	B	C	D
O(3)	–.066	.6998	.7002	.1414	1.298
O(4)	.107				
O(5)	.000				
O(6)	–.041				
C(1)	.019	–.1995	.4631	.8635	–2.440
C(2)	–.020				
C(3')	–.017				
C(4')	.018				
O(3)	.001	–.2128	.4850	.8482	–1.311
O(5)	–.001				
O(6')	–.001				
O(4')	.001				
V		.8359	.5159	–.1877	1.888
O(3)					
O(5)					
V		.4687	.7850	.4051	1.534
O(4)					
O(6)					

and 0.551 A found in the bisacetylacetonate.[16] The V–O(7) bond length, 1.619 A, for $Na_4[VO\text{-}dl\text{-}tart]_2 \cdot 12H_2O$ compares well with vanadyl group bond lengths found in other vanadyl(IV) compounds (see Table VI).[17]

Comparison of the Vanadyl(IV) *dl*-Tartrate Anion with the Vanadyl(IV) *d*-Tartrate Anion.—The V–V distance (4.082 A) for the *dl* dimer is somewhat shorter than that determined by Forrest and Prout[3] for the *dd* dimer (4.35 A). This difference is associated with the severe distortion from a normal square-pyramidal configuration to give an approximately trigonal-bipyramidal arrangement about the vanadium atom in the latter structure. In the vanadyl(IV) *d*-tartrate dimer, the two hydroxyl oxygen atoms are somewhat depressed while the two carboxyl oxygen atoms are raised relative to the *dl* dimer to give the pseudo-trigonal-bipyramidal configuration with the vanadyl oxygen and the two hydroxyl oxygen atoms occupying the equatorial positions. In Table VI, the differences between the vanadyl oxygen–vanadium–ligand oxygen angles observed by Forrest and Prout in the vanadyl(IV) *d*-tartrate anion and those angles observed for other vanadyl(IV) compounds are readily apparent. Note, however, that the hydroxyl oxygen–vanadium bonds are shorter than the carboxyl oxygen–vanadium bonds in both the *dd*- and *dl*-dimeric anions.

Molecular Packing and Hydrogen Bonding in the Crystal.—Figures 5 and 6 present stereoscopic drawings of the contents of the unit cell and the hydrogen and ionic bonding network, viewed along the *b* axis. The dimers lie in sheets parallel to the (100) plane with

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[16] These values were calculated by us from the atomic positions given by Hon, Belford, and Pfluger on the vanadyl(IV) bisbenzoylacetonate[13a] and the atomic positions determined by a further anisotropic refinement of the isotropic parameters given by Dodge, Templeton, and Zalkin on the vanadyl(IV) bisacetylacetonate (see footnote *d*, Table VI).

[17] Two additional crystal structure determinations give values for the vanadyl(IV) group bond length: 1.62 ± 0.06 A in diammonium oxotetrakisisothiocyanatovanadate(IV) pentahydrate [A. C. Hazell, *J. Chem. Soc.*, 5745 (1963)] and 1.76 ± 0.05 A in V_2O_4 [G. Andersson, *Acta Chem. Scand.*, **10**, 623 (1956)].

