structed. The N–O bond length for coordinated pyridine N-oxide (1.33 Å) falls in the steep portion of the curve where bond order is relatively insensitive to bond length but suggests that the π-bond character is small, of the order of 10–20%. This conclusion is consistent with the observed sizable twist of the pyridine rings out of the Ni–O–N planes. A further useful comparison is with the N–O bond length of 1.39 Å[29] in the aliphatic amine N-oxide, $(CH_3)_3NO$, where π bonding is impossible and the effect of charge separation[29] should roughly correspond to the present case. The pyridine N-oxide oxygens O(5) and O(6) are, respectively, 0.06 and 0.07 Å out of the least-squares planes through the pyridine rings. Similar deviations from planarity have been found for the N-oxide moiety in $C_5H_5NO \cdot HCl$[25] and $[CuCl_2(C_5H_5NO)]_2$.[4]

The bond lengths and angles of the acylacetonate chelate rings appear normal and compare well with those in the literature. The methyl carbons fall within 0.15 Å of the least-squares planes defined by the oxygens and carbons 2, 3, and 4 of the chelate rings. As has been noted in other acetylacetonate complexes,[9] the central metal does not lie exactly in the plane of the chelate ring. In the present structure the nickel atom falls 0.17 and 0.64 Å from the least-squares planes of chelate rings O(1)–C(2)–C(3)–C(4)–O(2) and O(3)–C(7)–C(8)–C(9)–O(4), respectively.

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CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY AND MATERIAL RESEARCH LABORATORY,
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The Crystal and Molecular Structure of Orthorhombic Vanadyl(IV) Pyridine-2,6-dicarboxylate Tetrahydrate[1]

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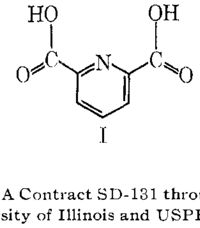
Optical spectra of polycrystalline vanadyl(IV) pyridine-2,6-dicarboxylate tetrahydrate (vanadyl(IV) 2,6-lutidinate tetrahydrate) have some interesting similarities to those of the low-symmetry vanadyl(IV) α-hydroxycarboxylates. The crystal structure of one form of vanadyl(IV) 2,6-lutidinate tetrahydrate has been determined to examine the effective symmetry of the chelate species involved and to obtain other structural information required to interpret the spectra of oriented crystals. The emerald green prismatic crystals are orthorhombic with $a = 8.68$, $b = 12.43$, and $c = 10.75$ Å. The space group is Pbcn and there are four units of $VOC_7H_3O_4N \cdot 4H_2O$ in the unit cell; $\rho_{\text{measd}} = 1.73$ g/cm³, $\rho_{\text{calcd}} = 1.733$ g/cm³; each molecule has C_2 symmetry. Three-dimensional intensity data were collected on multiple-film packs using the equiinclination Weissenberg technique. The structure was determined by Fourier methods and the positional and anisotropic thermal parameters were refined by least-squares methods to a final conventional R factor of 0.10 on 544 observed reflections. The vanadium atom is six-coordinated in a distorted octahedral site which closely approximates C_{2v} symmetry; one of the coordination positions is occupied by the vanadyl oxygen atom, two others are occupied by water molecules, and the remaining three, by the 2,6-lutidinate dianion acting as a tridentate ligand. The remaining two water molecules link the chelate molecules $(VOC_7H_3O_4N \cdot 2H_2O)$ by hydrogen bonding.

Introduction

There has been much interest in the very low-symmetry α-hydroxycarboxylate complexes with VO^{2+} since they exhibit four-band visible spectra[2] as opposed to the usual two or three strong bands observed in most vanadyl(IV) complexes. The Nujol mull spectrum (shown in Figure 1) of vanadyl(IV) complexed with pyridine-2,6-dicarboxylic acid (I) (hereafter referred to as 2,6-lutidinic acid)[3] reveals four bands similar to those of the low-symmetry α-hydroxycarboxylate species. We anticipated that the symmetry of the vanadyl(IV) 2,6-lutidinate complex might prove to be intermediate between that of ammonium vanadyl(IV) *d*-tartrate[4] which, from a spectroscopic examination, appears to be typical of low-symmetry vanadyl α-hydroxycarboxylate structures and the more usual case of approximately square-pyramidal local symmetry for vanadium in vanadyl structures.[5]



I

Difficulty in interpreting the spectra of the low-symmetry α-hydroxycarboxylates arises from the question-

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(1) Supported by ARPA Contract SD-131 through the Materials Research Laboratory at the University of Illinois and USPH GM 12470-03.

(2) J. Selbin and L. Murpurgo, *J. Inorg. Nucl. Chem.*, **27**, 673 (1965).

(3) The preparation of different hydrates of the potentially tridentate donor 2,6-lutidinic acid complexed with vanadyl(IV) has been reported by R. L. Dutta, S. Ghosh, and S. Lahiry, *Sci. Cult.* (Calcutta), **30**, 551 (1964).

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

(5) See, *e.g.*, R. E. Tapscott, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, **7**, 356 (1968).

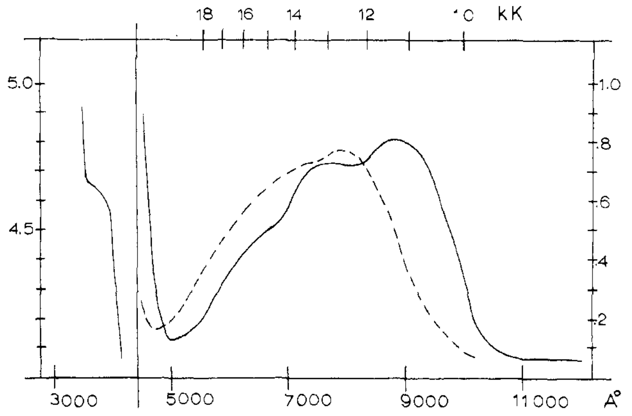

Figure 1.—Visible spectra of Nujol mulls of the two forms of $VOC_7H_8O_4N\cdot 4H_2O$ reported here. The solid curve refers to the green (orthorhombic) form; the dashed curve, to the blue (triclinic) form. The right-hand optical density scale applies to the visible spectra; the left-hand scale, to the ultraviolet segment.

able applicability of the high-symmetry models. Thus, a potentially useful aspect of the spectra of this compound is that it can perhaps serve as a comparative link between spectra of both the higher and lower symmetry compounds. Work on the oriented single-crystal spectra is now underway in our laboratory.

