

# Stereochemistry of Dioxovanadium(V) Complexes.

## I. The Crystal and Molecular Structure of Triammonium Bis(oxalato)dioxovanadate(V) Dihydrate<sup>1</sup>

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**Abstract:** The quantitative stereochemical description of the bis(oxalato)dioxovanadate(V) ion,  $[\text{O}_2\text{V}(\text{ox})_2]^{3-}$ , comes from the determination by X-ray analysis of the atomic arrangement in crystalline  $(\text{NH}_4)_3[\text{O}_2\text{V}(\text{ox})_2] \cdot 2\text{H}_2\text{O}$ . The  $\text{VO}_2$  group is in the cis configuration with an O-V-O angle of  $103.8^\circ$ ; the V-O distances of 1.648 (2) and 1.635 (2) Å imply substantial double bonding. Extraordinarily long complexing bonds, 2.185 and 2.235 Å, extend from the vanadium to the two carboxylate oxygen atoms occupying positions trans to the oxo oxygen atoms; the two other carboxylate oxygen atoms at 1.972 and 1.988 Å complete the octahedral coordination group. The observed close approach of the complex anion to  $C_2$  symmetry is not required by the space group,  $P2_12_12_1$ , utilized by the crystalline arrangement. The orthorhombic unit cell has  $a = 11.098$ ,  $b = 15.714$ , and  $c = 7.979$  Å. An experimental density of  $1.67 \text{ g/cm}^3$  compares favorably with a calculated density of  $1.667 \text{ g/cm}^3$  for a cell content of  $4(\text{NH}_4)_3[\text{O}_2\text{V}(\text{ox})_2] \cdot 2\text{H}_2\text{O}$ . The intensities of 2717 independent reflections having  $(\sin \theta)/\lambda \leq 0.743 \text{ \AA}^{-1}$  were measured with  $\text{Mo K}\alpha$  radiation by  $\theta$ - $2\theta$  scanning on a computer-controlled four-circle diffractometer; the 2566 data retained as statistically observable were employed for structure determination by direct methods followed by anisotropic full-matrix least-squares refinement to a conventional  $R$  of 0.041.

The chemistry of mononuclear vanadium(V) species in aqueous solution is limited by the ease of formation of polynuclear vanadates. The principal mononuclear species is thought to be the aquated  $\text{VO}_2^+$  cation, formed when metavanadate solutions are acidified.<sup>2,3</sup> Chelation of this cation by anions derived from ethylenediaminetetraacetic acid (EDTA;  $\text{H}_4\text{A}$ )<sup>4,5</sup> or by oxalate (ox)<sup>6,7</sup> leads to mononuclear complexes. Three classes of crystalline EDTA complexes have been prepared:<sup>4,5</sup>  $\text{M}_3[\text{O}_2\text{VA}] \cdot \text{XH}_2\text{O}$  and  $\text{M}[\text{O}_2\text{VAH}_2] \cdot \text{XH}_2\text{O}$ , with  $\text{M}^+ = \text{K}^+$ ,  $\text{NH}_4^+$  or  $\text{Na}^+$ , and  $\text{Na}_2[\text{O}_2\text{VAH}] \cdot 4\text{H}_2\text{O}$ . Reported stability constants<sup>4</sup> in aqueous solution are:  $\log K = 15.5$  for  $\text{VO}_2^+ + \text{A}^{4-} \rightarrow [\text{O}_2\text{VA}]^{3-}$ ,  $\log K = 9.60$  for  $\text{VO}_2^+ + \text{HA}^{3-} \rightarrow [\text{O}_2\text{VAH}]^{2-}$ , and  $\log K = 6.93$  for  $\text{VO}_2^+ + \text{H}_2\text{A}^{2-} \rightarrow [\text{O}_2\text{VAH}_2]^-$ . Crystalline  $(\text{NH}_4)_3[\text{O}_2\text{V}(\text{ox})_2] \cdot 2\text{H}_2\text{O}$  also has been prepared.<sup>6,7</sup> Complexes formed by 8-hydroxyquinoline with vanadium(V), by contrast, apparently utilize the protonated form,  $\text{OVOH}^{2+}$ , of the cation.<sup>8,9</sup>

Whether the configuration assumed by the  $\text{VO}_2^+$  ion is characteristically linear or bent and whether the two V-O bonds are sensibly equivalent are questions that have not been unequivocally answered by earlier workers. A linear configuration has been favored by Addison<sup>10</sup> and by Cartmell and Fowles,<sup>11</sup> on the basis

of a postulated theoretical model for the combined  $\sigma$  and  $\pi$  bonding. LaSalle and Cobble<sup>12</sup> concluded that a bent configuration was favored by their thermodynamic measurements and, to some degree, by the established structure for crystalline  $\text{KVO}_3 \cdot \text{H}_2\text{O}$ .<sup>13</sup> Dehnicke and Weidlein<sup>14</sup> considered that the infrared spectra from  $\text{VO}_2\text{Cl}$ ,  $\text{VO}_2\text{F}$ , and  $\text{VO}_2\text{SbF}_6$  were indicative of a bent configuration. Both linear and nonlinear configurations for the  $\text{VO}_2$  group in the EDTA and oxalato complexes have been suggested. Przyborowski, *et al.*,<sup>4</sup> formulated the typical EDTA complex as a quadridentate chelate of a bent  $\text{VO}_2^+$  ion. Sathyanarayana, *et al.*,<sup>7</sup> formulated the oxalato complex,  $[\text{O}_2\text{V}(\text{ox})_2]^{3-}$ , with a linear  $\text{VO}_2$  grouping in which one V-O bond was presumed to be much stronger than the other.

