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The Crystal Structure and Electronic Spectrum of a Vanadyl α-Hydroxycarboxylate Complex. Sodium Tetraethylammonium Bis(benzilato)oxovanadium(IV) Di-2-propanolate[1]

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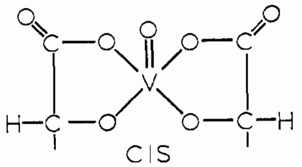
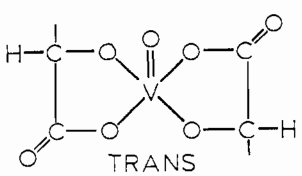
This paper presents the crystal structure of monomeric sodium tetraethylammonium bis(benzilato)oxovanadium(IV) di-2-propanolate, $Na[(C_2H_5)_4N]VO[(C_6H_5)_2COCO_2]_2 \cdot 2C_3H_7OH$, as determined by three-dimensional Fourier methods with the positional and isotropic thermal parameters refined by least-squares methods to a conventional R factor of 0.12 based on 2435 nonzero reflections. The data were collected on multiple films by the equiinclination Weissenberg technique. The purple platelike crystals are monoclinic, space group $P2_1/c$, with $a = 10.86 \pm 0.02$, $b = 24.32 \pm 0.04$, $c = 16.30 \pm 0.02$ Å, and $\beta = 98° 57' \pm 9'$. The density, as measured by flotation, is 1.23 ± 0.01 g/cm^3, in agreement with 1.238 g/cm^3 calculated assuming four molecules in the unit cell. The vanadium atom is in a 5-coordinate, distorted square-pyramidal environment with the vanadyl oxygen at the apex, and the two bidentate ligands arranged *trans* to one another. The solution, single-crystal, and polycrystalline optical spectra exhibit four bands similar to those of the *trans*-vanadyl(IV) *d*-tartrate system. Correlation of the structure of the vanadyl(IV) α-hydroxycarboxylates with their optical spectra suggests two possible orderings of the crystal field levels.

Introduction

The anionic complexes of VO^{2+} with α-hydroxycarboxylate anions are interesting because of both their varied stereochemistry[2-4] and their unusually rich visible spectra,[5] but heretofore only two of their structures,[2,3] both of dimeric tartrates, have been reported. *cis* and *trans* arrangements about the vanadyl group are reported for tetrasodium divanadyl(IV) *d*-tartrate *l*-tartrate dodecahydrate[3] and tetraammonium divanadyl(IV) bis-*d*-tartrate dihydrate,[2] respectively. Solution studies of these anionic dimeric complexes have shown the racemic tartrate complex (*cis*) to be the more stable.[4] Also, in another vanadyl structure[6] (vanadyl(IV) bisbenzoylacetonate) where *cis–trans* isomerism is possible, only the *cis* compound was obtained. The question then arose as to whether there is an extra stability associated with the *cis* arrangement about the vanadyl ion. Additional structural information was needed to aid in answering this question.



CIS



TRANS

The optical absorption spectra of the vanadyl(IV) *dl*-tartrate and *d*-tartrate salts are strikingly different. The *cis-dl* isomer exhibits a three-band spectrum in contrast to four bands displayed by the *trans-dd* isomer. Except for the *dl*-tartrate complex, all α-hydroxycarboxylate complexes in basic solution which have been investigated in our laboratories and elsewhere[5] have a characteristic four-band optical absorption spectrum. This fact implies that the other α-hydroxycarboxylic acid complexes also have a *trans* configuration about the vanadyl ion. If this is so, then these complexes might also show a distortion from the normal square-pyramidal geometry of other vanadyl compounds toward a distorted trigonal-bipyramidal structure as found for the *trans-d*-tartrate complex.[2]

Polarized crystal spectral studies on the two tartrate dimers are under way in our laboratories to help assign the electronic transitions giving rise to the optical spectrum. As the *trans-dd* isomer crystallizes in a tetragonal space group, making complete analysis of the spectrum into its molecular x, y, and z components impossible, we have determined the detailed geometrical structure of another α-hydroxycarboxylate complex expected to have a *trans* configuration. Accordingly, we report here the crystal structure and preliminary crystal spectra of the anionic complex vanadyl(IV) bisbenzilate. (The benzilate species involved is the dinegative anion oxydiphenylacetate, $O_2CC(O)(C_6H_5)_2{}^{2-}$, and is also called diphenylglycolate.)

Experimental Section

Preparation of the Compound.—Of the several α-hydroxycarboxylate complexes we prepared, only the benzilate produced

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[2] J. G. Forrest and C. K. Prout, *J. Chem. Soc., A*, 1312 (1967).

[3] R. E. Tapscott, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, **7**, 356 (1968), and R. E. Tapscott, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1967.

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

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

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

suitable crystals. Sodium tetraethylammonium bis(benzilato)-oxovanadium(IV) di-2-propanolate, $Na[(C_2H_5)_4N]VO[(C_6H_5)_2COCO_2]_2 \cdot 2C_3H_7OH$, was prepared by dissolving 0.02 mol of benzilic acid (supplied by Eastman Kodak) in 100 ml of 0.4 *M* sodium hydroxide. A second solution containing 0.01 mol of vanadyl sulfate and 0.02 mol of tetraethylammonium chloride in 50 ml of water was added dropwise with stirring to the first solution. Both solutions were purged with nitrogen before and during the addition to inhibit oxidation. The resulting purple solution was tested basic to litmus and then was placed in a vacuum desiccator over calcium chloride. After the solution had evaporated to near dryness, the remaining residue was dissolved under a nitrogen atmosphere in 100 ml of a hot 92% 2-propanol–8% water solution and then immediately filtered to remove the undissolved white inorganic salts. Evaporation of the filtrate in a desiccator produced purple crystals in 24–36 hr. The crystals are slightly moisture sensitive and tend to decompose in humid weather. The sodium and vanadium contents were analyzed as $NaVO_3$ combustion residue.[7] We also prepared the sodium and rubidium salts, but they formed very poor, extremely hygroscopic crystals.

Crystallographic Data.—The crystals belong to the monoclinic system. The cell parameters at 25°, as determined on a 60-mm precession camera (Mo Kα, λ 0.7107 Å), are $a = 10.86 \pm 0.02$, $b = 24.32 \pm 0.04$, $c = 16.30 \pm 0.02$ Å, $\beta = 98° 57' \pm 9'$. For a volume, $V = 4253 \pm 32$ Å^3, based on four molecules of $C_{42}H_{56}O_9NVNa$ (formula weight 792.7) per unit cell, the calculated density is 1.238 g/cm^3, which agrees well with 1.23 ± 0.01 g/cm^3 obtained by flotation in a mixture of carbon tetrachloride and cyclohexane. Inspection of Weissenberg and precession photographs shows systematic absences of the $0k0$ reflections when k is odd and $h0l$ reflections when l is odd; thus, the space group is uniquely determined as $P2_1/c$ (C_{2h}^5, no. 15). $F(000)$ is 1684.

Crystal Morphology.—The purple crystals are formed as flat parallelogram-shaped plates lying on the (010) face. The parallelogram has internal angles β and β^*. Growth is most rapid in the a direction, then the c direction, and slowest in the b direction, *i.e.*, the order of increasing axis length. All of the (010), (011), and (110) faces are well developed with occasional formation of the (001) and (100) faces. The extinction directions of the (010) face lie nearly along the a (light purple) and c (dark purple) axes. Figure 1 pictures the crystal habit for reference in this work and in a later report of single-crystal spectra.

Spectral Measurements.—The optical spectra were measured with monochromatic sample illumination in the range 14,000–3000 Å with a Cary Model 14 RI recording spectrometer. A lead sulfide detector was used in the 14,000–7000-Å region and a photomultiplier tube was used at 7000–3000 Å. The spectra obtained with the two detectors always coincided in the change-over region, 6500–7500 Å.

The solutions were prepared by dissolving weighed amounts of freshly prepared compound in water purged with nitrogen and diluting to about 80% of the required volume. The pH was adjusted to 8.5 with dilute sodium hydroxide and a Beckman Model G pH meter. Water was added to give a final 0.0400 *M* solution of VO^{2+}. The spectra were completed within 20 min of solution preparation to minimize air oxidation. The pH did not change more than 0.05 unit during any run.

The polycrystalline sample was prepared by grinding single crystals of the compound to a powder and suspending them in 2-propanol. The suspension was evaporated on a quartz plate under dry nitrogen. In the sample compartment a Nujol-impregnated filter paper was placed behind the sample plate and a similar paper was put in the reference side. A base line was determined by washing the sample plate and rerunning the spectrum. We believe that scattering does not greatly affect our results since powdered sodium chloride run on the sample plate gives an even base line to 3200 Å.