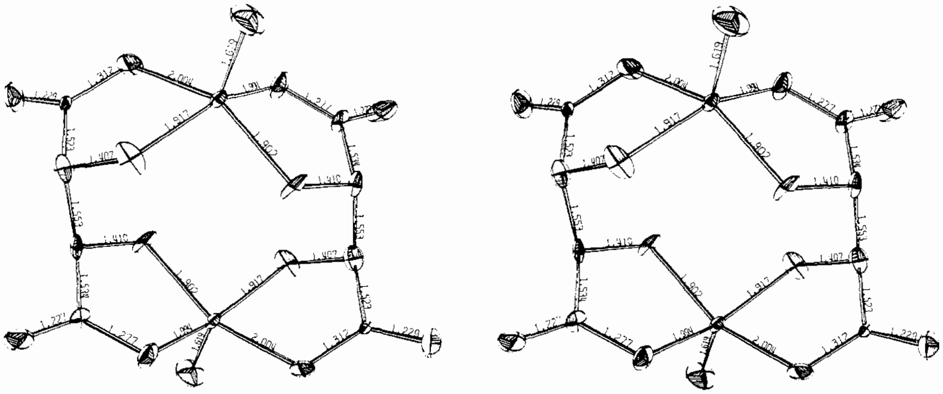

Figure 3.—Stereoscopic view of $[VO\text{-}dl\text{-tart}]_2^{4-}$ anion with bond lengths. See Table IV for standard deviations. This figure is best viewed with the aid of a simple stereoscopic viewer, such as an aerial photograph reader.

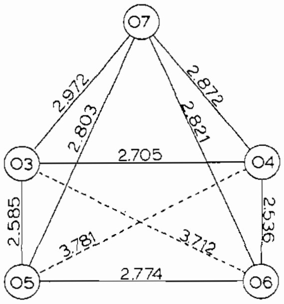

Figure 4.—Oxygen coordination pyramid.

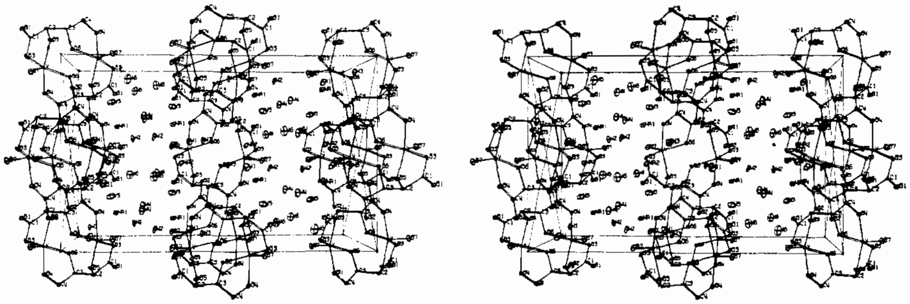

Figure 5.—Stereoscopic view (along *b* axis) of the contents of the unit cell.

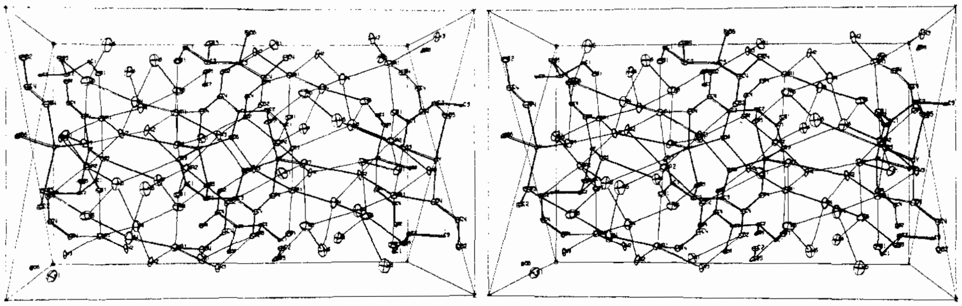

Figure 6.—Stereoscopic view (along *b* axis) of the hydrogen and ionic bonding network.

the V–V vector of the dimer approximately perpendicular to that plane. The dimer sheets are separated by layers of water molecules. Our earlier observation that (100) is the largest face of the crystal would indicate a preferred growth by addition of molecules to a sheet rather than by addition of dimer–water laminas. The greatest density of atoms should be within the dimer sheets.

The shortest V–V contacts between dimers are two for each vanadium at 7.351 A within a sheet and two for each vanadium at 8.142 A between sheets. Other V–V distances are two each at 8.641, 8.768, 9.105, and 9.402 A.

The sheets of dimers are held together by a rather complex system of hydrogen bonds, ion–dipole bonds, and ionic bonds. Our proposed hydrogen-bonding scheme, with the nearest neighbors of the sodium ions and oxygen atoms of the water molecules, is given in Table VII. One of these assigned hydrogen bonds, W(6) to O(3), is very long and implies, at most, a very weak interaction. In this case, however, either there is no acceptor atom at all for one of the hydrogens or W(6) or O(3) is acting as an acceptor. Assumption of a hydrogen bond between W(6) and O(3) gives a satisfactory tetrahedral geometry about this water molecule. The other assignments of hydrogen bonds appear reasonable.