We have prepared a green and a blue form of vanadyl(IV) 2,6-lutidinate tetrahydrate under different experimental conditions. This paper reports the crystal and molecular structure of the green form.

Experimental Section

Preparation of the Compound.—Vanadyl(IV) 2,6-lutidinate tetrahydrate, $VOC_7H_3NO_4\cdot 4H_2O$, was prepared by the action of the free acid on a slurry of freshly prepared vanadyl hydroxide. Green crystals grew from an aqueous solution of pH less than 1.8 under vacuum.[6] The crystals tended to break up with age taking on a mosaic-like structure. Under vacuum in solutions of pH above 2, bright blue prismatic crystals formed. (Note, however, that we have not been able to predict reliably whether the green or the blue form or both will crystallize from a given preparation.) This paper describes the crystal and molecular structure of the green form.[7]

Spectral Apparatus.—The optical Nujol mull spectrum was run with monochromatic sample illumination over the region 11,000–3000 Å using a Cary Model 14 RI spectrophotometer. A lead sulfide detector was used for the 6500–11,000-Å range, and a photomultiplier tube for the 6500–3000-Å range. Spectra coincided (within the thickness of the ink line) in the overlap of the detector regions.

Crystallographic Data.—The green prismatic crystals belong to the orthorhombic system. Cell parameters, as determined at 25° on a 60-mm precession camera using Mo Kα radiation (λ 0.7107 Å), are $a = 8.68 \pm 0.01$, $b = 12.43 \pm 0.01$, and $c = 10.75 \pm 0.02$ Å. The density, as measured by the flotation method in a mixture of bromoform and carbon tetrachloride, is 1.73 g/cm^3. Based on four formula units of $VOC_7H_3O_4N\cdot 4H_2O$ per unit cell, the calculated density is 1.733 g/cm^3. The systematic absences (as determined by inspection of $h0l$, hll, $0kl$, and $1kl$ precession photographs and $hk0$ and $hk1$ Weissenberg photographs) are $0kl$ when $k = 2n + 1$, $h0l$ when $l = 2n + 1$, and $hk0$ when $h + k = 2n + 1$ and uniquely determine the space group as Pbcn (D_{2h}^{14}, no. 60). The fact that the space group Pbcn requires eight general positions, together with the evidence of four monomeric formula units per cell, indicates that the molecule must contain either a center of inversion or a twofold rotation axis. Only the latter would be consistent with the known symmetry of the vanadyl group. $F(000)$ is 620.

Morphology of the Crystal.—The green prismatic crystals have well-developed {110} and {001} faces. Figure 2 shows the crystal habit used to calculate absorption corrections, gives the refractive indices, and indicates the dichroism. The refractive indices were measured using the immersion method with white light. The crystals show a strong tendency toward basal cleavage in the {001} faces. Measurements with a polarizing microscope yielded an approximate value for the optic angle, $2V$, of 45°.

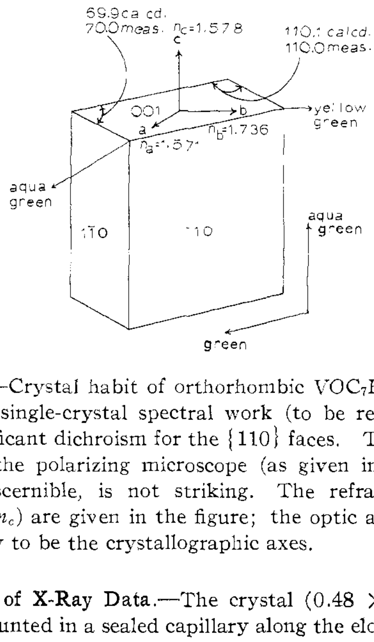

Figure 2.—Crystal habit of orthorhombic $VOC_7H_3O_4N\cdot 4H_2O$. Preliminary single-crystal spectral work (to be reported later) reveals significant dichroism for the {110} faces. The dichroism seen under the polarizing microscope (as given in the figure), although discernible, is not striking. The refractive indices (n_a, n_b, and n_c) are given in the figure; the optic axes are fixed by symmetry to be the crystallographic axes.

Collection of X-Ray Data.—The crystal (0.48 × 0.2 × 0.2 mm) was mounted in a sealed capillary along the elongated c axis and the reflected intensities were recorded on multiple films on the equiinclination Weissenberg camera using Cu Kα radiation (λ 1.5418 Å). Eight levels of data were taken ($hk0$–$hk7$) and 544 independent intensities were estimated visually. This represented approximately 55% of the possible independent reflections in the Cu Kα sphere. The various levels were initially placed on a common scale according to the exposure time. Lorentz, polarization, and absorption[8] correction factors were applied to the data. The linear absorption coefficient with Cu Kα radiation is 80 cm^{-1}.

Structure Determination.—The space group Pbcn has eight general positions, and the cell data indicate four vanadium atoms per unit cell; this information requires the vanadium atom to lie on a special position. Of the possible symmetry elements in the space group, only a twofold axis can accommodate the vanadyl group in an ordered fashion. From a three-dimensional Patterson synthesis,[9] we confirmed that the vanadium atom lies on a twofold axis. The first three-dimensional Fourier synthesis, carried out using the signs calculated on the basis of the contribution of the vanadium atom to the structure factors, revealed all atomic positions (other than those of H) except for the noncoordinated water molecules, which were revealed by a second Fourier synthesis. The conventional crystallographic R factor

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(6) *Anal.* Calcd for $VOC_7H_3O_4N\cdot 4H_2O$: C, 27.60; H, 3.62; N, 4.62. Found: C, 27.85; H, 3.99; N, 4.77.

