Stereochemistry of Dioxovanadium(V) Complexes. III. The Crystal and Molecular Structures of Trisodium (Ethylenediaminetetraacetato)dioxovanadate(V) Tetrahydrate[1]

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Received November 3, 1970

Abstract: A quantitative stereochemical description of the complex anion formed by the reaction of the VO_2^+ and ethylenediaminetetraacetate (A^{4-}) ions comes from determination by X-ray analysis of the atomic arrangement in the crystalline salt $Na_3[VO_2A]\cdot 4H_2O$. The VO_2 moiety is in the cis configuration with an OVO angle of 107.0° and V–O distances of 1.639 (2) and 1.657 (1) Å. Octahedral coordination around the vanadium atom is completed with two carboxylate oxygen atoms at 2.00 Å and, trans to the oxo ligands, the two nitrogen atoms at 2.36 Å. The anion, with two uncomplexed glycinate arms, approximates closely to C_2 symmetry. The unit cell of the monoclinic crystals contains $4Na_3[VO_2A]\cdot 4H_2O$, with $a = 10.593$, $b = 12.447$, $c = 15.003$ Å, and $\beta = 105.1°$. Calculated and measured densities are 1.78 and 1.75 g $(cm^3)^{-1}$, respectively. The space group is $P2_1/c$. The intensities of 7135 independent reflections having $(\sin\theta)/\lambda \lesssim 0.764$ Å^{-1} were measured with Mo Kα radiation by the θ–2θ scanning technique on an automated Picker four-circle diffractometer; the 6266 data retained as observable were employed for structure determination and anisotropic least-squares refinement to a conventional R of 0.048.

The genesis of our structural studies of the complexes formed by the VO_2^+ cation is set forth in the first paper of this series.[2] We report herein the crystal structure and molecular stereochemistry of trisodium (ethylenediaminetetraacetato)dioxovanadate(V) tetrahydrate ($Na_3[VO_2A]\cdot 4H_2O$).

Experimental Section

Crystalline $Na_3[VO_2A]\cdot 4H_2O$ was prepared according to the directions of Przyborowski, *et al.*[3] Specimens suitable for X-ray analysis were crystallized from aqueous solution. Preliminary X-ray examination of the crystals using precession and Weissenberg techniques, supported by a negative test for piezoelectricity, led us to the unique choice of $P2_1/c$ as the space group.[4] Angular settings for 38 reflections, distributed equally between $+2\theta$ and -2θ, were obtained from the automatic centering routine supplied with the computer-controlled four-circle diffractometer; the resolved Mo Kα_1 (λ 0.70926 Å) component was used. All measurements were made at the ambient laboratory temperature of 20 ± 1°. Least-squares refinement[5] of the setting angles gave the lattice constants $a = 10.593\,(2)$, $b = 12.477\,(2)$, $c = 15.003\,(2)$ Å, $\cos\beta = -0.2605\,(2)$, or $\beta = 105.10°$. The experimental density of 1.75 g/cm^3, determined by flotation in bromoform–chloroform, is to be compared with the calculated density of 1.78 g/cm^3 for four $Na_3[VO_2A]\cdot 4H_2O$ molecules per unit cell.

Intensity data were collected with Zr-filtered Mo Kα radiation using a takeoff angle of 1.5° on a computer-controlled four-circle diffractometer. The sample crystal with dimensions 0.26 × 0.40 × 0.40 mm was cut from a larger plate and was mounted so that the two large dimensions were roughly parallel and perpendicular to the φ axis; 7135 independent reflections for which $(\sin\theta)/\lambda \lesssim 0.764$ Å^{-1} were scanned by the θ–2θ technique. Each scan included a variable increment in angle above the minimum (1.8° at $2\theta = 0$) to allow for spectral dispersion and was taken at the rate of 1.0°/min. Background corrections were estimated as the average of two 40 sec counts taken at the limits of the scan. The intensity of three standard reflections, checked every 100 reflections, remained essentially constant throughout the data collection process. The intensity data were reduced to a set of relative squared amplitudes, $|F_o|^2$, by application of the standard Lorentz and polarization factors. The criterion previously specified[6] for retaining data as objectively observed was again employed; 6266 independent reflections thus retained were used for the determination and least-squares refinement of the structure. With a linear absorption correction for Mo Kα radiation of 0.70 mm^{-1} and the cited dimensions and mounting of the crystal, the maximum error in any amplitude was calculated to be <4%; thus no corrections for absorption were made.