In addition to the unanswered questions posed above, a further possibility to be considered is that the complex formed by the singly charged  $\text{VO}_2^+$  with the potentially sexadentate  $\text{A}^{4-}$  anion from EDTA might involve an expansion of coordination number above the usual six. The observed behavior in solution of the  $[\text{O}_2\text{VAH}_2]^-$  complex, a dibasic acid with  $\text{pK}$  values of 4.31 and 3.49, is quite compatible with two uncomplexed—or very loosely complexed—glycinato arms.<sup>4</sup> It is to be noted, however, that weak complexing of carboxylic acid arms to the central metal ion has been observed to occur more frequently than not in the crystalline EDTA chelates for which structural data are available.<sup>15</sup> Rather more convincing *a priori* objections against a coordination number greater than six are of a stereochemical nature; such expansion would ap-

(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.

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(10) W. E. Addison, "Structural Principles in Inorganic Compounds," Longmans, London, 1961, p 119.

(11) E. Cartmell and G. W. A. Fowles, "Valency and Molecular Structure," Butterworths, London, 1966, p 239.

(12) M. J. LaSalle and J. W. Cobble, *J. Phys. Chem.*, **59**, 519 (1955).

(13) C. L. Christ, J. R. Clark, and H. T. Evans, Jr., *Acta Crystallogr.*, **7**, 801 (1954).

(14) K. Dehnicke and J. Weidlein, *Angew. Chem., Int. Ed. Engl.*, **5**, 1041 (1966).

(15) For example, octahedrally complexed  $[\text{Ni}(\text{OH}_2)\text{AH}_2]$  has  $\text{H}_2\text{O}$  bonded to nickel and one complexed and one uncomplexed  $\cdot\text{CH}_2\text{COOH}$  arm: G. S. Smith and J. L. Hoard, *J. Amer. Chem. Soc.*, **81**, 556 (1959).

pear to require a tight V-shaped configuration for the VO<sub>2</sub> entity with an improbable combination of unduly small OVO angle and overlong V–O bonds.

A precise structure determination by X-ray diffraction analysis for the crystalline oxalato chelate (NH<sub>4</sub>)<sub>3</sub>[O<sub>2</sub>V(ox)<sub>2</sub>]·2H<sub>2</sub>O is detailed herein; equally precise structure determinations for the crystalline EDTA chelates NH<sub>4</sub>[O<sub>2</sub>VAH<sub>2</sub>]·3H<sub>2</sub>O and Na<sub>3</sub>[O<sub>2</sub>VA]·4H<sub>2</sub>O are presented in the accompanying papers, parts II and III.<sup>16,17</sup> A consistent stereochemical pattern for the dioxovanadium(V) complexes emerges from these studies. All three complexes utilize irregular octahedral coordination groups within which the VO<sub>2</sub> moiety preserves very nearly the same stereochemical parameters. The VO<sub>2</sub> group is strongly kinked; the OVO angle ranges from 104 to 107° and the six short V–O bonds average to 1.643 Å with a mean deviation of 0.010 Å and a maximum deviation of 0.020 Å. The abnormally long bonds to the two carboxylate oxygen atoms that are positioned opposite to the oxo ligands in the coordination group of the oxalato complex provide an unambiguous example of the structural trans effect. This effect is less cleanly, but unmistakably, to be seen in the EDTA complexes as well.<sup>16,17</sup>

### Experimental Section

Crystalline (NH<sub>4</sub>)<sub>3</sub>[O<sub>2</sub>V(ox)<sub>2</sub>]·2H<sub>2</sub>O was prepared by the method of Sathyanarayana, *et al.*<sup>7</sup> Well-formed crystals as large as 2 × 1 × 1 cm were readily grown from aqueous solution. Precession photographs from selected crystals displayed the symmetry and the extinctions uniquely demanded by the orthorhombic space group<sup>18</sup> P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>; this choice was supported by the strong positive test for piezoelectricity and by all subsequent developments during the determination of structure. Precise lattice constants were obtained by the least-squares refinement<sup>19</sup> of the angular settings for 40 reflections on a Picker computer-controlled four-circle diffractometer, using the automatic centering routine; negative values of 2θ were represented by 18 of the settings, all with |2θ| > 43°. The resolved Mo Kα<sub>1</sub> component (λ 0.70926 Å) was employed at the ambient laboratory temperature of 20 ± 1°. This procedure gave the lattice constants *a* = 11.098 (1), *b* = 15.714 (2), *c* = 7.979 (1) Å. For a cell content of 4(NH<sub>4</sub>)<sub>3</sub>[O<sub>2</sub>V(ox)<sub>2</sub>]·2H<sub>2</sub>O, the density was calculated to be 1.667 g/cm<sup>3</sup>; the experimental density, as measured by flotation, was found to be 1.67 g/cm<sup>3</sup>. These results are in good agreement with the lattice constants obtained by Sathyanarayana, *et al.*,<sup>7</sup> from X-ray powder methods.