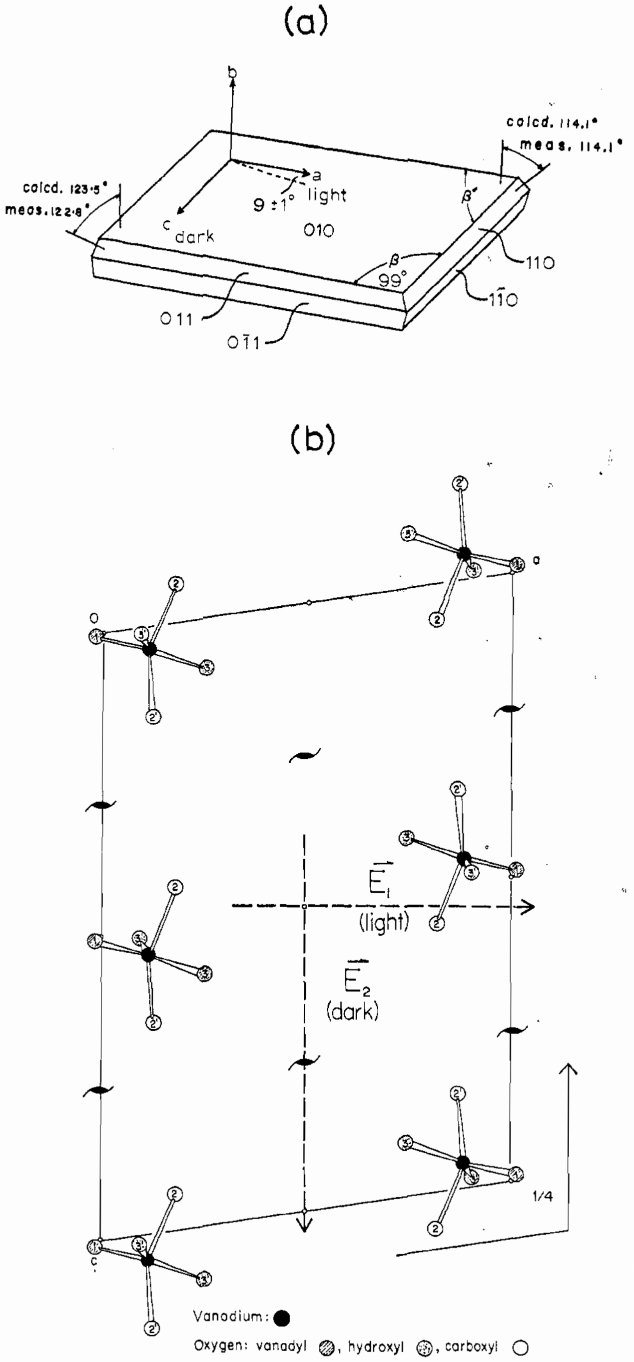

Figure 1.—(a) Crystal morphology. The dashed line denotes one extinction direction; the other lies along c. "Light" and "dark" refer to light and dark purple dichroism. (b) Projection of the VO_5 groups on the ac plane. Dashed arrows indicate the extinction directions as defined by the electric vector of plane-polarized light.

To obtain the room- and low-temperature single-crystal spectra, we mounted a crystal (dimensions, $2.402 \times 1.075 \times 0.158$ (± 0.005) mm) with the (010) face perpendicular to the incident polarized monochromatic light beam (path length, 0.158 mm) in an Air Products Joule–Thompson liquid helium cryostat equipped with quartz windows. The *dark* extinction direction (see Figure 1) was located through maximization of the absorbance at 13 kK by rotating a Rochon prism polarizer. A base line was determined by removing the crystal from the cryostat and rerunning the

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(7) *Anal.* Calcd for $Na[(C_2H_5)_4N]VO(C_{14}H_{10}O_3)_2 \cdot 2C_3H_8O$: V, 6.42; Na, 2.90; N, 1.77; C, 63.63; H, 7.11. Found: V, 6.55; Na, 2.96; N, 1.92; C, 63.46; H, 7.15.

spectrum. We measured the crystal dimensions with a Leitz stereoscopic microscope equipped with a graduated eyepiece.

Collection of X-Ray Data.—A crystal of dimensions 0.732 × 0.076 × 0.236 mm (all ±0.005 mm) was mounted on a glass rod along the *a* axis (0.732-mm length). The intensities were recorded on multiple films with an equiinclination Weissenberg camera (Ni filtered, Cu Kα, λ 1.5418 Å). Ten levels of data were taken ($0kl$–$9kl$) and the intensities were estimated visually by comparison with a calibrated film strip. Of an estimated 3800 independent reflections possible, with sin θ less than 0.70, 2435 were recorded above background. After the data collection, the crystal had a thin coating of decomposed material; however, the interior of the crystal still extinguished well under a polarizing microscope. Furthermore, during and after the data collection, other $h0l$ exposures were taken and served to test possible effects of crystal decomposition on the intensities. These photographs indicated that most decomposition probably occurred in the initial stages of data collection and that the only effect on the intensities was a uniform decrease. Since individual level scaling was employed in the subsequent analysis, it is unlikely that the crystal decomposition would significantly influence the results. Lorentz, polarization, and absorption[8] corrections were applied. The linear absorption coefficient μ(Cu Kα) is 25.6 cm^{-1}.[9] The transmission coefficients to be applied to the intensities had a maximum range of 0.55–0.82.

TABLE I

FINAL POSITIONAL AND ISOTROPIC PARAMETERS[a]

Atom	x	y	z	B(Å^2)	Root-Mean-Square Vibration Amplitude (Å)
V	.1164(2)	.2637(1)	.5272(1)	2.44(.05)	.18
O1	−.0120(9)	.2958(4)	.5104(6)	4.52(.23)	.24
O2	.1830(7)	.2687(3)	.4215(5)	3.08(.18)	.20
O3	.2572(7)	.3089(3)	.5629(4)	2.34(.17)	.17
O4	.3331(8)	.3046(3)	.3601(5)	3.82(.21)	.22
O2′	.1272(8)	.2384(4)	.6429(5)	3.61(.19)	.21
O3′	.0974(7)	.1858(3)	.5059(5)	2.65(.18)	.18
O4′	.0764(8)	.1693(3)	.7199(5)	3.60(.20)	.21
O5	.3257(9)	.1812(4)	.2280(6)	4.74(.23)	.24
O6	.0651(9)	.1662(4)	.3380(6)	4.74(.24)	.25
C1	.2739(14)	.3004(6)	.4206(9)	3.80(.32)	.22
C2	.3205(12)	.3344(5)	.5016(8)	3.08(.30)	.20
C3	.4535(12)	.3317(5)	.5277(8)	2.76(.28)	.19
C4	.5148(13)	.2802(6)	.5277(9)	3.83(.33)	.22
C5	.6429(16)	.2756(7)	.5579(11)	5.86(.43)	.27
C6	.7099(15)	.3204(7)	.5795(10)	5.24(.39)	.26
C7	.6536(17)	.3718(8)	.5810(11)	6.10(.44)	.28
C8	.5285(14)	.3769(6)	.5514(9)	4.58(.36)	.24
C9	.2661(12)	.3931(5)	.4838(8)	3.35(.30)	.21
C10	.2964(15)	.4219(7)	.4130(10)	5.10(.38)	.25
C11	.2427(18)	.4758(8)	.4029(12)	6.69(.48)	.29
C12	.1780(16)	.5000(8)	.4569(11)	5.82(.44)	.27
C13	.1531(15)	.4716(6)	.5238(10)	4.99(.39)	.25
C14	.2000(13)	.4170(6)	.5379(8)	3.53(.30)	.21
C15	.6403(21)	.3469(9)	.2151(14)	5.76(.55)	.27
C16	.5125(15)	.3200(7)	.2228(10)	5.57(.41)	.27
C17	.6569(21)	.3906(10)	.3634(15)	6.22(.55)	.28
C18	.6120(30)	.4465(14)	.3310(20)	13.43(.97)	.41
C19	.7507(23)	.3012(10)	.3490(16)	7.04(.62)	.30
C20	.8170(25)	.2591(12)	.2974(17)	11.30(.75)	.38
C21	.8378(22)	.3850(9)	.2807(14)	6.24(.56)	.28
C22	.9413(18)	.3934(8)	.3635(12)	6.56(.47)	.29
C23	.4464(18)	.1573(7)	.2577(12)	6.13(.44)	.28
C24	.4848(18)	.1766(8)	.3463(13)	7.10(.49)	.30
C25	.4350(23)	.0928(10)	.2513(15)	9.36(.63)	.34
C26	.0132(21)	.1116(9)	.3116(14)	7.18(.52)	.30
C27	−.1108(27)	.1023(11)	.3227(17)	8.89(.73)	.34
C28	.0421(26)	.1043(11)	.2227(17)	8.69(.70)	.33
C1′	.0974(12)	.1870(6)	.6527(8)	3.27(.30)	.20
C2′	.0916(11)	.1514(5)	.5747(7)	2.47(.27)	.18
C3′	−.0301(12)	.1207(5)	.5593(8)	2.87(.29)	.19
C4′	−.0367(16)	.0652(7)	.5618(10)	5.50(.41)	.26
C5′	−.1581(18)	.0395(8)	.5435(12)	6.64(.47)	.29
C6′	−.2645(16)	.0694(7)	.5256(10)	5.46(.41)	.26
C7′	−.2585(15)	.1248(7)	.5214(10)	4.81(.37)	.25
C8′	−.1396(14)	.1515(6)	.5389(9)	4.15(.34)	.23
C9′	.2071(11)	.1127(5)	.5859(7)	2.68(.27)	.18
C10′	.2350(14)	.0814(6)	.6550(9)	4.18(.34)	.23
C11′	.3383(14)	.0445(6)	.6640(10)	4.64(.37)	.24
C12′	.4130(14)	.0420(6)	.6037(10)	4.59(.36)	.24
C13′	.3883(15)	.0778(7)	.5333(10)	5.02(.38)	.25
C14′	.2821(13)	.1125(6)	.5275(8)	3.63(.31)	.21
N	.7244(11)	.3550(5)	.2990(7)	3.87(.27)	.22
Na	.1823(4)	.2357(2)	.2837(3)	3.78(.11)	.22
T1	.814(9)	.294(4)	.262(6)	7.1(2.4)	.30
T2	.604(8)	.337(3)	.312(6)	5.8(2.1)	.27
T3	.823(8)	.375(3)	.384(5)	4.8(1.8)	.25
T4	.749(7)	.402(3)	.223(5)	4.1(1.6)	.23
I	.053(8)	.082(4)	.348(6)	10.0(2.3)	.36