The position of the vanadium atom in the asymmetric unit of structure was deduced from a three-dimensional Patterson synthesis, and the remaining atoms were located during successive cycles of Fourier synthesis. The structure was then refined by full-matrix least-squares[7] using the inner 3000 data with isotropic thermal parameters. At this point, the position of the centroids of electron density were determined by the objective evaluation[8] of the peak positions of the Fourier synthesis using all of the observed data; the usually, but not invariably, trivial corrections for nonconvergence of the Fourier series were included. Least-squares refinement was then continued holding the atomic coordinates constant while refining the thermal parameters of the sodium and vanadium atoms anisotropically, and those of the light atoms isotropically. The amplitudes for 11 data found to be grossly in error owing to teletypewriter/puncher malfunctions were corrected. A Fourier difference synthesis then gave approximate positions for all hydrogen atoms in the chelate and for most of those in the water molecules as well. These hydrogen atoms were included in the subsequent refinement and structure factor calculations, with fixed positions and isotropic thermal parameters taken from those of the associated atoms. The apparent C–H distances ranged from 0.84 to 1.15 Å with an average value of 0.96 Å, and the apparent O–H distances lay between 0.91 and 1.05 Å. Block-diagonal least-squares refinement[9] of positional and aniso-

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(1) This investigation was supported in part by National Science Foundation Grant No. GP-6710X, Grant No. 2-RO1-GM09370 from the National Institutes of Health, General Medical Sciences, and by the Advanced Research Projects Agency.

(2) W. Robert Scheidt, C. Tsai, and J. L. Hoard, *J. Amer. Chem. Soc.*, **93**, 3867 (1971).

(3) L. Przyborowski, G. Schwarzenbach, and Th. Zimmerman, *Helv. Chim. Acta*, 48, 1556 (1965).

(4) "International Tables for X-ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965, pp 98–99.

(5) Use was made of the PICK-II computer program, a revision in this laboratory of W. C. Hamilton's MODE I program.

(6) W. R. Scheidt, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, **93**, 3873 (1971).

(7) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(8) (a) D. P. Shoemaker, J. Donohue, V. Shomaker, and R. B. Corey, *J. Amer. Chem. Soc.*, 72, 2328 (1950). Evaluation of a peak position utilized the least-squares fitting of a gaussian to 27 grid points immediately surrounding the peak. (b) See also D. M. Collins and J. L. Hoard, *ibid.*, **92**, 3761 (1970).

(9) The block-diagonal program REFINE, written by J. J. Park in this laboratory, was employed. Atomic form factors were from D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968),

tropic thermal parameters for all atoms (except that hydrogen contributions were handled as specified above) was then carried to convergence. Empirical weights ($w = 1/\sigma^2$) calculated by procedures described earlier[6] were employed. The final value of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.048, and that of $R_2 = [\Sigma w(|F_o| - |F_c|)^2]^{1/2}/(\Sigma w F_o^2)^{1/2}$ was 0.079; the estimated standard deviation of an observation of unit weight was 1.14, and the final parameter shifts were less than 10% of their estimated standard deviations during the last cycle.[10] The corresponding Fourier difference synthesis displayed no peak value larger than 5% of that observed for a carbon atom. A careful reevaluation of the peak positions in the Fourier synthesis of the 6266 independent F_o coefficients, with corrections (where needed) for finite termination of series, gave positional coordinates that generally were not significantly different from those obtained by least-squares refinement. Of interest, nevertheless, was any pattern of variation in the values of the V–O bond lengths within the VO_2 moiety (*vide infra*).

The coordinates and the associated thermal parameters for the atoms in the asymmetric unit of structure as derived from the least-squares refinement are listed in Tables I and II, respectively. Approximate positions for the hydrogen atoms are given in Table III.

Table I. Atomic Coordinates in Crystalline $Na_3VO_2A \cdot 4H_2O$[a]