Diffracted intensities were measured with Zr-filtered Mo Kα radiation at a takeoff angle of ~2° on a computer-controlled four-circle diffractometer. Two specimen crystals were employed: the first was a sphere 0.48 mm in diameter, the second a nearly cube-shaped specimen ~0.45 mm on an edge, cut from a larger crystal. All independent reflections, 2717, for which (sin θ)/λ ≤ 0.743 Å<sup>-1</sup> were scanned by the θ–2θ technique at the rate of 1.0°/min. All scans included a variable increment in angle to allow for spectral dispersion; background counts of 40-sec duration were taken at the extremes of the scan. Three standard reflections, periodically measured, displayed a gradual, nearly uniform, decrease in intensity. After some 1300 independent data had been observed, the decrease was approximately 10%; the second specimen was then aligned and data collection resumed. A similar gradual decrease in intensity of the three standard reflections, amounting to ~13% overall, was also observed for the second crystal. The average rate of decrease in the intensity of the standard reflections within each data set was used to correct for crystal decomposition; the validity of this procedure was checked by dividing the uncorrected

data sets into groups and calculating separate scale factors for each group by least-squares refinement. Such refinement was based on the already refined trial structure derived from the uncorrected data sets. The corrections suggested by both methods were virtually identical. Two scale factors, one for each data set, were used in the last stages of refinement.

The linear absorption coefficient of the crystal for Mo Kα radiation is 0.824 mm<sup>-1</sup>, yielding a μ<sub>R</sub> of 0.20 for the spherical crystal and a μ<sub>R</sub> of 0.19 for a spherical crystal having the same volume as the cube-shaped specimen used for intensity measurements. The absorption of X-rays for a spherical crystal having μ<sub>R</sub> = 0.2 is virtually independent of scattering angle, and deviations from this absorption occasioned by the use of the cube-shaped specimen are practically negligible except for a trivial fraction of the reflections. In these circumstances no absorption correction was made and the intensities were reduced to relative squared amplitudes, |F<sub>o</sub>|<sup>2</sup>, by application of the standard Lorentz and polarization factors (*Lp*). Of the 2717 reflections examined, 151 were rejected as objectively unobserved by applying the criterion |F<sub>o</sub>| < 1.35σ(|F<sub>o</sub>|), where σ(|F<sub>o</sub>|) is the standard deviation computed from σ<sup>2</sup>(|F<sub>o</sub>|) = (C*t* + *k*<sup>2</sup>*B*)/[4|F<sub>o</sub>|<sup>2</sup>*Lp*<sup>2</sup>] + (0.025|F<sub>o</sub>|)<sup>2</sup>, *Ct* being the total count from the scanning, *k* the ratio of scanning time to total background counting time, *B* the total background count, and *Lp* the Lorentz–polarization correction. The remaining 2566 observed intensities were used in the determination and refinement of structure.

Structure solution was achieved through the use of direct methods,<sup>20,21</sup> using the multiple-solution computer program MAGENC<sup>22</sup> and tangent-formula phase refinement.<sup>23</sup> A starting set of six reflections, which gave the eight possible phase combinations shown in Table I, was chosen; 158 reflections with |E| ≥ 1.5

Table I. Starting Set of Phase Assignments

<i>h</i>	<i>k</i>	<i>l</i>	<i>E</i>	Phase	Phase <sup>b</sup>
2	13	1	2.06	π/2 <sup>a</sup>	0.482π
4	3	2	1.94	0 <sup>a</sup>	-0.055π
1	0	5	1.76	π/2 <sup>a</sup>	0.5π
4	6	1	2.26	±π/2	-0.338π
8	4	1	1.82	±π/2	0.469π
4	10	1	1.74	±π/2	-0.618π

<sup>a</sup> Specifying the choice of origin. <sup>b</sup> From the squared-tangent formula.<sup>26</sup>

were expanded over the eight possible phase combinations using a computer-programmed multiple-solution procedure.<sup>22</sup> Of these eight sets, the one with phases π/2, 0, π/2, -π/2, π/2, -π/2, which had the largest consistency index  $\bar{c}$  = 0.89, and the largest  $\bar{\alpha}$  index, 63.5, was the best choice for a starting set. The  $\bar{\alpha}$  index<sup>20</sup> is given by  $\bar{\alpha} = \langle 2\sigma_3\sigma_2^{-2/2}|E_h|(A^2 + B^2)^{1/2} \rangle$  and the consistency index<sup>24</sup> by  $\bar{c} = \langle (A^2 + B^2)^{1/2}/\sum|E_k E_h - k| \rangle$ , where  $A = \sum|E_k E_h - k| \cos(\phi_k + \phi_h - k)$  and  $B = \sum|E_k E_h - k| \sin(\phi_k + \phi_h - k)$ . The same starting set with phases predicted by the squared-tangent formula<sup>25</sup> (Table I), using two-dimensional data, were expanded using the formula  $\phi_h = \langle \phi_k + \phi_h - k \rangle$ , and trial phases for 150 reflections with |E| ≥ 1.5 were obtained. These phases were expanded by application of the tangent formula; phases for 253 reflections with *E* ≥ 1.3 were thus obtained. An *E* map based on these 253 reflections gave the positions of all atoms in the [O<sub>2</sub>V(ox)<sub>2</sub>]<sup>3-</sup> anion; the Fourier synthesis with phasing based on the coordinates of the complex ion revealed the remaining nitrogen and oxygen atoms.

The structure was then refined by full-matrix least-squares techniques<sup>26</sup> with  $w = 1/\sigma^2(F_o)$ , anisotropic thermal parameters for

(20) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

(21) J. Karle, *ibid.*,  *Sect. B*, **24**, 182 (1968).