[a] Origin as defined in "International Tables for X-Ray Crystallography." Positional parameters in fractions of unit cell edge. Estimated standard deviations in parentheses (X10^4 for positional e.s.d. of atoms through Na; X10^3 for positional e.s.d. of last five atoms).

Structure Determination.—The space group P2$_1$/c and the cell data require one vanadium atom per asymmetric unit. Inspection of the Harker line, $P(0, v, {}^1/_2)$ of a three-dimensional Patterson synthesis,[10] allowed the assignment of the y coordinate of the vanadium atom, which was almost 0.25. We were unable to determine unambiguously the x and z coordinates from the Patterson map alone. The Harker section, $P(u, {}^1/_2, w)$, contained four strong peaks all of which had a corresponding vector peak at $2x$, $2y$, $2z$, as required by the space group P2$_1$/c. In an attempt to overcome this problem, we then employed the symbolic addition method for centrosymmetric space groups.[11,12] Comparison of several Fourier maps from the heavy-atom method and E maps from the symbolic addition method did not immediately reveal a structural solution. Finally, a comparison of the normal Patterson function with a sharpened function[13,14] enabled us to choose the most probable vanadium position. Based on only the vanadium position, the crystallographic R factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, was 0.59. From a three-dimensional Fourier synthesis, with structure amplitudes phased by the vanadium atom, we located two carbonyl groups, the sodium atom, and four coordinating oxygen atoms. From a second Fourier synthesis, using this information, we located the remaining atoms in the anion, the two 2-propanol oxygen atoms, the nitrogen, and four carbon atoms of the tetraethylammonium cation. A third Fourier synthesis revealed the rest of the atoms (except hydrogen). At this point the R factor was 0.25. Six cycles of least-squares refinement,[15] varying positional and isotropic temperature parameters with all reflections weighted[16] and minimizing $\Sigma w||F_o| - |F_c||^2$, with adjustment of interlevel scale factors such that $\Sigma|F_o| = \Sigma|F_c|$ for each level reduced R to 0.12 and R_2 $[(\Sigma w(|F_o| - |F_c|)^2)/\Sigma w|F_o|^2)^{1/2}]$ to 0.14. The structure is too large to permit full-matrix isotropic least-squares refinement on the computer available to us. Four of the six refinement cycles were carried out with the structure divided into two parts. In the first half, the phenyl rings C3–C8 and C3′–C8′ were refined with the remainder of the anion (minus the rings C9–C14 and C9′–C14′) and in the second half the phenyl rings C9–C14 and C9′–C14′ were refined with the tetraethylammonium ion, the two 2-propanol molecules, and the sodium ion. The atoms C9 and C9′ were common to both parts of the cycle. This procedure was repeated three more times, except that each time the roles of the phenyl rings C3–C8 and C3′–C8′ were interchanged with those of rings C9–C14 and C9′–C14′. Two of the six refinement cycles were carried out with the structure divided into three parts. One consisted of the tetraethylammonium cation, the two 2-propanol molecules, and the sodium ion. The other two each consisted of half of the anion containing one complete ligand and the vanadium atom with all of the coordinating

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(8) For absorption corrections, we used a modification of a program, GNABS, suitable for a crystal bounded by plane faces. The program was written by C. W. Burnham, Geophysical Laboratory, Carnegie Institute, Washington, D. C.

(9) Calculated from mass absorption coefficients for CuKα radiation: "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 162.

(10) All calculations were performed on the IBM 7094 and 360/75 computers at the University of Illinois. Patterson and Fourier calculations were computed with ERFR-2, written by W. G. Sly, D. P. Shoemaker, and J. H. van den Hende, Report No. CBRL-22M-62, Esso Research Engineering Co., 1962.

(11) For the symbolic addition method, we used a package of programs containing FAME and MAGIC written by E. B. Fleischer, A. L. Stone, and R. B. K. Dewar of the University of Chicago. FAME calculates normalized structure factors, E's, and MAGIC determines the signs of the E's using the Karle–Hauptman Σ_2 relationship and the symbolic addition procedure. The phased E's are used as coefficients in the Fourier synthesis.

(12) An authoritative review of this method is given by J. Karle and I. L. Karle, *Acta Cryst.*, **21**, 849 (1966).

(13) J. A. Wunderlich, *ibid.*, **19**, 200 (1965).

(14) R. A. Jacobson, J. A. Wunderlich, and W. N. Lipscomb, *ibid.*, **14**, 598 (1961).

(15) Using a modification of the program written by 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.

(16) We employed the weighting scheme $\sqrt{w} = 35.0/F_o$, when $F_o > 35.0$, and $\sqrt{w} = F_o/35.0$, when $F_o \leq 35.0$.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

k	l	F_o	F_c
**** H= 0 ****			
0	2	195	227
0	4	196	185
0	6	48	54
0	10	39	-38
0	14	38	28
1	2	54	-57
1	3	45	42
1	4	264	-260
1	5	48	-32
1	6	184	-173
1	7	11	-8
1	8	95	-101
1	9	22	28
1	10	77	-79
1	12	22	-26
1	13	13	-8
1	14	28	-30
2	1	89	97
2	2	10	-5
2	3	103	107
2	4	100	-101
2	5	28	-23
2	6	34	-31
2	7	6	-0
2	8	24	-24
2	11	14	18
2	13	13	-14
2	14	35	-38
3	1	75	-73
3	2	25	-31
3	3	64	-68
3	4	58	-60
3	5	49	42
3	6	34	-37
3	8	70	63
3	10	34	38
3	12	35	38
3	13	12	9
4	0	157	-117
4	1	40	40
4	2	108	81
4	3	139	132
4	4	16	-11
4	5	61	69
4	6	23	24
4	7	44	53
4	8	12	16
4	9	24	28
4	12	25	-20
4	13	28	28
5	1	177	186
5	2	26	-20
5	3	137	129
5	4	6	11
5	5	6	-3
5	6	33	29
5	7	20	-17
5	8	150	-150
5	9	41	-41
5	10	32	-36
5	12	39	-43
6	0	48	-38
6	1	68	47
6	2	58	-64
6	5	120	-113
6	6	17	-19
6	7	59	-55
6	8	13	8
6	9	28	-36
6	10	8	11
6	11	49	-54
6	12	29	30
7	1	83	-81
7	2	24	-19
7	3	63	-56
7	4	60	64
7	5	20	10
7	6	53	-51
7	7	16	14
7	8	89	94
7	9	20	15
7	12	18	23
8	0	18	-13
8	1	40	35
8	2	35	29
8	3	43	-43
8	4	29	34
8	5	95	86
8	6	21	-20
8	7	35	43
8	8	26	-25
8	10	14	14
8	11	45	48
8	12	38	-41
9	1	154	141
9	2	33	-34
9	3	38	36
9	4	65	-57
9	5	15	21
9	6	39	41
9	7	16	16
9	8	57	-64
9	9	15	-13
9	11	15	-22
9	12	10	-19
10	0	10	9
10	1	19	8
10	2	25	20
10	3	25	24
10	4	28	-25
10	5	43	-45
10	7	50	-49
10	8	14	22
10	9	22	-28
10	11	40	-42
10	12	21	20
11	2	22	32
11	3	19	-25
11	5	45	-48
11	6	10	-8
11	7	29	-32
11	8	35	36
11	10	31	36
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5	3	13	12
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15	1	20	-17
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16	-3	30	-29
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[a] The data are divided into groups having a common value of *h*.