Atom	10^4x	10^4y	10^4z
O_2	1106 (1)	3028 (1)	1961 (1)
O_1	3289 (2)	3435 (2)	3251 (1)
O_3	1233 (2)	2947 (1)	3865 (1)
O_4	−315 (2)	2278 (2)	4450 (1)
O_5	−1004 (2)	4644 (1)	581 (1)
O_6	−2311 (2)	3658 (2)	1185 (1)
O_7	3091 (2)	6502 (2)	1981 (1)
O_8	1944 (2)	5043 (1)	2096 (1)
O_9	3409 (2)	6624 (1)	5492 (1)
O_{10}	3722 (2)	5193 (2)	6403 (1)
N_1	−302 (2)	4462 (1)	2946 (1)
N_2	2267 (2)	5269 (1)	3888 (1)
C_1	27 (2)	2846 (2)	3888 (1)
C_2	−959 (2)	3478 (2)	3160 (1)
C_3	−1091 (2)	5047 (2)	2124 (1)
C_4	−1485 (2)	4387 (2)	1233 (1)
C_5	−82 (2)	5188 (2)	3760 (1)
C_6	1077 (2)	5917 (2)	3829 (1)
C_7	3197 (2)	5861 (2)	3493 (1)
C_8	2722 (2)	5822 (2)	2446 (1)
C_9	2878 (2)	4855 (2)	4830 (1)
C_{10}	3365 (2)	5644 (2)	5623 (1)
W_1[b]	4519 (2)	9026 (2)	3159 (2)
W_2[b]	3093 (3)	3404 (2)	178 (2)
W_3[b]	3527 (2)	1917 (2)	1742 (2)
W_4[b]	4906 (3)	6107 (2)	823 (2)
	10^5x	10^5y	10^5z
V	17493 (3)	37830 (3)	28760 (2)
Na_1	10577 (10)	40244 (9)	5028 (7)
Na_2	25256 (11)	66786 (8)	3818 (7)
Na_3	48824 (11)	75778 (10)	19587 (8)

[a] Figures in parentheses are the estimated standard deviations in the last significant figure. [b] Symbols used for water molecules.

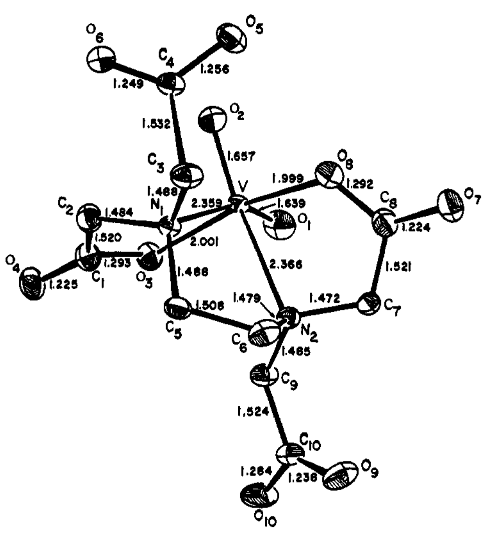

Figure 1. Model in perspective of the complex anion carrying the pertinent bond distances (Å). Atoms are represented as ellipsoids having the shapes and relative sizes concomitant with the data of Table II.

Discussion

The configuration established for the $[O_2VA]^{3-}$ ion, illustrated in Figure 1,[11] is so very similar to that of the related $[O_2VAH_2]^-$ anion in crystalline $NH_4[O_2VAH_2] \cdot 3H_2O$[6] that the larger part of the earlier discussion carries over with no significant alteration. Parameters[12] of the coordination octahedron and of the chelated framework in the $[O_2VA]^{3-}$ ion are listed in Tables IV and V, respectively. Comparison of these data with those given in paper II[6] shows that the one evidently significant difference in bonding parameters between the $[O_2VA]^{3-}$ and $[O_2VAH_2]^-$ ions is confined to the respective carboxylate and carboxylic acid groups of the uncomplexed glycinate and glycine residues. Thus the four C–O distances in the uncomplexed carboxylate groups of the $[O_2VA]^{3-}$ species average to 1.252 (8, 3) Å,[13] whereas the C–O distances to the protonated and unprotonated oxygen atoms in the uncomplexed arms of the $[O_2VAH_2]^-$ species carry averaged values of 1.321 (6, 4), and 1.207 (4, 4) Å.[6]

The $[O_2VA]^{3-}$ and $[O_2VAH_2]^-$ anions utilize the same basic configuration of quasi-C_2 symmetry and the amount of ring folding and/or kinking is comparable in the two species. The sums of the interior ring angles in the $[O_2VA]^{3-}$ anion are 520.9 and 521.2° in the glycinato rings and 515.0° in the ethylenediamine ring. All carboxylate groups are planar within the precision of the measurements. Averaged lengths of standard types of bonds, C–N = 1.483 (5, 2) Å,[13] C–C = 1.524 (4, 3) Å in glycinato rings, and 1.508 (3) Å in the ethylenediamine ring, closely parallel the analo-

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with corrections for anomalous dispersion in the vanadium form factor from D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(10) A table of observed and calculated structure amplitudes from this analysis has been deposited as Document No. NAPS-01309 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $5.00 for photoprints or $2.00 for microfiche. Advance payment is required. Make checks or money orders payable to: CCMIC–NAPS.