(22) C. Tsai, Ph.D. Thesis, Indiana University, 1968.

(23) J. Karle and H. Hauptman, *Acta Crystallogr.*, **9**, 635 (1956).

(24) M. G. B. Drew, D. H. Templeton, and A. Zalkin, *ibid.*,  *Sect. B*, **25**, 261 (1969).

(25) H. Hauptman, *ibid.*,  *Sect. B*, **26**, 531 (1970).

(26) Following 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. Atomic form factors were from D. T. Cromer and J. B. Mann, *Acta Crystallogr.*,  *Sect. A*, **24**, 321 (1968), with corrections, real and imaginary, for anomalous dispersion in the vanadium form factor from D. T. Cromer, *ibid.*, **18**, 17 (1965).

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

(17) W. R. Scheidt, R. Countryman, and J. L. Hoard, *ibid.*, **93**, 3878 (1971).

(18) "International Tables for X-ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965, p 105.

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

all atoms of the complex anion, and isotropic thermal parameters for the ammonium nitrogen atoms and water oxygen atoms. Isotropic extinction corrections, based on Zachariasen's recent formulation,<sup>27</sup> were included in the refinement. The absolute configuration of the complex anion was determined by anomalous scattering techniques. The calculated and observed structure factors of reflections used in the assignment are shown in Table II.

**Table II.** Calculated and Observed Differences in the Structure Factors of Friedel Pairs Using the Correct Absolute Configuration for the Complex Ion in the Crystal

Indices			$\Delta F  =  F_{hkl}  -  F_{\bar{h}\bar{k}l} $	
<i>h</i>	<i>k</i>	<i>l</i>	Calcd	Obsd
1	15	6	-0.76	-0.06
2	3	9	0.38	0.49
2	5	9	0.74	0.99
3	16	4	0.25	0.10
4	2	9	0.81	0.06
5	12	6	-1.68	-1.80
6	16	1	0.79	1.42
11	2	5	0.50	0.64

After the refinement had converged, a difference Fourier synthesis gave approximate positions for all hydrogen atoms. Apparent O-H distances ranged from 0.933 to 1.045 Å with an average value of 0.975 Å; apparent N-H distances ranged from 0.783 to 1.001 Å with an average value of 0.904 Å. Two more cycles of full-matrix least-squares refinement with anisotropic thermal parameters for all atoms of the complex anion, isotropic thermal parameters for the ammonium ions and water molecules, and fixed positional and thermal parameters ( $B = 4.0 \text{ \AA}^2$ ) for the hydrogen atoms gave a conventional *R* of 0.041 and a weighted *R* of 0.050. The estimated standard deviation of an observation of unit weight was 1.245. The final parameter shifts were less than 5% of their estimated standard deviation during the last cycle.<sup>28</sup>

The atomic coordinates within the asymmetric unit are given in Table III and the associated thermal parameters in Table IV. The

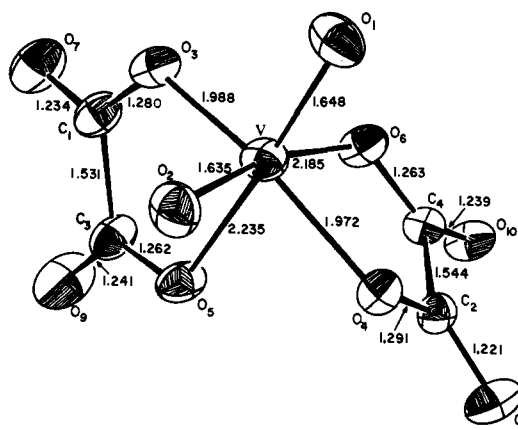
**Table III.** Atomic Coordinates in Crystalline  $(\text{NH}_4)_3[\text{VO}_2(\text{ox})_2] \cdot 2\text{H}_2\text{O}^a$

Atom	$10^4x$	$10^4y$	$10^4z$
O <sub>1</sub>	255 (2)	-1629 (1)	926 (3)
O <sub>3</sub>	-1621 (2)	-2462 (1)	-2317 (3)
O <sub>5</sub>	-1260 (2)	-3827 (1)	-590 (3)
O <sub>7</sub>	-3051 (3)	-3086 (2)	-3839 (3)
O <sub>9</sub>	-2685 (3)	-4546 (2)	-1986 (4)
C <sub>1</sub>	-2285 (3)	-3095 (2)	-2718 (4)
C <sub>3</sub>	-2071 (3)	-3903 (2)	-1688 (4)
O <sub>2</sub>	-1253 (2)	-2310 (1)	1143 (3)
O <sub>4</sub>	809 (2)	-3157 (1)	833 (3)
O <sub>6</sub>	666 (2)	-3167 (1)	-2402 (3)
O <sub>8</sub>	2127 (2)	-4232 (1)	815 (3)
O <sub>10</sub>	2019 (2)	-4220 (1)	2631 (2)
C <sub>2</sub>	1480 (2)	-3717 (2)	106 (3)
C <sub>4</sub>	1398 (3)	-3709 (2)	-1826 (4)
W <sub>1</sub> <sup>b</sup>	-468 (2)	-5445 (2)	421 (3)
W <sub>2</sub> <sup>b</sup>	29 (2)	-3572 (2)	-5754 (3)
N <sub>1</sub>	-1806 (3)	-952 (2)	-4175 (3)
N <sub>2</sub>	-2627 (3)	-3627 (2)	2799 (3)
N <sub>3</sub>	-571 (3)	-333 (2)	1208 (4)
	$10^5x$	$10^5y$	$10^5z$
V	-4150 (4)	-25372 (3)	-4800 (5)

<sup>a</sup> Figures in parentheses are the estimated standard deviations in the last significant figure. <sup>b</sup> Symbols used for water molecules.