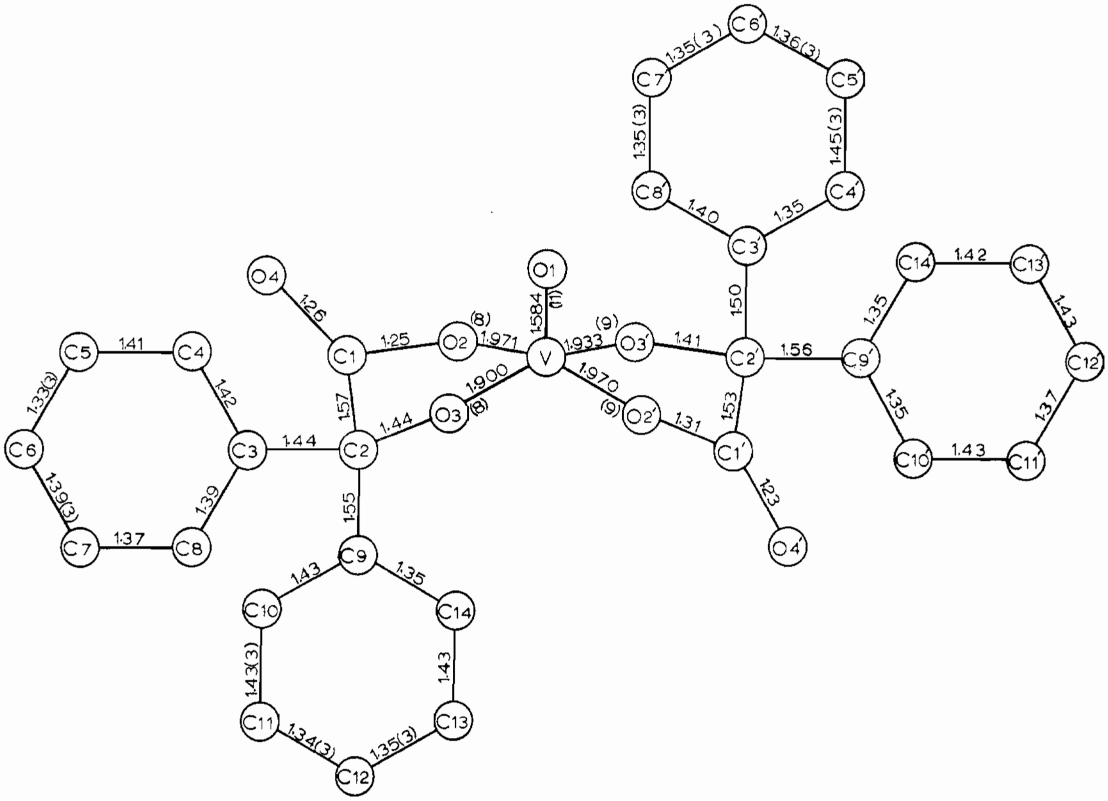


Figure 2.—Vanadyl bisbenzilate anion bond lengths. Estimated standard deviations are 0.02 Å unless given in parentheses (deviation in the last digit).

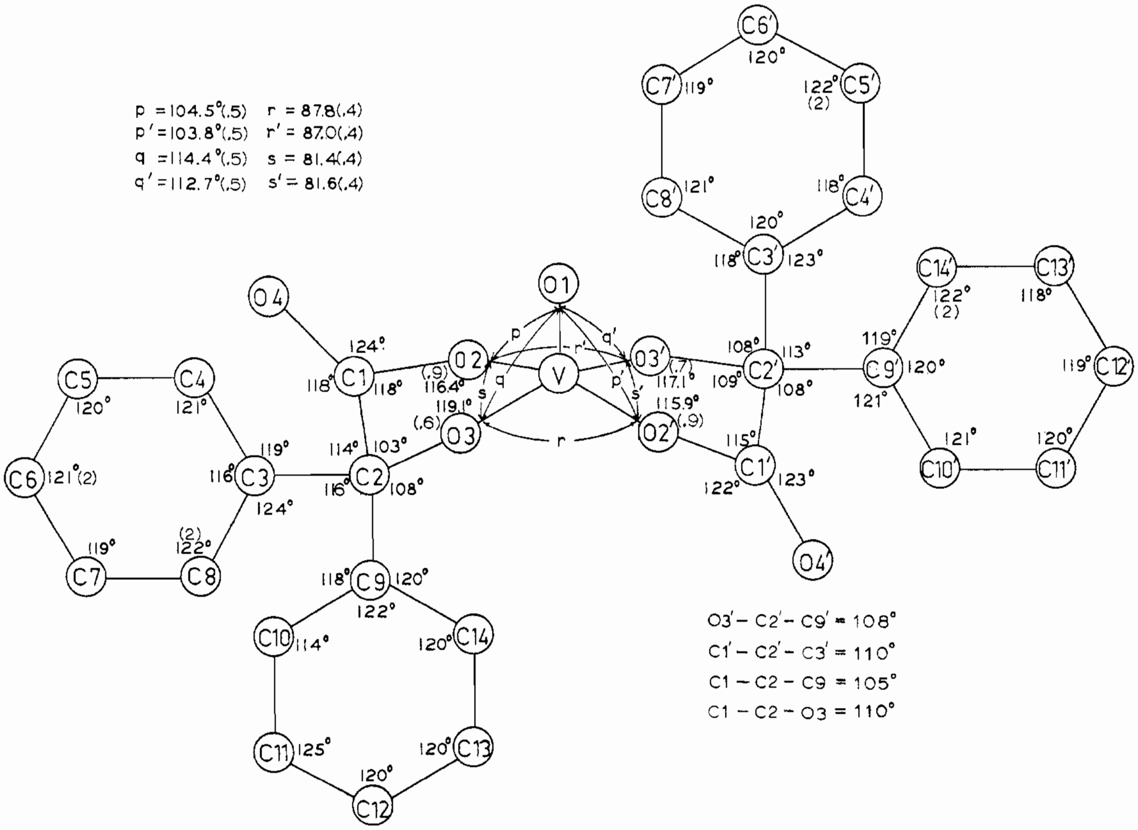


Figure 3.—Vanadyl bisbenzilate anion bond angles. The estimated standard deviations are 1° unless given in parentheses (deviation in the last digit).

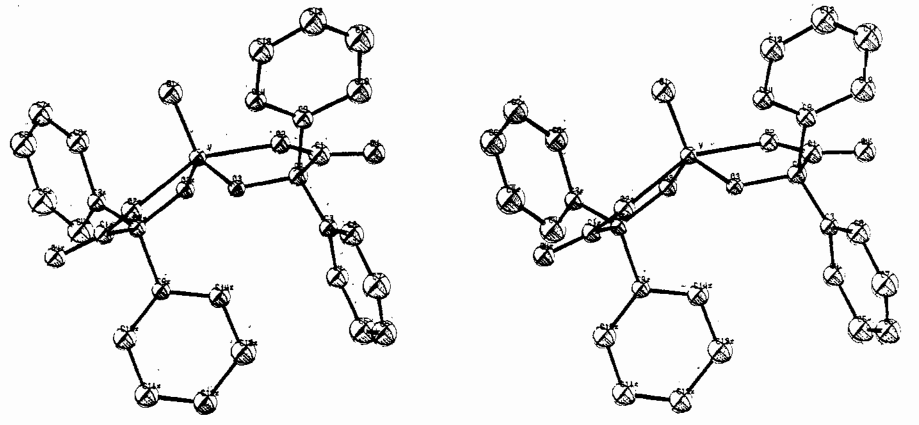


Figure 4.—Stereoscopic view of $VO[(C_6H_5)_2COCO_2]_2^{2-}$ anion. This figure is best viewed with the aid of a stereoscopic viewer, such as an aerial photograph reader. The symbol ‡ denotes the primes used elsewhere in the text.