(7) Preliminary studies in our laboratory show that the blue crystals are triclinic and have the same empirical formula and nearly the same density ($\rho_{meas} = 1.73$ g/cm^3) as the green orthorhombic form. The cell parameters are $a = 6.55$, $b = 9.11$, $c = 11.57$ Å, $\alpha = 113°\ 01'$, $\beta = 114°\ 07'$, $\gamma = 84°\ 02'$; the calculated density assuming 2 formula weights of $VOC_7H_3O_4N\cdot 4H_2O$ is 1.749 g/cm^3: M. H. Valek, R. L. Belford, and I. C. Paul, work in progress.

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

$(R = \Sigma||F_o| - |F_c||/\Sigma|F_o|)$ was 0.43 after inclusion of all atoms other than hydrogen in a structure factor calculation. Several cycles of isotropic least-squares refinement,[10] in which all reflections were weighted[11] and the quantity minimized was $\Sigma w||F_o| - |F_c||^2$, followed by adjustment of the interlevel scale factors, 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. Anisotropic temperature factors were then introduced for all atoms and four cycles of full-matrix least-squares refinement reduced R to 0.10 and R_2 to 0.12. In the final cycle, all parameter shifts were less than 10% of the estimated standard deviations. On a final three-dimensional difference synthesis, peaks were located which corresponded to reasonable positions for the hydrogen atoms attached to C(3) and C(4), and gave C–H distances between 1.1 and 1.2 Å. The heights of the peaks attributed to the hydrogen atoms were 0.33 and 0.38 electron/Å^3. We were unable to locate the hydrogen atoms associated with the water molecules. Two troughs of −0.6 electron/Å^3 were found at $x = \pm 0.093$, $y = 0.250$, and $z = 0.250$.

Tables I and II show the positional and thermal parameters used in the final structure factor calculation. 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.[12] Scattering factors for neutral V, O, C, and N were taken from "International Tables for X-Ray Crystallography."[13]

We made no correction for anomalous dispersion since the space group is nonpolar and the correction to the vanadium atomic scattering factor is small ($\Delta f' = 0.2$, $\Delta f'' = 2.3$).[14]

The introduction of anisotropic parameters is judged to be justified according to the simple significance test recommended by Hamilton.[15] On the basis of this test, the model allowing all atoms to have anisotropic temperature parameters leads to a significant improvement in the agreement between the observed and calculated structure factors. This improvement can be accepted at better than a 99.95% confidence level. These tests apply to random errors and do not take account of systematic errors as might arise from the collection of data about only one axis of rotation and treatment of interlevel scaling factors as adjustable parameters. The interlevel scale factors were not adjusted after introduction of anisotropic thermal parameters. Table II also gives the rms axial displacements and the direction of the most nearly unique axis of the thermal ellipsoids.

TABLE I

FINAL ATOMIC PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS (×10^4) IN FRACTIONS OF THE UNIT CELL EDGE. ORIGIN AS IN INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY[a]

	x	y	z
V	.0000	.2440(2)	.2500
O(1)	.0000	.1160(9)	.2500
O(2)	.1603(11)	.2926(7)	.1264(10)
O(3)	.2792(11)	.4194(8)	.0184(11)
N	.0000	.4197(9)	.2500
C(1)	.0909(13)	.4695(9)	.1744(13)
C(2)	.1877(15)	.3894(9)	.0992(15)
C(3)	.1013(19)	.5811(10)	.1690(16)
C(4)	.0000	.6365(13)	.2500
W(1)	−.1608(11)	.2611(7)	.1147(12)
W(2)	−.3874(14)	.4029(8)	.1271(14)

[a] No standard deviation is given for coordinates fixed by special positions.

TABLE II

Final Anisotropic Temperature Parameters (x 10^4)[a]

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	$B(A^2)^b$
V	57(3)	16(2)	33(4)	----	−0(.9)	----	1.48(.07)
O(1)	143(23)	18(8)	123(24)	----	76(47)	----	3.47(.30)
O(2)	80(15)	32(6)	50(14)	19(14)	56(20)	−15(14)	2.20(.18)
O(3)	112(19)	64(7)	65(16)	−11(17)	113(26)	3(17)	3.59(.25)
N	65(18)	19(8)	16(19)	----	−6(40)	----	1.57(.23)
C(1)	44(16)	27(8)	10(17)	18(16)	8(25)	11(16)	1.22(.21)
C(2)	69(16)	37(9)	20(19)	−3(18)	31(28)	11(19)	1.75(.23)
C(3)	121(24)	40(9)	53(21)	−15(25)	18(37)	−9(23)	2.77(.29)
C(4)	111(28)	34(13)	81(32)	----	−49(66)	----	3.23(.40)
W(1)	102(16)	45(7)	85(16)	2(18)	−67(22)	30(16)	3.17(.22)
W(2)	148(19)	60(8)	139(21)	−62(20)	−28(34)	−36(19)	4.54(.28)

Root-Mean-Square Amplitudes of Vibration (0.01A)

	Minimum	*Intermediate*	*Maximum*	*Direction Cosine*[c]			
V	11	14	15	.00	−1.00	.00	Min
O(1)	12	21	29	.00	1.00	.00	Min
O(2)	11	17	21	−.60	.49	.63	Min
O(3)	12	22	26	−.67	−.68	.73	Min
N	10	12	16	−1.00	.00	.10	Max
C(1)	8	12	16	−.53	−.82	−.21	Max
C(2)	9	17	17	−.38	−.18	.91	Min
C(3)	17	17	22	.92	−.27	.27	Max
C(4)	16	18	24	.62	.00	−.78	Max
W(1)	15	19	25	−.52	.28	.81	Max
W(2)	17	26	29	−.58	−.77	−.26	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. Dashes indicate terms constrained to zero by symmetry. [b] The B values given in the last column are those obtained in the final isotropic refinement before refining anisotropically. [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.