(27) W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967);  *Sect. A*, **24**, 324 (1968).

(28) A table of observed and calculated structure amplitudes from this analysis has been deposited as Document No. NAPS-01307 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.



**Figure 1.** Model in perspective of the  $[\text{O}_2\text{V}(\text{ox})_2]^{3-}$  anion.

positions of the hydrogen atoms are listed in Table V. All atoms are placed in the general positions of  $P2_12_12_1$ .

The space group  $P2_12_12_1$  requires that the four complex anions of the unit cell be congruent. Given the configuration established for the complex anion, there must be complete sorting during crystallization into enantiomorphic pairs; *i.e.*, each single crystal must contain only *d* or only *l* isomers. A crystal of  $(\text{NH}_4)_3[\text{O}_2\text{V}(\text{ox})_2] \cdot 2\text{H}_2\text{O}$  was crushed and dissolved in water as quickly as possible within a polarimetric cell of 10-cm path length; the cell was placed in a Perkin-Elmer Model 141 polarimeter and the solution was checked for optical activity with the 4360-Å line of Hg. The process of dissolution and measurement required  $\pm 30$  sec; no optical rotation was found, the presumed consequence of extremely fast racemization.

## Discussion

A model of the  $[\text{O}_2\text{V}(\text{ox})_2]^{3-}$  anion seen in perspective is illustrated in Figure 1; each atom is represented by an ellipsoid<sup>29</sup> having the shape, orientation, and relative size concomitant with the thermal parameters listed in Table II. The geometry of the octahedral coordination group and, indeed, of the entire complex is compatible with the point-group symmetry of  $C_2$  for the free ion, a stereochemical feature that cannot be required in the space group,  $P2_12_12_1$ . Examination of Figure 1 along with the listing in Table VI of the atomic displacements from the three principal (mean coordinate or axial) planes of the octahedron shows that the most striking departure from geometrical regularity is the displacement by  $\sim 0.40 \text{ \AA}$  of the vanadium atom from the effective octahedral center toward the pair of oxo ligands,  $\text{O}_1$  and  $\text{O}_2$ . The radial distances of the six coordinated oxygen atoms from the center lie in the range 1.90–1.93 Å.

Table VII is a listing of the complexing bond distances,<sup>30</sup> the octahedral edge lengths, and the angles subtended at the vanadium atom in the complex anion,  $[\text{O}_2\text{V}(\text{ox})_2]^{3-}$ . The  $\text{O}_1 \cdots \text{O}_2$  contact in the  $\text{VO}_2$  entity and the "bites" ( $\text{O}_3 \cdots \text{O}_5$  and  $\text{O}_4 \cdots \text{O}_6$ ) of the oxalato ligands are very short, 2.58–2.59 Å; indeed, only 2 of the 12 octahedral edges are as long as the van der Waals packing diameter of oxygen.<sup>31</sup> Irregularities

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

(30) Estimated standard deviations in the bond lengths and angles of  $(\text{NH}_4)_3[\text{O}_2\text{V}(\text{ox})_2] \cdot 2\text{H}_2\text{O}$  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.

(31) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

Table IV. Thermal Parameters<sup>a</sup>

Atom type	Anisotropic parameters, Å <sup>2</sup>						
	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$	$B, \text{Å}^2$ <sup>b</sup>
V	2.17 (2)	1.66 (2)	2.09 (2)	0.16 (2)	0.16 (2)	-0.07 (2)	1.95
O <sub>1</sub>	3.1 (1)	2.0 (1)	3.8 (1)	-0.3 (1)	1.2 (1)	-0.1 (1)	2.7
O <sub>3</sub>	2.8 (1)	2.4 (1)	3.0 (1)	0.3 (1)	-0.3 (1)	0.7 (1)	2.6
O <sub>5</sub>	2.9 (1)	2.0 (1)	2.9 (1)	-0.3 (1)	-0.8 (1)	0.3 (1)	2.5
O <sub>7</sub>	4.3 (2)	4.9 (2)	2.7 (1)	0.9 (1)	-1.3 (1)	-0.3 (1)	3.6
O <sub>9</sub>	4.8 (2)	2.4 (1)	6.9 (2)	-0.7 (1)	-2.4 (2)	-0.3 (1)	3.9
C <sub>1</sub>	3.2 (2)	2.8 (1)	2.1 (1)	0.9 (1)	-0.3 (1)	-0.2 (1)	2.6
C <sub>3</sub>	2.9 (2)	2.1 (1)	3.2 (2)	0.3 (1)	0.6 (1)	-0.3 (1)	2.7
O <sub>2</sub>	2.6 (1)	2.6 (1)	2.9 (1)	0.2 (1)	0.7 (1)	-0.1 (1)	2.6
O <sub>4</sub>	2.4 (1)	2.6 (1)	1.8 (1)	0.6 (1)	-0.1 (1)	-0.4 (1)	2.2
O <sub>6</sub>	3.0 (1)	2.7 (1)	1.8 (1)	0.9 (1)	0.1 (1)	0.0 (1)	2.3
O <sub>8</sub>	3.9 (1)	2.4 (1)	2.7 (1)	0.8 (1)	-0.9 (1)	0.1 (1)	2.8
O <sub>10</sub>	3.6 (1)	2.6 (1)	2.5 (1)	1.1 (1)	0.5 (1)	-0.3 (1)	2.7
C <sub>2</sub>	2.0 (1)	1.9 (1)	1.9 (1)	-0.1 (1)	-0.3 (1)	0.0 (1)	1.9
C <sub>4</sub>	2.3 (1)	1.8 (1)	1.9 (1)	0.1 (1)	0.1 (1)	-0.2 (1)	2.0
W <sub>1</sub> <sup>c</sup>							3.5 (1)
W <sub>2</sub> <sup>c</sup>							3.6 (1)
N <sub>1</sub> <sup>c</sup>							2.7 (1)
N <sub>5</sub> <sup>c</sup>							2.9 (1)
N <sub>8</sub> <sup>c</sup>							3.1 (1)