TABLE III

INTERATOMIC DISTANCES AND ANGLES NOT GIVEN IN FIGURES 2 AND 3[a]

Distances (Å)

N-C15, C17, C19, C21: 1.54, 1.62, 1.55, 1.50(.03)
N-T1, T2, T3, T4: 1.92, 1.43, 1.68, 1.73(.10)

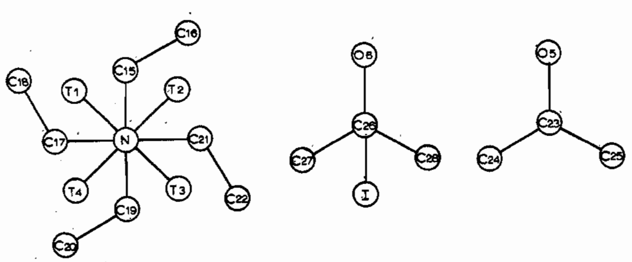
C15-C16	1.56(.03)	C23-O5	1.45(.02)	C26-C27	1.40(.04)
C17-C18	1.51(.04)	C23-C24	1.52(.03)	C26-C28	1.54(.04)
C19-C20	1.57(.04)	C23-C25	1.58(.03)	C26-I	0.99(.10)
C21-C22	1.63(.03)	C26-O6	1.48(.03)		

Na-02, 04, 05, 06, 02′, 04′: 2.38, 2.53, 2.33, 2.37, 2.37, 2.67(.01)

Angles (deg)

C15-N-C17	112(1)	N-C19-C20	109(2)	O2′-Na-O4	110.4(.4)
C15-N-C19	113(1)	N-C21-C22	112(1)	O2′-Na-O5	81.8(.3)
C15-N-C21	106(1)			O2′-Na-O6	118.9(.3)
C17-N-C19	100(1)	O5-C23-C24	107(1)		
C17-N-C21	110(2)	O5-C23-C25	109(2)	O4′-Na-O2	87.5(.4)
C19-N-C21	115(2)	C24-C23-C25	112(1)	O4′-Na-O4	78.5(.3)
				O4′-Na-O5	130.1(.4)
T1-N-T2	109(5)	O6-C26-C27	116(2)	O4′-Na-O6	120.8(.4)
T1-N-T3	101(4)	O6-C26-C28	105(2)		
T1-N-T4	98(4)	C27-C26-C28	116(2)	O2-Na-O4	53.6(.4)
T2-N-T3	116(5)	O6-C26-I	112(5)	O2-Na-O5	130.8(.4)
T2-N-T4	124(5)	C27-C26-I	98(6)	O2-Na-O6	79.1(.4)
T3-N-T4	104(4)	C28-C26-I	110(6)		
				O4-Na-O5	98.5(.4)
N-C15-C16	113(1)	O2′-Na-O4′	54.5(.3)	O4-Na-O6	129.2(.4)
N-C17-C18	114(2)	O2′-Na-O2	142.0(.4)	O5-Na-O6	99.8(.4)

Atom Numbering for the Tetraethylammonium Ion and the Isopropanol Molecules



[a] Estimated standard deviations are in parentheses.

oxygen atoms. The scale factor was varied in each part of each refinement cycle.

After the first three refinement cycles ($R = 0.13$), all of the inner carbon atoms and two terminal carbon atoms of the tetraethylammonium ion had excessively large temperature parameters, 10.0–12.0 Å². The bond lengths and angles of the ion were also unreasonable. Disorder is not uncommon for tetraethylammonium ions.[17] A difference map, based on structure factors calculated on all previously located atoms, showed four peaks in an approximate tetrahedral arrangement about the nitrogen. We found no peaks corresponding to alternate positions for the terminal carbon atoms within the resolution of the difference map. We attempted to describe the disorder with the nitrogen and terminal carbon atoms occupying nearly the same positions in two different orientations of the tetraethylammonium ion. From the difference map, we estimated the occupancy of the four tetrahedral "ghost" peaks (designated as T1–T4) to be 20% of a carbon atom. Another "ghost" peak (designated as I) was found near one 2-propanol molecule. This 2-propanol molecule also had poor bond lengths and two terminal carbon atoms with large temperature factors. We could best account for disorder in this instance by an approximate threefold rotation about the central carbon–oxygen bond, with each terminal carbon atom occupying the "ghost" position about 15% of the time. Thus, we further refined the structure with five additional atomic positions and thermal parameters, the tetraethylammonium ion now having two sets of tetrahedral carbon atoms with 20% (T1–T4) and 80% (C15, C17, C19, C21) occupancy and the 2-propanol molecule having three terminal carbon atoms with 85% (C27), 85% (C28), and 30% (I) occupancy. Refinement did not improve the bond lengths and angles significantly, but the anomalous temperature factors improved as expected. With the existing data, better definition of this portion of the structure is not possible. While we are confident that the disorder is real, we judge that the quality and relatively small amount of data do not warrant variation of occupancy or other attempts to describe better this portion of the structure.

During the final refinement cycle, no parameter changed more than 50% of the estimated standard deviation. A final difference map contained no peaks greater than 20% of a typical carbon atom. There was no conclusive evidence for anisotropy.

The structure amplitudes calculated for the unobserved data indicated that these reflections should be too weak to be observed.[18] Atomic scattering factor curves for neutral V, O, C, and N and for Na⁺ were taken from ref 19. No correction was made for anomalous dispersion since the space group is nonpolar and the terms are too small to be of significance in the present analysis.[20]

Results

Molecular Structure of Sodium Tetraethylammonium Bis(benzilato)oxovanadium(IV) Di-2-propanolate.—

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[17] See, for example, G. D. Stucky, J. B. Folkers, and T. J. Kistenmacher, *Acta Cryst.*, **23**, 1064 (1967).

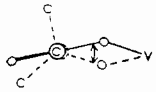
[18] Forty-nine low-order reflections were obscured by the beam stop.

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

[20] For V with Cu Kα, $\Delta f' = 0.2$ and $\Delta f'' = 2.3$: C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

TABLE IV

COMPARISON OF VANADIUM ENVIRONMENT IN SODIUM TETRAETHYLAMMONIUM BIS(BENZILATO)OXOVANADIUM(IV) DI-2-PROPANOLATE WITH OTHER OXYGEN-COORDINATED VANADYL(IV) COMPOUNDS[a]

	Na(Et$_4$N)[VO(benzilate)$_2$] ·2C$_3$H$_7$OH	(NH$_4$)$_4$[VO*d*-tart]$_2^2$ ·2H$_2$O	Na$_4$[VO*dl*-tart]$_2^3$ ·12H$_2$O	VO(2, 6-lutidinate) ·4H$_2$O		VO(acac)$_2^d$	VO(bzac)$_2^{e,6}$
				Orthorhombic[b]	Triclinic[c]		
			V-O Bond Lengths				
Vanadyl Oxygen	1.584(.011)	1.60(.02)	1.619(.007)	1.591(.011)	1.592(.010)	1.571(.010)	1.612(.010)
Ligand Oxygens	1.971(.008)	2.01(.02)	2.004(.006)	2.017(.010)	2.055(.009)	1.974(.008)	1.952(.008)
	1.970(.009)	2.03(.02)	1.994(.006)	2.017(.010)	2.022(.009)	1.955(.008)	1.946(.008)
						1.983(.007)	
	1.900(.008)	1.93(.02)	1.917(.006)	2.027(.012)	2.013(.012)	1.962(.007)	1.986(.007)
	1.933(.008)	1.79(.02)	1.902(.006)	2.027(.012)	2.077(.012)		1.982(.008)
			Vanadyl Oxygen-V-Ligand Oxygen Angles (deg)				
	104.5(.5)	99(1)	109.8(.3)	107.4(.3)	107.1(.5)	104.8(.4)	106.9(.4)
	103.8(.5)	99(1)	104.8(.3)	107.4(.3)	107.0(.5)	106.2(.4)	106.0(.4)
						108.4(.4)	
	114.4(.5)	122(1)	104.6(.3)	96.0(.3)	97.2(.5)	105.6(.4)	104.0(.4)
	112.7(.5)	115(1)	106.2(.3)	96.0(.3)	95.7(.5)		106.6(.4)
			Angles Between Planes (deg)[f]				
V, O2, O3 V, O2′, O3′	127.7	122.0	136.1	143.3	143.8	134.7	135.6
O1, V, O3, O3′;[g] O1, V, O2, O2′	86.6	86.3	86.1	90.1[h]	90.1[h]	92.0	91.8
			Dihedral Angles (deg)				
	12.3	20.0	15.0	----	----	----	----
	11.1	5.8	1.0	----	----	----	----

[a] Estimated standard deviations are in parentheses. Distances and angles involving equivalent atoms are grouped together (carboxyl oxygens first, then hydroxyl oxygens where appropriate).