Results and Discussion

The Molecular Structure of Vanadyl (IV) 2,6-Lutidinate Tetrahydrate.—Figure 3 shows the atom numbering used in this study (not the conventional numbering of the heterocyclic ring) and also the bond distances; Table IV lists distances and angles with estimated standard deviations. Bond angles are also shown diagrammatically in Figure 4. The molecule possesses effective C_{2v} symmetry; the twofold axis, passing through V, O(1), N, and C(4), is required by the space group symmetry, but the σ_v planes are not. The coordination geometry around the vanadium atom is a distorted octahedron with two V–O (water) distances of 2.027 Å, two V–O (carboxyl) distances of 2.017 Å, a V–N distance of 2.184 Å, and a V–O (vanadyl oxygen) length of 1.591 Å. The two water molecules are in *trans* positions to each other. Some bond lengths and angles which define the vanadium environment in this and other structures are listed in Table V. The vanadyl bond length agrees closely with the corresponding distances found in other structures. The configuration of the five oxygen atoms about the vanadium atom can be described as a distorted trigonal bipyramid similar to that found in the vanadyl *d*-tartrate ion.[4] In the

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[10] 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.

[11] Using $\sqrt{w} = |F_o|/50.0$ when $|F_o| \leq 50.0$ and $\sqrt{w} = 50.0/|F_o|$ when $|F_o| > 50.0$.

[12] The following reflections were obscured by the beam stop: $h = 0$, $k = 0$, $l = 2, 4, 6$. The following observed reflections were inadvertently omitted from the least-squares computations but are properly accounted for as shown by their $|F_o/F_c|$: $(h, k, l|F_o|F_c) = (9, 7, 0|23|31)$, $(9, 7, 1|20|25)$, $(4, 4, 2|66|65)$, $(7, 9, 2|16|21)$, $(9, 2, 2|16|21)$, $(6, 9, 3|14|16)$, $(2, 7, 7|14|16)$, $(5, 6, 7|17|17)$.

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

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

[15] W. C. Hamilton, *ibid.*, **18**, 502 (1965).

Table III

Observed and Calculated Structure Factors[a]