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

Table V. Hydrogen Atom Parameters

Atom <sup>a</sup>	10 <sup>3</sup> x	10 <sup>3</sup> y	10 <sup>3</sup> z
H <sub>1</sub> W <sub>1</sub>	-69	-480	35
H <sub>2</sub> W <sub>1</sub>	-112	-583	65
H <sub>1</sub> W <sub>2</sub>	45	-325	-660
H <sub>2</sub> W <sub>2</sub>	40	-335	-480
H <sub>1</sub> N <sub>1</sub>	-120	-80	-480
H <sub>2</sub> N <sub>1</sub>	-225	-92	-525
H <sub>3</sub> N <sub>1</sub>	-210	-55	-340
H <sub>4</sub> N <sub>1</sub>	-175	-150	-370
H <sub>1</sub> N <sub>2</sub>	-278	-345	375
H <sub>2</sub> N <sub>2</sub>	-210	-330	235
H <sub>3</sub> N <sub>2</sub>	-330	-365	230
H <sub>4</sub> N <sub>2</sub>	-250	-417	325
H <sub>1</sub> N <sub>3</sub>	-20	-35	235
H <sub>2</sub> N <sub>3</sub>	-70	0	50
H <sub>3</sub> N <sub>3</sub>	-20	-75	60
H <sub>4</sub> N <sub>3</sub>	140	-42	140

<sup>a</sup> The notation specifies the water molecule (W<sub>i</sub>) or the nitrogen atom (N<sub>i</sub>) with which the hydrogen atom is associated.

Table VI. Equations of the Three Principal Planes of the Coordination Octahedron and the Atomic Displacements Therefrom

Plane I (O<sub>1</sub>, O<sub>3</sub>, O<sub>4</sub>, O<sub>5</sub>):<sup>a</sup>  $0.565X - 0.336Y - 0.754Z = 1.629^b$   
 Plane II (O<sub>2</sub>, O<sub>3</sub>, O<sub>4</sub>, O<sub>6</sub>):<sup>a</sup>  $0.444X + 0.891Y - 0.092Z = -4.012^b$   
 Plane III (O<sub>1</sub>, O<sub>2</sub>, O<sub>5</sub>, O<sub>6</sub>):<sup>a</sup>  $-0.692X + 0.288Y - 0.662Z = -0.565^b$

Atom type	Displacements from mean planes, Å		
	Plane I	Plane II	Plane III
V	0.26	-0.29	0.01
O <sub>1</sub>	0.05	-1.92	-0.12
O <sub>2</sub>	1.89	-0.07	0.12
O <sub>3</sub>	-0.05	0.07	-1.92
O <sub>4</sub>	-0.05	0.08	1.92
O <sub>5</sub>	0.05	1.93	-0.11
O <sub>6</sub>	-1.90	-0.08	0.11

<sup>a</sup> The coordinates of these atoms were employed for the determination by a least-squares fitting of the equation of the mean plane. <sup>b</sup> X, Y, and Z are orthogonal coordinates measured in ångströms along the respective a, b, and c axes of the orthorhombic unit of structure.