TABLE VI

COMPARISON OF VANADIUM ENVIRONMENT IN $Na_4(VO\text{-}dl\text{-}tart)_2\cdot 12H_2O$ WITH THAT OBSERVED IN OTHER OXYGEN-COORDINATED VANADYL(IV) COMPOUNDS BY X-RAY DIFFRACTION TECHNIQUES[a]

	$Na_4[VOdl\text{–}Tart]_2$ $\cdot 12H_2O$	$(NH_4)_4[VOd\text{–}Tart]_2$ $\cdot 2H_2O$[b]	$VOSO_4$[c]	$VO(acac)_2$[d]		$VO(bzac)_2$[e]	$VOMoO_4$[f]
				Isotropic	Anisotropic		
			V–O BOND LENGTHS(A)				
Vanadyl Oxygen	1.619(.007)	1.60(.02)	1.594(.017)	1.56(.01)	1.571(.010)	1.612(.010)	1.677(.016)
Ligand Oxygens	2.004(.006)	2.01(.02)	2.056(.018)	1.97(.01)	1.974(.008)	1.952(.008)	1.972(.013)
	1.994(.006)	2.03(.02)	2.056(.018)	1.96(.01)	1.955(.008)	1.946(.008)	1.972(.013)
			2.005(.015)	1.98(.01)	1.983(.007)		1.972(.013)
	1.917(.006)	1.93(.02)	2.016(.013)	1.96(.01)	1.962(.007)	1.986(.007)	1.972(.013)
	1.902(.006)	1.79(.02)				1.982(.008)	
			VANADYL OXYGEN–V–LIGAND OXYGEN ANGLES (deg)				
	109.8(.3)	99.2(.8)	99.5(.6)	104.5	104.8(.4)	106.9(.4)	102.4(.6)
	104.8(.3)	98.8(.8)	99.5(.6)	106.3	106.2(.4)	106.0(.4)	102.4(.6)
			96.4(.5)	108.2	108.4(.4)		102.4(.6)
	104.6(.3)	122.1(.8)	99.8(.5)	105.6	105.6(.4)	104.0(.4)	102.4(.6)
	106.2(.3)	114.6(.8)				106.6(.4)	

[a] Estimated standard deviations are in parentheses. Distances and angles involving equivalent atoms are grouped together.

[b] J. G. Forrest and C. K. Prout, private communication. The angles and their standard deviations are those we calculate from the reported atomic positions with deviations and agree with the angles which they reported with one less significant figure. The first two atomic distances and bond angles involving the tartrate oxygen atoms, given above for the *dl*-isomer and the *dd*-isomer, are for the carboxyl oxygens - the second two are for the hydroxyl oxygens.

[c] P. Kierkegaard and J. M. Longo, *Acta Chem. Scand.*, *19*, 1906 (1965). The bond angles and standard deviations given are those we calculate from the reported atom positions and deviations as all the angles were not explicitly given in their paper. We disagree slightly in the first two angles given in the table. We obtain 99.5° whereas they report 99.9°. There is a coordinating oxygen in the axial position (opposite the vanadyl oxygen) with a bond length to vanadium of 2.284 A.

[d] Vanadyl (IV) bisacetylacetonate. R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, *35*, 55 (1961). The anisotropic values are those calculated by a further anisotropic refinement of the reported isotropic parameters by Hon, Belford, and Pfluger [P. K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.*, *43*, 3111 (1965)]. The angles obtained in the isotropic refinement are reported by Dodge, *et.al.*, to have standard deviations of about 1° or less.

[e] Vanadyl (IV) bisbenzoylacetonate. P. K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.*, *43*, 1323 (1965).

[f] Vanadyl (IV) molybdate. H. A. Eick and L. Kihlborg, *Acta Chem. Scand.*, *20*, 722 (1966). There is also a coordinating oxygen atom in the sixth position at a distance of 2.588 A from the vanadium atom.