(11) C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustration," ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(12) Estimated standard deviations in these bond lengths and angles were calculated following W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(13) The first of the figures in parentheses is the mean deviation from the average; the second is the root-mean-square value of the standard deviation for the individual datum.

Table II. Thermal Parameters[a]

Atom type	Anisotropic parameters, Å^2 B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B, Å$^{2\,b}$
V	1.43 (1)	1.42 (1)	1.24 (1)	0.20 (1)	0.58 (1)	−0.10 (1)	1.28
O_2	2.71 (7)	2.32 (6)	2.15 (6)	−0.25 (5)	0.57 (5)	−0.54 (5)	2.34
O_1	2.02 (6)	2.91 (7)	2.70 (7)	0.55 (5)	0.79 (5)	−0.29 (5)	2.40
Na_1	2.36 (4)	2.76 (4)	2.21 (3)	0.21 (3)	0.84 (3)	0.36 (3)	2.35
Na_2	3.10 (4)	2.32 (4)	1.57 (3)	−0.38 (3)	0.25 (3)	−0.22 (3)	2.26
Na_3	2.11 (4)	3.32 (5)	3.02 (4)	−0.73 (3)	0.44 (3)	0.66 (4)	2.66
N_1	1.44 (5)	1.61 (5)	1.21 (5)	−0.05 (4)	0.35 (4)	−0.02 (4)	1.44
N_2	1.60 (5)	1.78 (6)	1.34 (5)	−0.03 (4)	0.41 (4)	−0.00 (4)	1.56
O_3	1.94 (5)	2.15 (5)	2.11 (5)	0.26 (4)	0.61 (4)	0.48 (4)	2.01
O_4	2.76 (7)	3.15 (8)	2.57 (7)	−0.16 (6)	0.83 (5)	1.20 (6)	2.57
O_5	2.43 (6)	2.62 (6)	1.56 (5)	−0.07 (5)	0.86 (4)	0.12 (4)	2.04
O_6	3.26 (8)	3.65 (8)	1.81 (6)	−1.59 (7)	0.75 (5)	−0.57 (5)	2.53
O_7	2.79 (7)	3.16 (7)	2.12 (6)	−0.83 (6)	0.74 (5)	0.55 (5)	2.47
O_8	2.30 (6)	2.35 (6)	1.50 (5)	−0.39 (5)	0.54 (4)	0.04 (4)	1.98
O_9	3.31 (8)	1.86 (6)	2.41 (6)	0.06 (5)	0.22 (6)	−0.40 (5)	2.48
O_{10}	4.16 (9)	3.02 (7)	1.48 (5)	0.37 (7)	0.20 (5)	0.04 (5)	2.70
C_1	2.07 (7)	1.73 (6)	1.80 (6)	−0.08 (5)	0.56 (5)	0.25 (5)	1.83
C_2	1.68 (6)	2.00 (7)	1.82 (6)	−0.18 (5)	0.55 (5)	0.26 (5)	1.79
C_3	2.13 (7)	2.00 (7)	1.44 (6)	0.11 (6)	0.20 (5)	−0.05 (5)	1.86
C_4	1.79 (6)	2.07 (7)	1.19 (5)	−0.02 (5)	0.29 (5)	0.05 (5)	1.66
C_5	1.87 (6)	2.08 (7)	1.35 (6)	0.05 (5)	0.59 (5)	−0.34 (5)	1.66
C_6	1.86 (7)	1.52 (6)	1.70 (6)	0.07 (5)	0.20 (5)	−0.31 (5)	1.70
C_7	1.81 (7)	2.44 (8)	1.54 (6)	−0.55 (6)	0.40 (5)	−0.12 (6)	1.86
C_8	1.60 (6)	2.16 (7)	1.69 (6)	−0.03 (5)	0.50 (5)	0.23 (5)	1.78
C_9	2.16 (7)	1.88 (7)	1.21 (6)	0.10 (5)	0.16 (5)	−0.01 (5)	1.73
C_{10}	1.71 (6)	2.09 (7)	1.55 (6)	0.25 (5)	0.22 (5)	−0.38 (5)	1.75
W_1	3.11 (9)	4.78 (11)	3.66 (9)	0.42 (8)	0.97 (7)	0.94 (8)	3.70
W_2	3.60 (10)	4.69 (12)	4.40 (11)	0.65 (9)	1.17 (8)	0.72 (9)	4.12
W_3	3.61 (9)	3.46 (9)	3.75 (9)	−0.04 (7)	0.81 (7)	−1.18 (7)	3.49
W_4	4.14 (11)	4.12 (11)	4.26 (11)	0.73 (9)	1.63 (9)	0.31 (8)	4.00