Table VII. Parameters of the Coordination Octahedron

Type	A. Bond and Edge Lengths, Å <sup>a</sup>			
	Length		Length	
O <sub>2</sub> -O <sub>1</sub>	2.584 (3)	O <sub>3</sub> -O <sub>6</sub>	2.771 (3)	
O <sub>2</sub> -O <sub>3</sub>	2.801 (3)	O <sub>4</sub> -O <sub>5</sub>	2.769 (3)	
O <sub>2</sub> -O <sub>4</sub>	2.659 (3)	O <sub>4</sub> -O <sub>6</sub>	2.587 (3)	
O <sub>2</sub> -O <sub>5</sub>	2.757 (3)	V-O <sub>1</sub>	1.648 (2)	
O <sub>1</sub> -O <sub>3</sub>	2.697 (3)	V-O <sub>2</sub>	1.635 (2)	
O <sub>1</sub> -O <sub>4</sub>	2.849 (3)	V-O <sub>3</sub>	1.988 (2)	
O <sub>1</sub> -O <sub>6</sub>	2.728 (3)	V-O <sub>4</sub>	1.972 (2)	
O <sub>5</sub> -O <sub>6</sub>	2.782 (3)	V-O <sub>5</sub>	2.235 (2)	
O <sub>3</sub> -O <sub>5</sub>	2.581 (3)	V-O <sub>6</sub>	2.185 (2)	
Type	B. Bond Angles Subtended at the V(V) Atom			
	Angle, deg <sup>a</sup>		Angle, deg <sup>a</sup>	
O <sub>2</sub> VO <sub>1</sub>	103.8 (1)	O <sub>1</sub> VO <sub>5</sub>	165.0 (1)	
O <sub>2</sub> VO <sub>4</sub>	94.5 (1)	O <sub>4</sub> VO <sub>3</sub>	152.2 (1)	
O <sub>2</sub> VO <sub>3</sub>	100.8 (1)	O <sub>4</sub> VO <sub>6</sub>	76.8 (1)	
O <sub>2</sub> VO <sub>6</sub>	165.5 (1)	O <sub>4</sub> VO <sub>5</sub>	82.0 (1)	
O <sub>2</sub> VO <sub>5</sub>	89.5 (1)	O <sub>3</sub> VO <sub>6</sub>	83.1 (1)	
O <sub>1</sub> VO <sub>4</sub>	103.4 (1)	O <sub>3</sub> VO <sub>5</sub>	75.1 (1)	
O <sub>1</sub> VO <sub>3</sub>	95.3 (1)	O <sub>6</sub> VO <sub>5</sub>	78.0 (1)	
O <sub>1</sub> VO <sub>6</sub>	89.6 (1)			

<sup>a</sup> The figure in parentheses is the estimated standard deviation.

in this tightly packed coordination group and, most particularly, the displacement of the vanadium atom from the octahedral center are responsible for the markedly nonstandard bond angles listed in Table VII.

The off-center positioning of the vanadium atom is attributable to the retention in the octahedral complex of a VO<sub>2</sub> entity having very short V-O bonds (~1.64 Å) and an OVO angle (103.8°) that is ~14° larger than the standard octahedral value (90°). Comparison with the sum of the ionic radii<sup>31</sup> (1.99 Å) for V<sup>5+</sup> and O<sup>2-</sup> suggests a bond order approaching two for the V-O linkages in the VO<sub>2</sub> group. Noting that the 1.64-Å bond distance is not much larger than that reported for the complexing linkage in the vanadyl (VO<sup>2+</sup>) ion (1.57-1.62 Å),<sup>32</sup> it appears that π bonding

(32) (a) J. G. Forrest and C. K. Prout, *J. Chem. Soc. A*, 1312 (1967); (b) P. K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.*, **43**,

plays a similarly major role in stabilizing both structural entities.

The four complexing bonds to oxalato oxygen atoms divide into two distinctive pairs accordingly as the position occupied by oxalato oxygen is cis to both oxo ligands or is trans to one and cis to the other. The V–O bond lengths to the first pair (in carboxylate groups A) average to 1.980 (8, 2) Å,<sup>33</sup> a rational value for a pure  $\sigma$  bond, whereas those to the second pair (in carboxylate groups B) average to the substantially larger value, 2.210 (25, 2) Å.<sup>33</sup> This lengthening (by  $\sim 0.23$  Å) and weakening of the complexing bonds to the atoms lying trans to the oxo ligands provides a striking example of the well-known structural trans effect;<sup>34</sup> it is the more striking because two ligands are thus affected. Through a synergistic mechanism the  $\pi$  bonding to the oxo oxygen atoms presumably induces a strengthening of the  $\sigma$  bonding to these same ligands at the expense of the  $\sigma$  bonding to the carboxylate oxygen atoms occupying the trans positions.<sup>35</sup> The weaker complexing of type B carboxylate oxygen relative to type A is supported by the pattern of C–O bond lengths in the oxalato ligands (*vide infra*).

The familiar kinetic trans effect on the rate of certain substitution reactions<sup>36</sup> is expected whenever there is a demonstrable structural trans effect. The converse of this proposition, a rational expectation, is not so readily established by experiment for those complexes in which the structural trans effect is inherently small, *e.g.*, the complexes of Pt(II). In one group of Pt(II) complexes, however, the existence at a modest level of the anticipated structural differences is well documented.<sup>37–39</sup>

The trans effect provides a rational explanation for the apparently quite rapid racemization of the optically pure  $[\text{O}_2\text{V}(\text{ox})_2]^{3-}$  ion. A chelate ring opening–closing mechanism of racemization for oxalato complexes was originally suggested by Werner<sup>40</sup> and demonstrated by Long<sup>41</sup> by exchange experiments. The chelate ring opening–closing process (I of Figure 2) has been suggested as the mechanism of racemization of  $[\text{Cr}(\text{ox})_3]^{3-}$  on the basis of <sup>18</sup>O exchange between the solvent water and the complex.<sup>42</sup> A mechanism involving chelate ring opening and closing seems quite appropriate in the present case with the trans labilized bonds in-

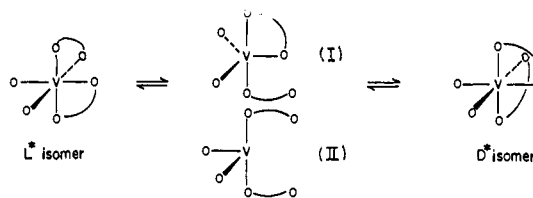


Figure 2. Bond-breaking mechanisms for the racemization of the  $[\text{O}_2\text{V}(\text{ox})_2]^{3-}$  complex anion.

involved in the rupture. Either process I or II of Figure 2 is plausible; however, a single-bond rupture with a five-coordinate intermediate is probably the path with the lower activation energy.