[b] Vanadyl (IV) 2, 6-pyridine dicarboxylic acid tetrahydrate (orthorhombic). B. H. Bersted, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, in press. There is nitrogen coordination in the sixth position at a distance of 2.18 Å from the vanadium atom.

[c] Vanadyl (IV) 2, 6-pyridine dicarboxylic acid tetrahydrate (triclinic). M. H. Valek, R. L. Belford, and I. C. Paul, to be published. There is nitrogen coordination in the sixth position at a distance of 2.15 Å from the vanadium atom.

[d] Vanadyl (IV) bisacetylacetonate. Isotropic parameters reported by R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961). The table values are based on anisotropic parameters obtained from further refinement of the reported isotropic parameters by P. K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.*, **43**, 3111 (1965).

[e] Vanadyl (IV) bisbenzoylacetonate.

[f] Planes involving more than three atoms are "best" planes. The average distances of atoms from the best planes in all the structures are ± 0.01 Å except in the case of Na$_4$[VO*dl*-tart]$_2$·12H$_2$O where it is ± 0.02 Å.

[g] This angle is measured internal to the bridging ligand. [h] Has no internal angle as defined in g.

Table I shows the positional and isotropic thermal parameters used in the final structure factor calculations. Table II lists the final calculated and observed structure amplitudes. Figure 1b shows the VO$_5$ groups projected on the *ac* face of the crystal with extinction directions marked. Figures 2 and 3 and Table III give the atom numbering and some bond distances and angles. Figure 4 presents a stereoscopic view of the VO[(C$_6$H$_5$)$_2$COCO$_2$]$_2^{2-}$ anion.[21]

While we treated the disorder in the tetraethylammonium ion and one of the 2-propanol molecules in a limited way, the agreement among chemically equivalent bond lengths and angles of the anion (except for the anomalously short C2–C3 bond) gives us confidence that this portion of the structure is essentially correct. The disorder in the tetraethylammonium ion and one 2-propanol molecule is reflected in the bond lengths and angles given in Table III.

The anion has a *trans* arrangement about the vanadyl group (as expected, since steric hindrance involving the two phenyl groups on each ligand makes a *cis* arrangement very unlikely). The vanadium–oxygen bond lengths are typical of other vanadyl structures (see Table IV), with the vanadium–hydroxyl oxygen

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[21] 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 V

BEST PLANES THROUGH GROUPS OF ATOMS WITH DISTANCES[a]

Plane 1	$.4743X + .8455Y + .2453Z = 8.068$ Å					
Atoms:	V	O1	O2	O2′		
Distances:	.006	−.001	−.002	−.002 Å		
Plane 2	$-.1197X - .1477Y + .9818Z = 7.143$ Å					
Atoms:	V	O1	O3	O3		
Distances:	.004	−.001	−.002	−.001 Å		
Plane 3	$.1755X + .1402Y - .9744Z = -5.6350$ Å					
Atoms:	C3	C4	C5	C6	C7	C8
Distances:	−.020	.021	−.023	.024	−.023	.021 Å
Plane 4	$.8393X + .3600Y + .4075Z = 8.881$ Å					
Atoms:	C9	C10	C11	C12	C13	C14
Distances:	−.014	.020	−.022	.011	−.001	.006 Å
Plane 5	$.0869X - .0478Y - .9951Z = -9.284$ Å					
Atoms:	C3′	C4′	C5′	C6′	C7′	C8′
Distances:	−.006	.000	.009	−.013	.007	.003 Å
Plane 6	$.5721X + .7182Y + .3960Z = 6.911$ Å					
Atoms:	C9′	C10′	C11′	C12′	C13′	C14′
Distances:	−.026	.025	.003	−.021	.015	.004 Å
Plane 7	$-.6114X + .7448Y - .2673Z = 1.920$ Å					
Atoms:	C1	C2	O2	O4		
Distances:	.017	−.006	−.006	−.005 Å		
Plane 8	$.9677X - .2280Y + .1075Z = 1.102$ Å					
Atoms:	C1′	C2′	O2′	O4′		
Distances:	−.002	.000	.001	.001 Å		

[a] The (X, Y, Z) axis system is the unit cell system orthogonalized and normalized to 1 Å; *i.e.*, $(X, Y, Z) = (x \cdot a \cdot \sin\beta, y \cdot b, z \cdot c + x \cdot a \cdot \cos\beta)$.

distances significantly shorter than vanadium–carboxyl oxygen distances (1.92 *vs.* 1.97 Å). Vanadyl oxygen–vanadium–ligand oxygen angles differ by about 10° for the carboxyl and hydroxyl oxygen atoms (104 *vs.* 114°). The anion, excepting the phenyl rings, has approximate C_2 symmetry (see Figure 4).

Discussion

Ligand Features.—The "best" planes (by a least-squares method with all atoms equally weighted) through various groups of atoms are given in Table V. In all cases, the groups of atoms are planar within the accuracy of the analysis as shown by the fact that the distance of each atom from the plane is never more than twice the standard deviation in position. The root-mean-square deviation of the 24 C–C distances in the phenyl rings is 0.044 Å which is larger than the average estimated standard deviation of 0.025 Å from the least-squares refinement. The low estimate of the standard deviations from least squares is probably a result of the partial matrix refinement procedure which should most seriously affect the phenyl ring portion of the structure. Each carboxyl carbon atom is the center of an essentially planar four-atom fragment. The phenyl rings on both halves of the anion are similarly oriented, with interplanar angles between neighboring phenyl rings of 68° (planes 5 and 6) and 78° (planes 3 and 4), respectively. The angles between phenyl planes C3–C8, C9–C14 and plane C1–C2–O3 for the two halves of the anion are 86, 117 and 85, 121°, respectively. These relationships involving the phenyl rings can best be seen in Figure 4.

Comparison of the Vanadyl(IV) Bisbenzilate Anion with Other Vanadyl(IV) Compounds. A. Bond Lengths.—Table IV lists parameters of other vanadyl(IV) structures for comparison. The average differences between vanadium–hydroxyl oxygen (∼1.9 Å) and vanadium–carboxyl oxygen (∼2.0 Å) distances are 0.06, 0.16, and 0.09 Å for the vanadyl(IV) bisbenzilate, *d*-tartrate, and *dl*-tartrate α-hydroxycarboxylate complexes, respectively. The large value of 0.16 Å for the *d*-tartrate chelate probably is not significantly different from the others, in view of the lower accuracy of that structure and the anomalously short vanadium–hydroxyl oxygen bond (1.79 Å). Of all of the vanadium–ligand bond distances found thus far, the vanadium–α-hydroxyl oxygen linkages are the shortest. The vanadium–ligand oxygen bond lengths for the β-diketonate compounds ($VO(acac)_2$ and $VO(bzac)_2$) are somewhat intermediate between those of the two types in the α-hydroxycarboxylates.

B. Bond Angles.—The difference between the O1–V–hydroxyl oxygen and O1–V–carboxyl oxygen angles is most pronounced in vanadyl(IV) *d*-tartrate (average 17°). Because of this extreme depression of hydroxyl oxygen atoms, the *trans-d*-tartrate complex has been described as having a distorted trigonal-bipyramidal geometry, with the vanadyl oxygen and the hydroxyl oxygens in the equatorial positions.[2] In contrast, the hydroxyl oxygens in the *cis-dl*-tartrate compound are not depressed; consequently, it is similar to the β-diketone chelates in having square-pyramidal geometry. The vanadium atom in these compounds lies about 0.54 Å above the pyramid base. The structure of vanadyl(IV) bisbenzilate is intermediate between the trigonal-bipyramidal and square-pyramidal geometries.