****		L= 0	****	8	0	75	72	3	10	31	30	0	4	91	-104	4	8	108	-104	1	3	34	10	6	3	18	26	3	1	73	-61	0	8	20	12	6	2	19	-18	2	12	60	-54	1	1	108	144
0	2	108	-117	8	2	31	-38	3	11	68	74	0	6	91	86	4	9	21	-19	1	4	107	116	6	4	43	-44	3	2	66	60	0	10	88	-98	6	4	44	46	3	0	29	-27	1	2	10	12
0	4	32	31	8	4	34	35	4	1	16	-7	0	8	110	-113	4	10	59	57	1	5	99	111	6	6	19	17	3	3	59	45	1	1	101	-117	6	8	38	37	3	3	33	28	1	3	66	-78
0	6	288	-372	8	6	55	-62	4	2	85	-71	0	10	69	74	4	12	29	-34	1	6	42	-41	6	8	29	-31	3	5	20	-19	1	2	14	6	6	10	24	-24	3	4	20	16	1	4	10	-14
0	8	108	117	8	8	28	34	4	4	56	49	0	12	35	-40	5	4	27	-19	1	7	107	-115	6	10	58	56	3	6	30	-25	1	3	16	10	7	1	60	-57	3	7	18	13	1	5	87	96
0	12	53	59	8	10	32	-36	4	5	48	-48	1	0	87	-101	5	5	31	-32	1	8	52	-48	7	1	41	40	3	7	45	43	1	4	52	54	7	2	39	-37	3	9	49	-46	1	6	34	34
1	1	109	-110	9	3	28	-31	4	6	19	-15	1	1	107	90	5	6	35	35	1	9	49	45	7	2	37	-36	4	0	289	314	1	5	77	-87	7	3	19	11	3	11	21	24	1	7	102	-112
1	3	26	-29	9	9	32	36	4	7	14	10	1	2	72	-58	5	8	26	-25	1	10	52	-50	7	3	21	-20	4	1	46	-36	1	6	15	17	7	5	63	-67	4	0	125	-121	1	9	14	10
1	9	32	40	10	0	57	72	4	8	23	23	1	3	49	53	5	9	31	-36	1	11	56	-56	7	5	42	43	4	2	94	-94	1	7	116	133	7	7	46	44	4	1	42	37	1	11	64	-60
2	0	126	115	****		L= 1	****	4	9	22	-22	1	4	52	42	5	10	28	33	2	1	54	51	7	7	59	-58	4	3	15	-15	1	9	20	-17	7	9	28	-30	4	2	44	40	2	1	20	-17
1	5	77	-71	0	2	72	84	4	10	77	-84	1	5	35	-33	5	11	25	30	2	2	17	-23	7	8	41	40	4	4	54	51	1	11	69	65	8	7	31	32	4	3	18	-13	2	2	25	19
1	7	31	26	0	4	41	36	4	11	23	26	1	6	36	-38	5	12	27	-27	2	3	62	60	7	9	30	31	4	6	142	-161	1	12	13	-14	9	1	55	-61	4	4	53	-50	2	4	53	-48
2	2	66	-61	0	6	83	87	5	1	174	-171	1	8	44	47	6	0	106	-106	2	4	50	-46	7	10	26	23	4	8	64	66	2	1	38	41	9	3	38	43	4	6	65	65	2	10	71	69
2	4	63	62	0	8	27	-25	5	2	15	13	1	9	60	-57	6	1	41	-35	2	6	35	-29	7	11	34	-35	4	10	32	-28	2	2	45	-41	9	5	46	-48	4	7	21	-21	2	11	20	-16
2	6	68	-60	0	12	44	46	5	3	39	37	1	10	40	-45	6	2	84	79	2	7	30	29	9	1	67	78	4	12	51	51	2	3	84	84	9	7	35	46	4	8	59	-57	3	1	18	12
2	8	118	111	1	1	191	-238	5	4	56	50	1	11	32	34	6	4	37	-35	2	8	18	17	9	3	33	-35	5	1	39	40	2	5	35	-35	****		L= 6	****	4	10	46	45	3	2	36	-34
2	10	78	-80	1	2	89	113	5	5	92	-89	1	12	38	37	6	6	85	82	2	10	51	48	9	5	54	57	5	2	17	16	2	6	29	21	0	2	118	173	4	12	39	-36	3	3	37	-45
2	12	40	44	1	3	185	202	5	7	128	142	2	0	285	-397	6	7	21	25	2	11	49	53	9	7	48	-53	5	3	55	-47	2	7	25	-26	0	4	42	-42	5	1	78	72	3	4	34	-30
3	1	11	5	1	4	32	29	5	10	12	-12	2	1	199	208	6	8	58	-56	2	12	26	-24	****		L= 4	****	5	4	17	-12	2	9	61	-65	0	6	72	77	5	3	24	22	3	5	48	52
3	3	114	-99	1	5	165	-183	5	11	50	49	2	2	65	52	6	10	46	42	3	1	233	251	0	2	21	12	5	5	18	-18	2	10	47	-46	0	8	106	-121	5	5	43	-45	3	7	39	-39
3	5	131	118	1	6	31	24	6	1	14	15	2	3	45	-41	6	12	45	-43	3	2	19	14	0	4	16	10	5	7	28	-31	2	11	20	20	0	10	48	46	5	6	14	-18	3	8	24	24
3	7	54	-46	1	7	105	91	6	3	37	31	2	4	22	-16	7	0	15	-17	3	3	162	-153	0	6	57	-62	5	9	55	59	3	1	185	-173	0	12	28	-30	5	8	14	19	3	9	51	47
3	9	96	98	1	8	28	-20	6	5	15	16	2	5	55	-46	7	1	17	-24	3	5	151	139	0	8	55	57	6	0	47	44	3	2	16	-8	1	0	36	-41	5	9	19	-19	3	10	24	21
3	11	54	-58	1	9	105	-105	6	6	12	15	2	6	193	184	7	2	15	9	3	6	55	-51	0	10	82	-90	6	1	13	11	3	3	108	111	1	1	24	-25	5	10	21	-22	3	11	50	-47
4	0	41	35	1	11	34	30	6	8	37	-37	2	7	57	-51	7	4	46	45	3	7	141	-131	0	12	70	67	6	2	16	-5	3	4	16	-8	1	2	24	-31	5	11	29	24	4	2	51	48
4	2	83	-60	2	1	32	-33	6	9	12	-19	2	8	92	-87	7	7	21	24	3	8	43	-40	1	0	18	11	6	4	16	13	3	5	124	-125	1	3	26	-22	5	12	22	23	4	3	22	-21
4	4	17	9	2	2	106	-105	6	10	50	-47	2	9	37	34	7	10	34	-35	3	9	60	59	1	1	9	9	6	6	44	-45	3	7	81	88	1	5	27	-29	6	0	162	-159	4	4	28	-24
4	6	76	-69	2	3	73	-62	7	1	99	-99	2	10	46	51	8	0	78	-81	3	10	22	-20	1	3	29	-33	6	8	53	55	3	8	26	25	1	6	50	51	6	1	18	-15	4	7	17	17
4	8	74	75	2	4	78	69	7	2	35	32	2	11	27	28	8	1	20	-24	3	11	35	-30	1	4	55	53	6	10	46	-48	3	9	41	-41	1	7	13	11	6	2	31	21	4	8	58	-53
4	10	63	-70	2	5	41	46	7	3	72	79	2	12	64	-59	8	2	43	46	4	1	29	-26	1	5	73	77	6	12	38	40	3	10	36	34	1	8	14	-16	6	4	35	-32	4	9	16	-16
4	12	44	48	2	6	17	19	7	5	72	-72	3	1	22	-20	8	3	20	-21	4	2	13	-12	1	6	12	12	7	0	43	-36	3	11	40	38	1	9	15	-20	6	6	100	83	4	10	28	21
5	1	26	22	2	7	20	-19	7	7	74	77	3	2	31	-29	8	4	24	-26	4	3	37	-31	1	7	42	-43	7	1	37	-34	3	12	17	20	1	10	21	26	6	8	54	-48	5	1	92	102
5	3	75	59	2	8	57	55	7	8	24	-26	3	4	74	-65	8	6	60	57	4	4	23	-14	1	9	47	53	7	2	36	-29	4	1	19	-21	1	11	21	26	6	10	30	31	5	2	17	16
5	5	37	29	2	9	17	20	7	9	17	-22	3	5	20	-5	8	8	49	-48	4	6	32	-25	1	10	17	-13	7	3	21	-23	4	3	53	-53	1	12	38	-34	7	0	25	22	5	3	23	-11
5	7	24	-21	2	10	64	-62	8	2	15	-21	3	6	38	-33	8	10	29	29	4	8	28	25	1	11	41	-43	7	5	49	55	4	4	37	32	2	0	134	-145	7	10	13	22	5	4	33	33
5	9	14	-10	2	11	58	-60	8	3	17	-17	3	7	30	28	9	0	34	32	4	9	60	58	2	0	206	217	7	9	29	32	4	6	28	27	2	1	60	-52	8	0	60	-51	5	5	78	79
5	11	21	-24	2	12	24	26	8	4	21	17	3	8	29	23	9	1	23	27	4	10	35	38	2	1	82	-80	8	0	88	90	4	10	27	-28	2	2	83	85	8	2	59	51	5	7	64	-61
6	0	172	150	3	1	50	-48	8	9	30	33	3	9	28	-33	9	5	20	-23	5	1	68	62	2	2	191	-192	8	1	37	36	4	11	35	-34	2	3	47	47	8	4	51	-49	5	9	49	45
6	2	201	-185	3	2	144	-126	8	10	29	-34	3	10	19	19	10	0	54	-63	5	2	35	27	2	3	47	-42	8	2	47	-51	4	12	28	25	2	4	49	-48	8	5	24	-27	6	1	14	15
6	4	83	82	3	3	58	-33	9	1	19	-19	3	11	19	19	****		L= 3	****	5	3	71	-74	2	4	87	92	8	4	33	31	5	1	50	-41	2	5	26	24	8	6	39	35	6	6	31	-29
6	6	87	-88	3	4	99	-82	9	3	28	32	4	0	130	-117	0	2	160	239	5	5	94	94	2	6	87	-97	8	6	57	-53	5	2	32	29	2	6	103	103	8	8	36	-33	6	7	12	-12
6	8	86	84	3	5	92	-95	9	5	39	-38	4	1	30	26	0	4	48	-49	5	7	59	-55	2	7	35	34	8	8	48	46	5	3	83	77	2	7	31	35	****		L= 7	****	7	1	68	64
6	10	34	-35	3	6	39	37	9	6	23	4	4	2	156	150	0	8	112	-110	5	8	26	-23	2	8	103	115	10	0	45	49	5	5	66	-64	2	8	55	-55	0	2	27	-36	7	3	77	-69
7	3	18	20	3	7	100	102	9	9	29	-40	4	3	75	56	0	10	88	86	5	9	36	36	2	10	50	-51	****		L= 5	****	5	7	38	33	2	9	24	-25	0	4	11	9	7	5	68	66
7	7	16	23	3	8	71	63	****		L= 2	****	4	5	24	-17	1	1	95	-107	5	11	68	-66	2	12	27	29	0	4	77	87	5	9	73	-75	2	10	55	49	0	8	58	63	7	7	35	-27
7	9	10	11	3	9	33	-33	0	2	96	112	4	6	87	75	1	2	98	85	6	2	42	43	3	0	112	106	0	6	38	-34	5	11	24	27	2	11	14	-19	0	10	39	38	7	9	36	43