[a] The number in parentheses that follows each B_{ij} value is the estimated standard deviation in the last significant figure. The B_{ij}'s (Å^2) are related to the dimensionless β_{ij}'s employed during refinement as $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$. [b] Isotropic thermal parameter calculated from $B = 4[V^2\det(\beta_{ij})]^{1/3}$.

Table III. Hydrogen Atom Parameters

Atom[a]	10^3x	10^3y	10^3z
H_1C_1	−121	301	259
H_2C_1	−166	355	342
H_1C_3	−56	564	198
H_2C_3	−158	512	224
H_1C_5	10	477	422
H_2C_5	−79	558	372
H_1C_6	122	632	439
H_2C_6	83	632	334
H_1C_7	338	657	376
H_2C_7	415	539	378
H_1C_9	209	446	499
H_2C_9	361	450	467
H_1W_1	398	927	257
H_2W_1	385	878	337
H_1W_2	352	301	68
H_2W_2	243	297	−35
H_1W_4	498	555	123

[a] The notation specifies the carbon atom (C_i) or the water molecule (W_i) with which the hydrogen atom is associated.

gous data from the $[O_2VAH_2]^-$ species. C–O bond lengths in the coordinated carboxylate groups of $[O_2VA]^{3-}$, 1.293 (1, 2)[13] and 1.224 (1, 2) Å to complexed and uncomplexed oxygen atoms, respectively, are indicative of bonding interactions quite as strong as those in the $[O_2VAH_2]^-$ anion.

The VO_2 moiety takes the same bent configuration as in both the $[O_2VAH_2]^-$ and the $[O_2V(ox)_2]^{3-}$ complexes, with an OVO angle of 106.96 (8)°. Bond lengths of V–O_1 = 1.639 (2) and V–O_2 = 1.657 (1) Å from the least-squares refinement are to be compared with the respective values of 1.647 and 1.655 Å from the Fourier synthesis, with the 1.623 (2) and 1.657 (2) Å in the $[O_2VAH_2]^-$ ion, and with the 1.635 (2) and 1.648 (2) Å in the $[O_2V(ox)_2]^{3-}$ species.[2] The objectively assigned standard deviations suggest that a difference $\gtrsim$0.009 Å between any two of the V–O bond lengths should be highly significant; in these terms the least-squares values of V–O_1 and V–O_2 are objectively different within each of the three complexes as these exist in the crystals—their otherwise close approximations to C_2 symmetry notwithstanding. Lacking any obvious basis in electronic theory for anticipating a nearly trivial nonequivalence of the V–O_1 and V–O_2 bonds in the unconstrained complexes, we might ascribe the small differences observed in the crystals to interactions with the asymmetric environments. None of the crystalline arrangements, however, displays a clearly satisfactory correlation of asymmetric interactions with differences in the V–O_1 and V–O_2 bond lengths; the absence of such correlation is most striking for the $[O_2VAH_2]^-$ ion wherein the V–O_1 and V–O_2 distances exhibit the largest apparent difference, 0.034 Å.

We now point out that so long as least-squares refinement utilizes spherically symmetric form factors

Table IV. Parameters of the Coordination Octahedron

A. Bond and Edge Lengths, Å[a]

Type	Length[b]	Type	Length[b]	Length[c]
O_2–O_1	2.649 (2)	O_8–N_1	3.064 (2)	
O_2–O_3	2.826 (2)	O_8–N_2	2.635 (2)	
O_2–O_8	2.651 (2)	N_1–N_2	2.900 (2)	
O_2–N_1	2.957 (2)	V–O_1	1.639 (2)	1.647
O_1–O_3	2.647 (2)	V–O_2	1.657 (1)	1.655
O_1–O_8	2.784 (2)	V–O_8	1.999 (2)	1.996
O_1–N_2	2.800 (2)	V–O_3	2.001 (2)	2.001
O_3–N_1	2.632 (2)	V–N_1	2.359 (2)	2.359
O_3–N_2	3.088 (2)	V–N_2	2.366 (2)	2.369