C. Angles between Planes.—Comparison of the angles between the vanadium–ligand oxygen planes (*i.e.*, V–O2–O3 and V–O2′–O3′) illustrates very well the differences in geometry of these compounds. In each of the square-pyramidal structures ($VO(dl\text{-tart})^{2-}$, $VO(acac)_2$, and $VO(bzac)_2$), the angle between these planes is about 135°; it is 122° in the distorted trigonal-bipyramidal vanadyl(IV) *d*-tartrate (120° is expected for a perfect trigonal bipyramid). Vanadyl(IV) bisbenzilate is intermediate, with a value of 127.7°. Angles (internal to the bridging ligand) between the planes O1–V–O3–O3′ and O1–V–O2–O2′ are markedly different for the α-hydroxycarboxylates (86°) and the β-diketonates (92°). Relative to a six-membered chelate ring, formation of a five-membered ring compresses this angle.[3] In the case of the $VO(2,6\text{-lut}) \cdot 4H_2O$ molecule (lut = lutidinate), where

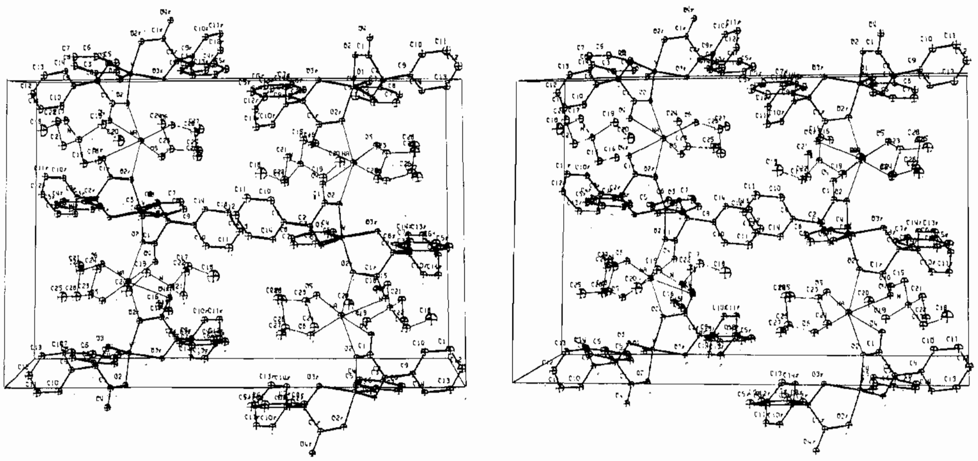


Figure 5.—Stereoscopic view (along [$\bar{1}$00]) of the contents of the unit cell. For clarity of presentation the radii of the thermal spheres have been uniformly scaled down.

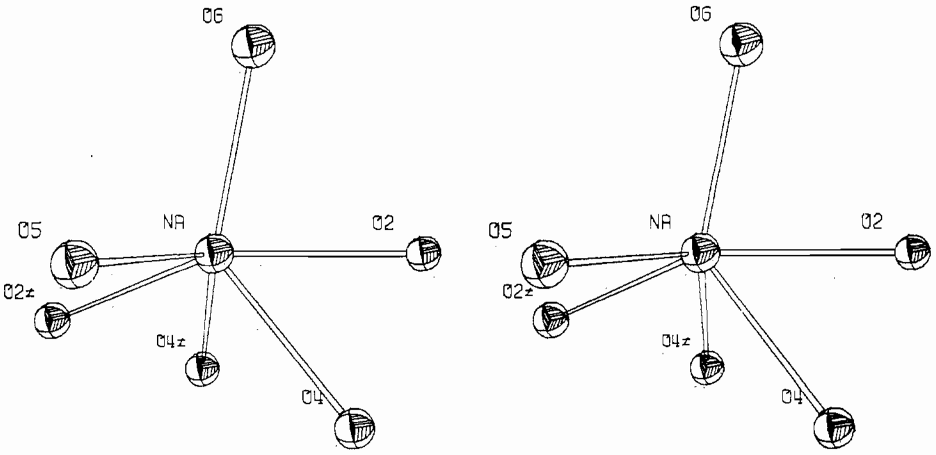
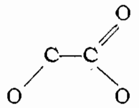


Figure 6.—Sodium coordination polyhedron. O_2, O_4, O_2', and O_4' belong to carboxylate groups while O_5 and O_6 belong to 2-propano molecules.

no ring formation of this type occurs, the molecule relaxes to the expected right-angle geometry in both crystal modifications (see Table IV).

D. Dihedral Angles.—The dihedral angles between coordinating ligand oxygen atoms about the C1–C2 bond axis are essentially the same (11 and 12°) for both ligands of the vanadyl(IV) bisbenzilate anion, as expected of a chelate having near-C_2 symmetry and approximately planar



groups. The dihedral angle differences for the two ligands in both the *d*-tartrate and *dl*-tartrate vanadyl(IV) complexes reflect differences in the depression angles $O1–V–O_n$ and $O1–V–O_m$ of chemically equivalent ligand oxygen atoms (O_n and O_m) of the two halves of the anion (see Table IV).

Molecular Packing.—A stereoscopic view of the unit cell is given in Figure 5. van der Waals, ion–ion, and Na^+ ion–dipole forces and hydrogen bonds all must be involved in the crystal binding. The sodium ion is in a six-coordinate, very distorted octahedral environment (see Figure 6) and lies between two vanadyl(IV) bisbenzilate anions related by the glide plane. It coordinates to the four oxygen atoms of the two crystallographically independent carboxyl groups in these anions. Two 2-propanol oxygen atoms occupy the other two coordinating positions. Some bond lengths and angles are given in Table III.

The shortest V–V distances are two at 8.18 Å (glide plane along *c*), two at 10.86 Å (unit cell translation along *a*), and one at 11.77 Å (inversion center). The angle between symmetry-related vanadyl groups is 59.0° (glide plane or screw axis); *i.e.*, each VO group makes an angle of 60.5° with the *b* axis.

The two 2-propanol molecules are hydrogen-bonded to the hydroxyl oxygen atoms of the benzilate ligands. The lengths O5–O3 and O6–O3′ are 3.07 and 2.75 Å, respectively; the corresponding angles, C23–O5–O3 and C26–O6–O3′, are 100.3 and 115.4°, respectively. (O3 is related by x, $^1/_2 - y$, $^1/_2 + z$ to the position given in Table I.)

Stability of *cis* and *trans* Isomers.—The question of

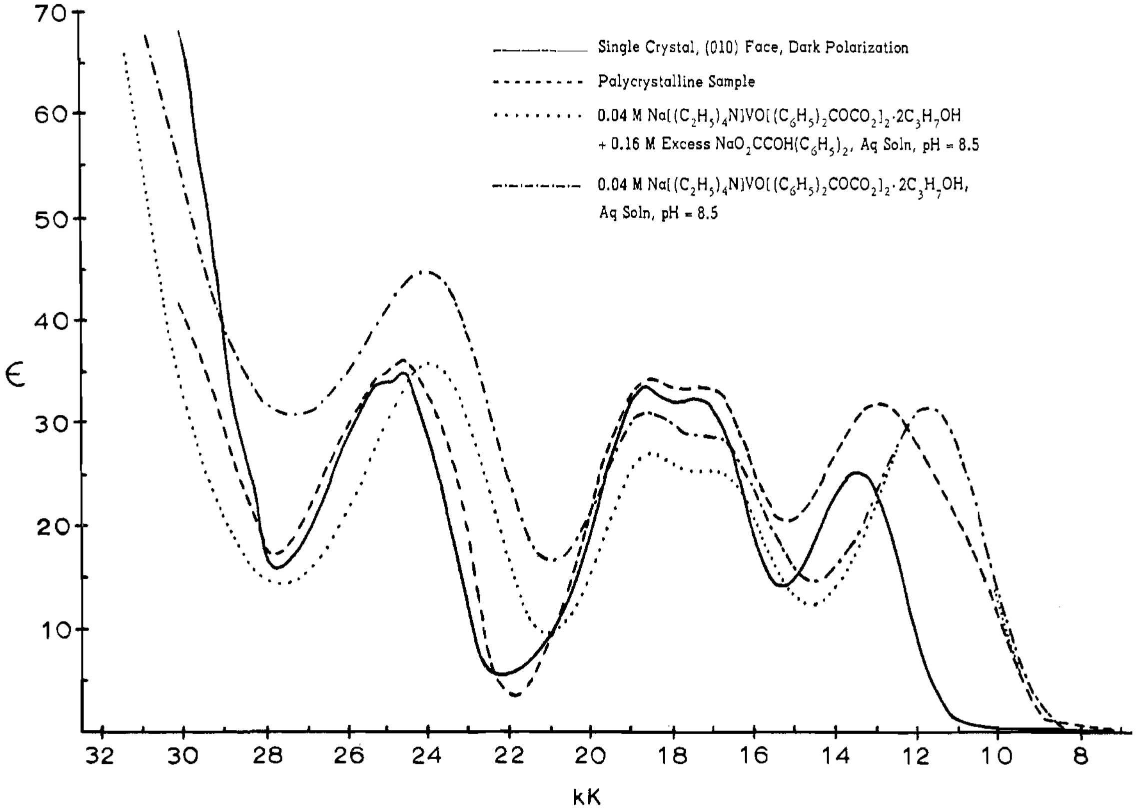


Figure 7.—Sodium tetraethylammonium bis(benzilato) oxovanadium(IV) di-2-propanolate spectra. Decadic molar extinction coefficient (l./cm mol) *vs.* frequency (1 kK = 1000 cm^{-1}). Extinction coefficients for the polycrystalline sample were obtained by arbitrarily scaling the 13-kK band absorbance to that of the solution spectrum.