[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. For other information, see footnote 12.

Table IV

Interatomic Distances and Angles for Vanadyl(IV) 2,6-Lutidinate Tetrahydrate[a,b]

Distances (A)

V–O(1)	1.591(.011)	C(2)–C(1)	1.533(.018)
V–W(1)	2.027(.012)	C(2)–O(3)	1.235(.018)
V–O(2)	2.017(.010)	C(1)–N	1.291(.014)
V–N	2.184(.012)	C(1)–C(3)	1.391(.017)
C(2)–O(2)	1.261(.014)	C(3)–C(4)	1.417(.018)

Angles (deg)[c]

O(1)–V–O(2)	107.4(.3)	O(2)–C(2)–C(1)	113.2(.6)
O(1)–V–W(1)	96.0(.3)	O(3)–C(2)–C(1)	121.8(1.2)
W(1)–V–O(2′)	88.3(.4)	C(2)–C(1)–C(3)	126.2(.8)
W(1)–V–O(2)	88.0(.4)	N–C(1)–C(3)	123.0(1.2)
W(1)–V–W(1′)	168.0(.3)	C(2)–C(1)–N	110.8(1.0)
O(2)–V–O(2′)	145.2(.3)	C(1)–C(3)–C(4)	114.8(1.1)
W(1)–V–N	84.0(.3)	C(3)–C(4)–C(3′)	121.8(1.0)
O(2)–V–N	72.6(.3)	C(1)–N–V	118.7(.5)
V–O(2)–C(2)	124.6(.7)	C(1)–N–C(1′)	122.7(.8)
O(2)–C(2)–O(3)	124.9(.8)		

[a] Bond lengths are given to three decimal places to avoid the rounding error, although the estimated standard deviations are at least ten parts in the last place. [b] Standard deviations given in parentheses. [c] The primed atoms are those related to the unprimed by the twofold molecular symmetry.

present structure, however, the distortion of the four quasi-equatorial oxygen atoms from the "ideal" equatorial plane is less severe than in the above-mentioned d-tartrate complex. The tridentate mode of chelation for the 2,6-lutidinate moiety results in some large distortions in bond angles at the ring carbon atoms which are bonded to the carboxylate groups. The NC(1)C(2) angle is 110.8° and the C(3)C(1)C(2) angle is 126.2°.

The planes (best by an equal weight least-squares criterion) through various groups of atoms are given in Table VI. The question of how close the molecule approaches C_{2v} symmetry is quite important in the subsequent interpretation of the crystal spectra. The plane containing the vanadyl oxygen atom and the two chelating carboxyl oxygen atoms, the best plane through the chelate ring atoms, and the best plane through the pyridine ring correspond within 1.5° (Figure 5). Looking down the vanadyl axis, one sees that the planes containing O(1), O(2), O(2′) and O(1), W(1), W(1′) are almost perpendicular. Thus, since the amount of "twist" is at most 1.5°, there is very nearly a vertical

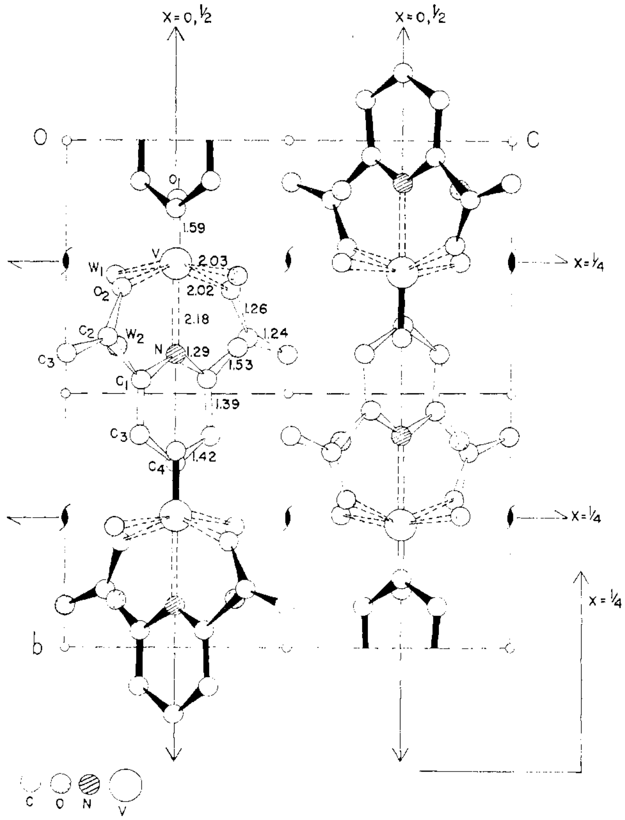

Figure 3.—Molecular packing diagram (as viewed along the a axis) showing the atom numbering used in this study (not the conventional numbering of the heterocyclic ring) and also the principal bond distances. See Table IV for a full listing of interatomic distances with estimated standard deviations.