B. Bond Angles Subtended at the V(V) Atom[a]

Type	Angle, deg	Type	Angle, deg
O_1VO_2	106.96 (8)	O_2VN_2	162.21 (9)
O_1VO_8	99.39 (8)	O_8VO_3	158.64 (10)
O_1VO_3	92.75 (7)	O_8VN_1	88.95 (6)
O_1VN_1	157.70 (11)	O_8VN_2	73.74 (5)
O_1VN_2	86.72 (7)	O_3VN_1	73.75 (5)
O_2VO_8	92.47 (7)	O_3VN_2	89.60 (6)
O_2VO_3	100.76 (7)	N_1VN_2	75.73 (5)
O_2VN_1	93.18 (7)		

[a] The figures given in parentheses are the estimated standard deviations. [b] Calculated from atomic coordinates determined by least squares. [c] Calculated from atomic coordinates determined by Fourier techniques.

Table V. Bond Parameters of the EDTA Chelate

A. Bond Lengths, Å[a]

Bond	Length[b]	Length[c]	Bond	Length[b]	Length[c]
O_3–C_1	1.293 (2)	1.296	N_2–C_6	1.479 (2)	1.482
O_4–C_1	1.225 (2)	1.226	N_2–C_7	1.472 (2)	1.469
C_1–C_2	1.520 (3)	1.519	N_2–C_9	1.485 (2)	1.486
N_1–C_2	1.484 (2)	1.482	C_7–C_8	1.521 (3)	1.523
N_1–C_3	1.488 (2)	1.485	C_8–O_8	1.292 (2)	1.293
N_1–C_5	1.488 (2)	1.485	C_8–O_7	1.224 (2)	1.223
C_8–C_4	1.532 (3)	1.539	C_9–C_{10}	1.524 (2)	1.529
C_4–O_6	1.249 (3)	1.247	C_{10}–O_9	1.238 (3)	1.234
C_4–O_5	1.256 (2)	1.262	C_{10}–O_{10}	1.264 (2)	1.267
C_5–C_6	1.508 (3)	1.517			

B. Bond Angles, Deg[a]

Type	Value	Type	Value	Type	Value
$N_2C_6C_5$	110.0 (1)	VO_8C_1	122.3 (1)	C_3N_1V	117.6 (1)
$N_1C_5C_6$	111.9 (1)	$O_4C_1O_3$	123.2 (2)	$C_2N_1C_5$	107.8 (1)
$N_2C_7C_8$	108.9 (1)	$O_4C_1C_2$	121.5 (2)	C_2N_1V	101.7 (1)
$O_7C_8O_8$	123.6 (2)	$O_3C_1C_2$	115.4 (2)	C_5N_1V	107.7 (1)
$O_7C_8C_7$	119.9 (2)	$N_1C_2C_1$	108.0 (1)	$C_9N_2C_7$	112.7 (1)
$O_8C_8C_7$	116.6 (2)	$N_1C_3C_4$	115.3 (1)	$C_9N_2C_6$	113.6 (1)
C_8O_8V	120.2 (1)	$O_5C_4O_6$	124.1 (2)	C_9N_2V	108.1 (1)
$N_2C_9C_{10}$	119.6 (2)	$O_5C_4C_3$	118.0 (2)	$C_7N_2C_6$	110.6 (1)
$O_{10}C_{10}O_9$	124.7 (2)	$O_6C_4C_3$	117.9 (2)	C_7N_2V	101.5 (1)
$O_{10}C_{10}C_9$	113.3 (2)	$C_3N_1C_2$	112.9 (1)	C_6N_2V	109.6 (1)
$O_9C_{10}C_9$	122.0 (2)	$C_3N_1C_5$	108.5 (1)		

[a] The figure in parentheses is the estimated standard deviation. [b] Calculated from atomic coordinates determined by least squares. [c] Calculated from atomic coordinates determined by Fourier techniques.

for the three atoms (at rest) in the very compact VO_2 entity, the derived V–O bond lengths should be expected to depend upon the scope of the X-ray data, *i.e.*, upon the range in $(\sin \theta)/\lambda$ within which the intensities of objectively observed reflections are measured with reasonable precision. The very short complexing bonds must be associated with markedly nonspherical distributions of electron density in the valence shells of the three atoms and, consequently, with somewhat nonspherical form factors carrying low maximum symmetries. Standard least-squares refinement, which achieves the best overall fit between calculated and observed structure amplitudes (while employing spherically symmetrical form factors), takes implicit cognizance of the bonding electron density by yielding an effective centroid of electron density for each oxygen atom that is shifted from the nuclear position toward the (almost unaffected) position of the vanadium atom. The magnitude of this shortening of the apparent V–O bond length should decrease with increasing scope of the X-ray data as the direct consequence of the rapidly diminishing importance of the scattering from valence shells with increasing $(\sin \theta)/\lambda$. Improved definition of such real physical differences as may exist in the lengths of the symmetry-nonequivalent V–O_1 and V–O_2 bonds in each crystal also is concomitant with increasing scope of the data.