the relative stability of *cis vs. trans* arrangements about the vanadyl ion (see Introduction) is partly clarified by this work. In addition to the *trans*-vanadyl bisbenzilate and *d*-tartrate complexes, the *trans*-2,6-lutidinate (green orthorhombic form, note *b*, Table IV) exhibits a four-band spectrum. The presence of four distinct bands in the optical spectrum seems to be diagnostic of a *trans* configuration and perhaps trigonal distortion about the vanadyl group. In view of their characteristic spectra, all vanadyl α-hydroxycarboxylate complexes, except the *cis-dl*-tartrate complex,[3] probably have a *trans* configuration. One does not know how far each of these compounds is distorted toward a trigonal bipyramid. Since vanadyl bisbenzilate is much less distorted than vanadyl *d*-tartrate, it is entirely possible that a simple α-hydroxycarboxylate complex with no large steric requirements, such as vanadyl bisoxoacetate, is only slightly distorted. The greater stability of the *cis-dl*-tartrate complex over the *trans-d*-tartrate complex then may be due to the severe trigonal distortion from the (normally preferred) square-pyramidal geometry.[22] Tapscott[8] suggested that the *d*-tartrate complex distorts toward trigonal-bipyramidal geometry to relieve strain associated with an eclipsed conformation about the central C–C bond of the bridging tartrate chain. To achieve a staggered conformation, the *d*-tartrate complex must distort from a square-pyramidal geometry about the vanadium atom, while the *dl* complex need not.

The structure of bistrimethylamineoxovanadium(IV) dichloride, VOCl$_2$·2N(CH$_3$)$_3$, has just been reported to have a *trans* configuration and basically trigonal-bipyramidal geometry with oxygen and chlorine atoms in the equatorial positions.[23] The authors attribute the molecular geometry to nonbonded intramolecular interactions (steric hindrance) between trimethylamine ligands and the chlorine and oxygen atoms. The compound exhibits a five-band spectrum, the fifth band at 36,000 cm^{-1} being assigned to a charge-transfer transition.

Spectral Properties.—The solid and solution spectra of vanadyl(IV) bisbenzilate are presented in Figure 7. The polycrystalline sample [alkaline solution] exhibits four bands at 13.0 [11.8], 16.9 [16.7],[24] 18.5 [18.5], and 24.7 [24.0] kK, with the bands shifted to higher energy in the solid. Contamination of the solution spectrum by more than one species is evident from the

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[22] The following compounds have a distorted octahedral geometry (or a square-pyramidal geometry excepting the oxygen coordination in the sixth position which is at a larger distance from the vanadium atom than the equatorial ligands): vanadyl sulfate, VOSO$_4$, sixth position distance of 2.28 Å [P. Kierkegaard and J. M. Longo, *Acta Chem. Scand.*, **19**, 1906 (1965)], vanadyl molybdate, VOMoO$_4$, sixth position distance of 2.59 Å [H. A. Eick and L. Kihlborg, *ibid.*, **20**, 722 (1966)], diammonium oxotetrakisisothiocyanatovanadate pentahydrate, (NH$_4$)$_2$VO(NCS)$_4$·5H$_2$O, sixth position distance of 2.22 Å [A. C. Hazell, *J. Chem. Soc.*, 5745 (1963)], and vanadyl sulfate pentahydrate, VOSO$_4$·5H$_2$O, preliminary results, sixth position distance of 2.223 Å [C. J. Ballhausen, B. F. Djurinskij, and K. J. Watson, *J. Am. Chem. Soc.*, **90**, 3305 (1968)].

[23] J. E. Drake, J. Vekris, and J. S. Wood, *J. Chem. Soc., A*, 1000 (1968).

[24] This band occurs as a shoulder; therefore, its precise location is uncertain.

spectral changes attending addition of excess ligand. The similarities in the principal features of the solid and solution spectra indicate that like species are present.

Owing to the similarity in intensity and shape of the four optical bands, our first reaction is that they are all likely to be basically of "d–d" origin. A tentative interpretation of the optical spectrum is suggested by a correlation of structural differences in the ammonium vanadyl(IV) *d*-tartrate, the sodium tetraethylammonium vanadyl(IV) bisbenzilate, and the sodium vanadyl(IV) *dl*-tartrate salts with their solid-state spectra. In light of the systematic change from roughly trigonal-bipyramidal to square-pyramidal geometries for these compounds and the *cis–trans* differences in the vanadyl tartrate systems, crystal field arguments suggest the two possible energy level schemes in Figure 8. Here the z axis is taken to lie along the vanadyl bond and the x and y axes lie approximately along the vanadium–hydroxyl oxygen and vanadium–carboxyl oxygen atom directions, respectively. Without the present structural information, Selbin and Morpurgo[5] had suggested the energy level scheme having $x^2 - y^2 < xz, yz$ as a possible but unlikely explanation for the spectra of the vanadyl α-hydroxycarboxylates.

There is a marked difference in the low-energy band (~13 kK) of the mull and (010) face dark polarization spectra. It is possible that this band has two electronic components, in which case the above energy level schemes are not applicable. Another interesting feature is the splitting of the high-energy band (~25 kK) by about 700 cm^{-1} in the (010) face dark polarization at room temperature. At liquid nitrogen temperature we observed fine structure, consisting of at least 12 small peaks superimposed on the main band and the following charge-transfer region. The details of the spectra between room and liquid helium temperatures will be reported at a later date.

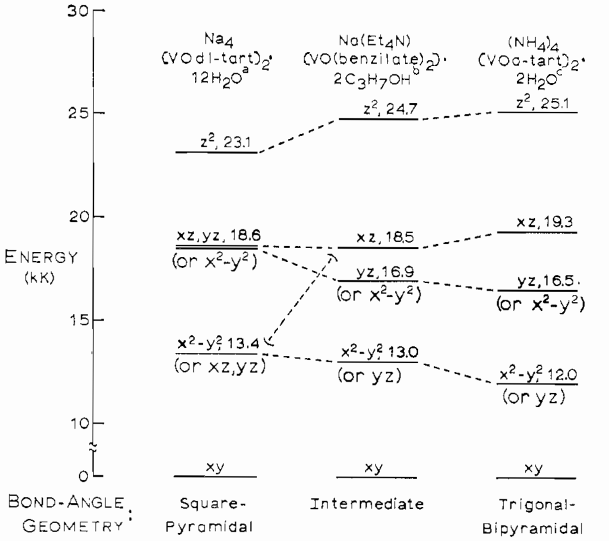

Figure 8.—Two possible orderings of the crystal field energy levels and band maxima, for three α-hydroxycarboxylate complexes: (a) Nujol mull spectrum; (b) polycrystalline spectrum; (c) reflectance spectrum reported in ref 5. Our Nujol mull spectrum is in agreement with the reported reflectance spectrum. The terms "square-pyramidal" and "trigonal-bipyramidal" are not intended to imply C_{4v} or D_{3h} symmetry but refer only to the approximate angular geometry of the coordination polyhedron about the vanadium atom. See the text for the definition of the coordinate system.

The vanadyl(IV) bisbenzilate, *d*-tartrate, and *dl*-tartrate complexes offer a special opportunity to probe systematically the ligand field energy levels of oxovanadium(IV) compounds. Hopefully, comparison of geometrical effects on the polarized crystal spectra and electron resonance parameters will aid considerably in the elucidation of the origin of the optical transitions and bonding in vanadyl compounds in general and α-hydroxycarboxylates in particular.[25,26]

Acknowledgments.—The authors wish to thank Mr. J. S. McKechnie and Mrs. S. M. Johnson for their assistance with the X-ray equipment and programs and Mrs. S. F. Eilers for the stereoscopic drawings.

[25] Reviews of this area can be found in J. Selbin, *Chem. Rev.*, **65**, 153 (1965), and *Coord. Chem. Rev.*, 293 (1966).

[26] Leading spectral references are given by C. J. Ballhausen, B. F. Djurinskij, and K. J. Watson, *J. Am. Chem. Soc.*, **90**, 3305 (1968).