All of the oxygen atoms of the water molecules, except W(1), have a pseudo-tetrahedral environment. W(1) is in an approximately trigonal-planar environment and is 0.23 A out of the plane of the Na(2), O(7), and O(2) atoms. The vibration of this oxygen atom, W(1), appears to be primarily normal to the plane of these three atoms (Table II). Na(1) and Na(2) both have six oxygen atoms about them with approximately octahedral geometry.

Clark[18] gives weighted averages (according to the estimated standard deviations) for the observed O···H–O–H···O angles and O···O distances in hydrated crystals of salts of organic acids and related compounds. These values are 109° (low 57°, high 137°) for an average of 26 values and 2.84 A (low 2.49, high 3.01) for an average of 53 values. Excluding the somewhat doubtful W(6) to O(3) hydrogen bond, our values range from 87 to 136° for the O···H–O–H···O angles and from 2.66 to 3.04 A for the O···O distances.

All of the oxygen atoms in the anionic complex are either involved in hydrogen bonding to water molecules or are in close contact to sodium ions. The sodium ions aid directly in bonding within a dimer sheet and they also indirectly aid in bonding between sheets since they bond to water molecules by ion–dipole interaction and thus contribute to the over-all intermolecular bonding network.

Discussion.—As noted in our earlier paper[2] on vanadyl(IV) tartrates, the optical absorption spectra of solutions of vanadyl(IV) *dl*-tartrate salts differ markedly from those of the vanadyl(IV) *d*-tartrate salts—the *dl* isomer exhibiting a three-band spectrum and the *dd* isomer exhibiting a four-band spectrum. Selbin and Morpurgo[19] have published visible spectral data for solutions of several other vanadyl(IV) α-hydroxycarboxylate salts. These exhibit four-band spectra very similar to that observed for the vanadyl(IV) *d*-tartrate anion. With the exception of vanadyl(IV) *dl*-tartrate salts, all aliphatic α-hydroxycarboxylic acid complexes of vanadyl(IV) which we have examined (around pH 7, in solution) have also shown four-band visible spectra.

Since we know that the vanadyl(IV) *d*-tartrate anion has a *trans* configuration whereas the vanadyl(IV) *dl*-tartrate anion has a *cis* configuration about the vanadyl group, the question immediately arises whether these other α-hydroxycarboxylate complexes have a *trans* configuration about the vanadyl(IV) ion as in the *d*-

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(18) J. R. Clark, *Rev. Pure Appl. Chem.*, **13**, 50 (1963).

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

TABLE VII

ENVIRONMENT OF SODIUM IONS AND WATER MOLECULES AND PROPOSED HYDROGEN-BONDING SCHEME[a]

Distances (A)

Na(1)–W(2)	2.358(.008)	Na(2)–W(6)	2.381(.009)
Na(1)–O(4)	2.364(.007)	Na(2)–W(1)	2.408(.009)
Na(1)–O(1)	2.415(.007)	Na(2)–W(3)	2.422(.008)
Na(1)–W(4)	2.423(.008)	Na(2)–W(2)	2.427(.008)
Na(1)–O(3)	2.463(.007)	Na(2)–O(1)	2.435(.007)
Na(1)–W(3)	2.496(.007)	Na(2)–O(2)	2.442(.007)

		Hydrogen
W(1) Na(2)	2.408(.009)	
W(1) → O(7)	2.908(.010)	H(3)
W(1) → O(2)	2.898(.010)	H(4)
W(2) Na(1)	2.358(.008)	
W(2) Na(2)	2.427(.008)	
W(2) → O(7)	2.874(.010)	H(5)
W(2) → W(4)	2.817(.011)	H(6)
W(3) Na(1)	2.496(.007)	
W(3) Na(2)	2.422(.008)	
W(3) → O(2)	2.984(.009)	H(7)
W(3) → O(6)	2.790(.009)	H(8)
W(4) Na(1)	2.423(.008)	
W(4) ← W(2)	2.817(.011)	H(6)
W(4) → W(5)	2.760(.011)	H(9)
W(4) → W(6)	2.844(.012)	H(10)
W(5) ← W(4)	2.760(.011)	H(9)
W(5) ← W(6)	2.745(.012)	H(14)
W(5) → O(7)	3.036(.010)	H(11)
W(5) → O(5)	2.663(.010)	H(12)
W(6) Na(2)	2.381(.009)	
W(6) ← W(4)	2.844(.012)	H(10)
W(6) → O(3)	3.230(.010)	H(13)
W(6) → W(5)	2.745(.012)	H(14)