In the VO_2 groups of the $[O_2VAH_2]^-$, $[O_2V(ox)_2]^{3-}$, and $[O_2VA]^{3-}$ species, the respective averaged values from least-squares refinements of the V–O bond distances are 1.640 (17, 2), 1.642 (7, 2), and 1.648 (9, 2) Å,[13] as derived from data carried to the respective maximum values of $(\sin \theta)/\lambda$ of 0.670, 0.743, and 0.764 $Å^{-1}$; the Fourier value for this averaged bond length in the $[O_2VA]^{3-}$ ion is 1.651 Å, with a mean deviation of just 0.004 Å. The most pertinent comparisons involve the EDTA complexes wherein the complexing bonds to nitrogen and carboxylate oxygen atoms are effectively structural invariants. Taking the volume of the Cu Kα sphere in reciprocal space as the unit, the $[O_2VAH_2]^-$ and $[O_2VA]^{3-}$ data sets correspond to 1.10 and 1.63 such spheres, respectively; the shell of higher resolution data added in the latter case has increased the total number of independent, objectively observed reflections by 35%.

The foregoing analysis suggests that the best value derivable from the X-ray data for the averaged *internuclear* V–O distance in the VO_2 entity of the $[O_2VA]^{3-}$ species is the 1.651 Å given by the objective determination of the positions of the pertinent maxima of electron density in the nearly convergent Fourier synthesis. Inasmuch as the objective procedure for the determination of peak positions probably does not entirely eliminate the effects of nonspherical electron densities in the valence shells of the bonded atoms, the derived value for the averaged V–O distance may still be an underestimate of the internuclear separation. It seems improbable that protonation of the carboxylate groups in the uncomplexed glycinate residues of the $[O_2VA]^{3-}$ ion should more strongly affect the bonds in the VO_2 entity than the much weaker complexing bonds to nitrogen and carboxylate oxygen atoms. In view of the apparently trivial alterations in these weaker bonds that attend protonation, it appears that the apparent reduction to 1.640 Å for the averaged V–O distance in the VO_2 group of the $[O_2VAH_2]^-$ species is, as outlined above, the probable consequence of employing X-ray data of rather too limited scope. On this basis

Table VI. Intermolecular Distances and Angles in the Crystal

A. Interatomic Distances Involving the Sodium Ions[a]

Bond	Length, Å	Bond	Length, Å
Na_1-O_5	2.313 (2)	Na_2-O_6	2.486 (2)
Na_1-O_5'	2.347 (2)	Na_2-O_4	2.532 (2)
Na_1-O_4	2.458 (2)	Na_2-W_4	2.536 (3)
Na_1-W_2	2.456 (2)	Na_3-W_3	2.367 (2)
Na_1-O_2	2.504 (2)	Na_3-O_1	2.304 (2)
Na_1-O_8	2.652 (2)	Na_3-O_7	2.329 (2)
Na_2-O_9	2.300 (2)	Na_3-W_4	2.506 (2)
Na_2-O_7	2.327 (2)	Na_3-O_9	2.545 (2)
Na_2-O_6	2.339 (2)	Na_3-W_1	2.646 (3)

B. Hydrogen-Bonding Parameters[a]

Bond	Length, Å	Bond angle	Value, deg
W_1-O_{10}	2.728 (3)	O_{10}-W_1-O_6	108.72 (9)
W_1-O_6	2.802 (3)	O_{10}-W_1-W_4	98.91 (9)
W_2-O_3	2.928 (3)	O_6-W_1-W_4	92.27 (9)
W_2-W_3	2.930 (3)	O_3-W_2-W_3	96.51 (9)
W_2-W_4	2.963 (3)	O_3-W_2-W_4	102.82 (10)
W_3-O_{10}	2.693 (3)	W_3-W_2-W_4	123.53 (10)
W_3-O_2	3.006 (3)	O_{10}-W_3-W_2	117.96 (9)
W_3-O_1	3.009 (2)	O_{10}-W_3-O_2	125.37 (9)
W_4-O_7	2.948 (3)	O_{10}-W_3-O_1	141.26 (10)
W_4-W_1	2.988 (3)	W_2-W_3-O_2	80.58 (8)
		W_2-W_3-O_1	100.32 (9)
		O_2-W_3-O_1	52.25 (5)
		O_7-W_4-W_2	157.91 (10)
		O_7-W_4-W_1	85.48 (8)
		W_2-W_4-W_1	141.09 (9)