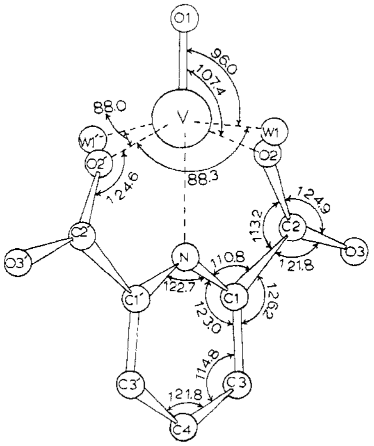

Figure 4.—$VOC_7H_3O_4N \cdot 2H_2O$ molecular unit with atom designations and bond angles. See Table IV for estimated standard deviations.

TABLE V

COMPARISON OF VANADIUM ENVIRONMENTS IN VANADYL(IV) 2,6-LUTIDINATE TETRAHYDRATE AND TWO OTHER VANADYL(IV) COMPOUNDS[a,b]

	VO 2,6-lutidinate	Na_4[VO *dl*-Tart][b]	$(NH_4)_4$[VO *dd*-Tart]$_2$[c]
	V–O Bond Lengths (A)		
Vanadyl Oxygen	1.591(.011)	1.619(.007)	1.60(.02)
Ligand Oxygens[d]	2.017(.012)	2.004(.006)	2.01(.02)
	2.017(.012)	1.994(.006)	2.03(.02)
	2.027(.010)	1.917(.006)	1.93(.02)
	2.027(.010)	1.902(.006)	1.79(.02)
	Vanadyl Oxygen–V–Ligand Oxygen Angles (deg)		
	107.4(.3)	109.8(.3)	99.2(.8)
	107.4(.3)	104.8(.3)	98.8(.8)
	96.0(.3)	104.8(.3)	122.1(.8)
	96.0(.3)	106.2(.3)	114.6(.8)

[a] Estimated standard deviations are in parentheses. Distances and angles involving equivalent atoms are grouped together. [b] A more complete table of comparison between the tartrates and other vanadyl species is given by R. E. Tapscott, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, **7**, 356 (1968). [c] J. G. Forrest and C. K. Prout, *J. Chem. Soc., A*, 1312 (1967). [d] The first two ligand oxygen atoms listed in both the bond length and angle tables above are carboxyl oxygen atoms. The other two are water molecules and hydroxyl oxygen atoms for the lutidinate and tartrate complexes, respectively.

TABLE VI

BEST PLANES THROUGH GROUPS OF ATOMS WITH DEVIATIONS (DISTANCES TO PLANE, Å)[a]

Plane 1	$.7217X + .0359Y + .6913Z = 2.077$ A							
Atoms:	O(3)	C(1)	O(2)	C(2)				
Deviations:	−.004	−.003	−.003	.010				
Plane 2	$.7096X + .0000Y + .7046Z = 1.893$ A							
Atoms:	N	C(1)	C(1')	C(3)	C(3')	C(4)		
Deviations:	.000	−.012	.012	.011	−.011	.000		
Plane 3	$.7012X + .0000Y + .7130Z = 1.915$ A							
Atoms:[b]	V	O(2)	O(2')	C(2)	C(2')	C(1)	C(1')	N
Deviations:	.000	.029	−.029	−.013	.013	−.026	.026	.000
Plane 4	$.6905X + .0000Y + .7234Z = 1.943$ A							
Atoms:[c]	O(1)	O(2)	O(2')					

[a] The X,Y,Z-axis system is the orthonormal system defined by $(X, Y, Z) = (xa, yb, zc)$. [b] Deviations of atoms C(3) and O(3), not used in defining plane 3, are −0.004 and −0.075, respectively. [c] Deviations of atoms C(2), C(1), C(3), and O(3), not used in defining plane 4, are −0.047, −0.043, −0.022, and −0.126, respectively.

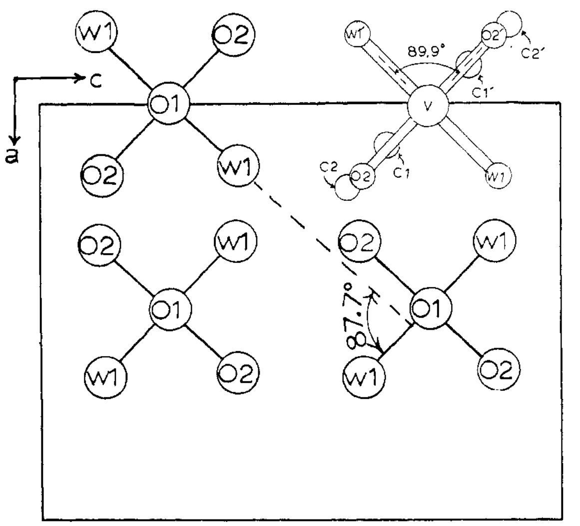

Figure 5.—View down the b axis (i) showing that any electric vector makes nearly equal projections on the two equatorial molecular axes and (ii) indicating (in the upper right-hand molecule) the approach to molecular C_{2v} symmetry.

reflection plane giving the molecule C_{2v} symmetry (see also Table VI, footnote c).

Table II contains the lengths of the axes of the rms thermal ellipsoids together with the direction cosines of the most nearly unique axis. This table and Figure 6 reveal that most atoms are vibrating roughly perpendicular to chemical bonds. This result is to be expected and helps to reinforce our belief that anisotropic refinement was justified. The only thermal ellipsoids strongly at variance with the foregoing statement are associated with the oxygen atoms of the uncoordinated water molecules. However, as the hydrogen atoms were omitted from our analysis and the probable hydrogen-bonding network is only a hypothesis, the expected thermal vibrations of these oxygen atoms are uncertain.