Acceptor-Donor-Acceptor Angles

O(7)–W(1)–O(2)	136.0(.3)
O(7)–W(2)–W(4)	87.2(.2)
O(2)–W(3)–O(6)	117.6(.3)
W(5)–W(4)–W(6)	109.0(.4)
O(7)–W(5)–O(5)	131.4(.2)
O(3)–W(6)–W(5)	120.0(.2)

[a] Estimated standard deviations are given in parentheses. Arrows are drawn from the hydrogen donors to the hydrogen acceptors proposed.

tartaric acid complex and, if so, whether they also show the distortion from the square-pyramidal geometry exhibited by the *dd* dimer. Single-crystal X-ray diffraction studies of some of the salts of the vanadyl(IV) α-hydroxycarboxylates should aid in answering these questions.[20]

The *dd* and *dl* isomers of vanadyl(IV) tartrate present ideal systems for comparison of polarized crystal spectra since the two molecular species are both dimeric and both have a fourfold coordination to the vanadyl(IV) ion with two coordinating hydroxyl oxygen atoms and two coordinating carboxyl oxygen atoms. The major differences between the two species appear to be the *cis* or *trans* arrangement of the coordinating oxygen atoms and the pseudo-trigonal-bipyramidal configuration about the vanadium in the vanadyl(IV) *d*-tartrate anion. We hope, therefore, to make assignments of the bands observed in the electronic spectra of the *dd* and *dl* species by comparison of the polarized crystal spectra for the two isomers and by calculations of the changes in spectra which we should observe due to the two different geometries about the vanadium nuclei. Polarized crystal spectral studies are now in progress toward this end.

A third area of interest in this system is the observed V–V coupling in the vanadyl(IV) *dl*-tartrate anion.[2] We are, at present, doing low-temperature epr studies and magnetic susceptibility studies to determine the magnitude of the exchange coupling in this isomer and to determine whether such coupling also occurs in the *dd* isomer. This is the first such coupling to be observed by epr hyperfine splitting in vanadyl(IV) complexes and thus is of great theoretical interest.

The structure of the [VO-*dl*-tart]$_2^{4-}$ ion serves as an interesting comparison to some results reported on antimony tartrate compounds.[21–24] The crystal structure of $(NH_4)_2[Sb_2(C_4H_2O_6)_2]\cdot 4H_2O$[22] shows this crystal to consist of dimers composed of two antimony(III) ions bridged with *trans* configuration either by two *d*-tartrate or two *l*-tartrate tetranegative ions. A crystallographic twofold axis relates one half of the dimer to the other. A preliminary note[23] on the structure of racemic potassium antimony tartrate indicates a monomeric structure in contrast to that found for the ammonium salt.

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(20) Such a crystal structure study is underway in these laboratories on the mixed tetraethylammonium-sodium salt of vanadyl(IV) benzilate (diphenylglycolate): N. D. Chasteen, R. L. Belford, and I. C. Paul, work in progress.

(21) G. A. Kiosse, N. I. Golovastikov, and N. V. Belov, *Kristallografiya*, **9**, 402 (1964).

(22) G. A. Kiosse, N. I. Golovastikov, and N. V. Belov, *Dokl. Akad. Nauk SSSR*, **155**, 545 (1964). The authors give the formula $(NH_4)_2Sb_2(C_4H_4O_6)_2\cdot 4H_2O$, but to preserve electroneutrality, the tartrate ions must be tetranegative $C_4H_2O_6$ ions.

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