[a] The figures in parentheses are the estimated standard deviations.
[b] W_i is the symbol employed for the *i*th water molecule.

the near identity of all corresponding bond parameters in the coordination groups of the unconstrained $[O_2VAH_2]^-$ and $[O_2VA]^{3-}$ species is highly probable.

It is perhaps surprising to find that substitution of charged carboxylate oxygen for neutral amino nitrogen in the trans positions of the coordination group has no significant effect on the averaged V–O bond length in the VO_2 entity. That this parameter should have nearly or exactly the same value in the $[O_2V(ox)_2]^{3-}$ species as in the EDTA complexes lends strong support to the conclusion that the latter pair utilize the same quantitative pattern of complexing bond parameters. As pointed out in paper I,[2] the substitution of oxide oxygen for carboxylate oxygen atoms does have a significant, if not large, effect on the bond distances in the VO_2 entity.

We note further that the deviations of the V–O_1 and V–O_2 bond lengths from their averaged values as given by least-squares refinements of the three structures tend generally (with one minor exception) to decrease with increasing range of the X-ray data in $(\sin \theta)/\lambda$. This observation together with the fact that the mean deviation has dropped to just 0.004 Å for the values derived from Fourier synthesis[14] of the most nearly complete set of structure amplitudes strongly support chemical and structural equivalence of the V–O_1 and V–O_2 bonds in the unconstrained complexes.

Interatomic distances involving the sodium ions and the parameters describing the hydrogen bonding are listed in Table VI. All three structural types of sodium ions are in six-coordination with bond distances to carboxylate oxygen atoms and water molecules lying in the range 2.300 (2)–2.652 (2) Å.

(14) See ref 8b and references cited therein for a discussion of the advantages accruing from the use of very nearly convergent Fourier synthesis for the precise determination of atomic positions.

Trifluoromethyl Hydroperoxide. Properties and Reactions with Some Acid Fluorides

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Abstract: A convenient preparation of trifluoromethyl hydroperoxide, CF_3OOH, is described and its physical and chemical properties are reported. Trifluoromethyl hydroperoxide behaves as a weak protic acid and readily forms trifluoromethyl peroxides with a variety of reactants. With acid fluorides trifluoromethylperoxy esters are formed in high yield. The synthesis and properties of the new compounds $CF_3C(O)OOCF_3$, $CH_3C(O)OOCF_3$, $CF_3OOC(O)CF_2CF_2CF_2C(O)OOCF_3$, $CF_3OOC(O)CF_2CF_2CF_2C(O)F$, and $CF_3CF(OF)OOCF_3$ are discussed.

Trifluoromethyl hydroperoxide, CF_3OOH, was first prepared by Talbott,[1] who obtained the compound in small amounts by hydrolysis of trifluoromethyl fluoroformyl peroxide, $CF_3OOC(O)F$.[1,2] The synthesis of $CF_3OOC(O)F$ was difficult and there have been no reports on the chemistry of CF_3OOH. Recently an improved method for the preparation of the formyl peroxide was found,[3,4] which permits us to undertake an investigation of its properties and reactions.

Trifluoromethyl hydroperoxide is a weak acid in water and reacts with a variety of compounds forming trifluoromethyl peroxides. For example, it reacts with N_2O_5 forming CF_3OONO_2 and $HONO_2$,[5] cleaves $P_2O_3F_4$

(1) R. L. Talbott, *J. Org. Chem.*, **33**, 2095 (1968).
(2) R. L. Cauble and G. H. Cady, *ibid.*, **33**, 2099 (1968).
(3) D. D. DesMarteau, *Inorg. Chem.*, **9**, 2179 (1970).
(4) L. R. Anderson and W. B. Fox, *ibid.*, **9**, 2182 (1970).
(5) F. A. Hohorst and D. D. DesMarteau, manuscript in preparation.