Molecular Packing and Hydrogen Bonding.—Figure 3 is a packing diagram which shows the unit cell, as viewed along the a axis, with the bond lengths. Figure 6 is a stereoscopic projection of the unit cell, viewed along the c axis, which clearly shows our proposed hydrogen-bonding scheme. The molecules lie along twofold rotation axes (the C(4)–N–V–O(1) lines) parallel to the b axis. In our proposed hydrogen-bonding scheme, the molecules in the crystal are joined by a network in which each water is at the apex of a flattened trigonal pyramid. Table VII contains the pertinent bond distances and angles, with standard deviations. We assume that each coordinated water molecule forms two hydrogen bonds to proton acceptors. There are only two possible acceptors (a noncoordinated carbonyl oxygen, O(3), of another molecule, and a water of hydration, W(2)) at reasonable distances and making reasonable angles about W(1). For the same reason, the two hydrogen-donor bonds from W(2) must link uncoordinated oxygen atoms (O(3)) on different molecules. Thus, the carbonyl bond and the three hydrogen-bonding linkages ascribed to O(3) form an approxi-

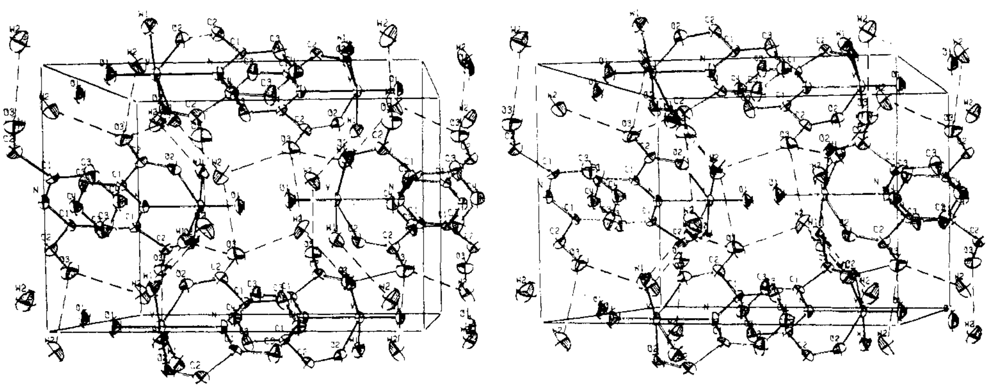

Figure 6.—Stereoscopic view of $VOC_7H_9O_4N \cdot 4H_2O$ with atom designations. The view is along [00$\bar{1}$], [0$\bar{1}$0] is to the right, and [100] is toward the top of the paper. The hydrogen bonds are depicted as broken lines. All other chemical bonds are shown as thicker cylindrical bonds. This figure is best viewed with the aid of a simple stereoviewer such as an aerial map reader. This figure was 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 VII

BOND ANGLES AND LENGTHS FOR PROPOSED HYDROGEN-BONDING SCHEME[a,b]

Distances (A)

$W(1)_1 \rightarrow W(2)_1$	2.645(.015)	$W(2)_1 \rightarrow O(3)_3$	2.864(.016)
$W(1)_1 \rightarrow O(3)_2$	2.711(.015)	$W(2)_1 \rightarrow O(3)_4$	3.129(.016)

Angles (deg)

$W(2)_1-W(1)_1-O(3)_2$	115.8(.6)	$C(2)_1-O(3)_1-W(1)_5$	104.2(1.0)
$W(2)_1-W(1)_1-V$	123.1(.6)	$C(2)_1-O(3)_1-W(2)_3$	145.9(.8)
$O(3)_2-W(1)_1-V$	115.1(.5)	$C(2)_1-O(3)_1-W(2)_6$	108.7(.9)
$W(1)_1-W(2)_1-O(3)_4$	135.5(.6)	$W(1)_5-O(3)_1-W(2)_3$	106.7(.3)
$W(1)_1-W(2)_1-O(3)_3$	104.0(.6)	$W(1)_5-O(3)_1-W(2)_6$	89.2(.4)
$O(3)-W(2)_1-O(3)_4$	92.8(.4)	$W(2)_3-O(3)_1-W(2)_6$	86.1(.5)

[a] Standard deviations are given in parentheses. Since the hydrogen-bonding scheme connects atoms of different molecules, refer to the text and figures for identification. [b] The subscripts 1, 2, 3, 4, 5, and 6 indicate that if Table I gives the position of the designated atom as (x, y, z), the position of the specific atom designated here is (x, y, z), ($x - 1/2$, $1/2 - y$, $-z$), ($-x$, $1 - y$, $-z$), ($x - 1$, y, z), ($1/2 + x$, $1/2 - y$, $-z$), and ($1 + x$, y, z), respectively.

mate tetrahedron (see Table VII). One of the postulated hydrogen bonds appears to be relatively long[16] (3.12 Å) and thus weak.

Spectral Properties.—The spectra of the two forms of vanadyl(IV) 2,6-lutidinate (Figure 1) are similar except that the spectrum of the blue form is shifted to higher energy and the 15-kK band in the green compound is not observed; it is perhaps buried under one of the other shifted bands. Four bands in all are evident in the green lutidinate crystal spectrum, ~11.2, 13.5, 15, and 27 kK. As in the low-symmetry vanadyl(IV) α-hydroxycarboxylates, the first band appears at an unusually low energy; in most vanadyl(IV) compounds, the first strong band occurs in the 12–14-kK range. For example, the first band lies at 11.2 kK in the case of ammonium vanadyl(IV) *d*-tartrate.[2] The remaining spectral bands of the *d*-tartrate complex are at 16.8, 18.9, and 25.0 kK. The oriented crystal spectra of the vanadyl(IV) 2,6-lutidinates and the ammonium vanadyl(IV) *d*-tartrate are currently under investigation in this laboratory. One problem in interpreting spectral data on the lutidinate is evident from the structure reported here. It appears that it will not be possible to detect equatorial molecular anisotropy in optical absorption, since (as seen in Figure 5) the relative orientation of neighboring molecules is such that any electric vector will have nearly equal projections on the molecular x and y axes. However, the b spectrum gives clearly the molecular z spectrum (parallel to VO), and any spectrum perpendicular to b is a perpendicular spectrum. Thus, this study offers the attractive possibility of assisting in the interpretation of the spectra of both high- and low-symmetry complexes of vanadyl(IV) by providing polarized crystal spectra of a compound of intermediate symmetry.

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(16) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, pp 278–280.