$\text{VO}_2$  groups, with nonlinear configurations similar to those of the dioxovanadium(V) complexes reported here, occur as structural entities in several oxovanadate(V) compounds. Both  $\text{KVO}_3$ ,<sup>43</sup> with a tetrahedral array of oxygen donors, and  $\text{KVO}_3 \cdot \text{H}_2\text{O}$ ,<sup>13</sup> with a trigonal-bipyramidal coordination group, have  $\text{VO}_2$  groups with V–O lengths of  $\sim 1.66$  Å and an O–V–O angle of  $\sim 107^\circ$ . A similar grouping occurs within some of the  $\text{VO}_6$  octahedra of the decavanadate ion in the salts  $\text{K}_2\text{Zn}_2\text{V}_{10}\text{O}_{28} \cdot 16\text{H}_2\text{O}$ <sup>44</sup> and  $\text{Ca}_3\text{V}_{10}\text{O}_{28} \cdot 16\text{H}_2\text{O}$ .<sup>45</sup> A structural trans effect is also observed in these octahedra: the  $\text{VO}_2$  group has V–O = 1.69 Å and O–V–O =  $107^\circ$ ; the V–O distances involving the oxygen atoms cis to the  $\text{VO}_2$  group average to 1.93 Å, while those involving the trans pair of oxygen atoms average to 2.10 Å.

It is clear, however, that the bond parameters of the  $\text{VO}_2$  group are somewhat sensitive to the differing environments provided in the several complexes. The fact that both the minimum and the maximum values of the bond length in the  $\text{VO}_2$  entity are attained in octahedral coordination groups, *i.e.*, in the respective  $[\text{O}_2\text{V}(\text{ox})_2]^{3-}$  and decavanadate ions, suggests that the effect of the added ligands is rather more dependent upon their complexing power than on their number. The sensitivity of the bond distance in either the  $\text{VO}_2^+$  or the  $\text{VO}_2^{2+}$  ion to complexing by a range of complexing agents appears to be smaller by an order of magnitude than that which characterizes the uranyl ion ( $\text{UO}_2^{2+}$ ) in similar circumstances.<sup>46</sup> Further discussion of this point and of a possible chemical nonequivalence of the bonds in the  $\text{VO}_2$  entity is postponed to paper III,<sup>17</sup> following presentation of the structural results for the two EDTA complexes of dioxovanadium(V).

Table VIII lists the parameters of the oxalato groups in the chelate rings 1 (odd subscripts) and 2 (even subscripts) of Figure 1. The sum of the bond angles subtended at each of the four carbon atoms is  $360.0^\circ$ , corresponding to flat carboxylate groups. No atom of ring 1 departs by more than 0.004 Å from the mean plane. Ring 2 departs appreciably from planarity, the consequence of a  $10.7^\circ$  folding along the  $\text{O}_4 \cdots \text{O}_8$

1323 (1965); (c) R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961); (d) N. D. Chasteen, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, **8**, 408 (1969); (e) R. E. Tapscott, R. L. Belford, and I. C. Paul, *ibid.*, **7**, 356 (1968); (f) M. Mathew, A. J. Carty, and G. J. Palenik, *J. Amer. Chem. Soc.*, **92**, 3197 (1970).

(33) The figures in parentheses are, respectively, the mean deviation from the average and the estimated standard deviation of an individual bond length in the last significant figure of the datum.

(34) The usual preference evinced by vanadyl complexes for square-pyramidal five-coordination of the vanadium atom with no ligand trans to the oxo oxygen represents a rather extreme case of the structural trans effect. A similar conclusion obtains for high-spin iron porphyrins; *cf.* J. L. Hoard in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, pp 573–594.

(35) *Cf.* (a) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966); (b) L. M. Venanzi, *Chem. Brit.*, **4**, 162 (1968), for a discussion of such synergistic mechanisms.

(36) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

(37) G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, **6**, 725 (1967).

(38) R. Eisenberg and J. A. Ibers, *ibid.*, **4**, 773 (1965).

(39) G. G. Messmer and E. L. Amma, *ibid.*, **5**, 1775 (1966).

(40) A. Werner, *Justus Liebigs Ann. Chem.*, **386**, 1 (1912); *Ber.*, **45**, 1228, 3061 (1912).

(41) F. A. Long, *J. Amer. Chem. Soc.*, **61**, 570 (1939); **63**, 1353 (1941).

(42) C. A. Bunton, J. H. Carter, D. R. Llewellyn, C. O'Connor, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4615 (1964).

(43) H. T. Evans, Jr., *Z. Kristallgr., Kristallogeometrie, Kristallphys., Kristallchem.*, **114**, 17 (1960).

(44) H. T. Evans, Jr., *Inorg. Chem.*, **5**, 967 (1966).

(45) H. T. Evans, Jr., A. G. Swallow, and W. H. Barnes, *J. Amer. Chem. Soc.*, **86**, 4209 (1964).

(46) The probability that the bond distance in the uranyl entity must be strongly dependent upon the character of additionally coordinated ligands was first pointed out by J. L. Hoard and S. Geller, *Ann. Rev. Phys. Chem.*, **1**, 215 (1950); the reality of this dependence was subsequently confirmed in detail by W. H. Zacharisen, *Acta Crystallogr.*, **7**, 795 (1954).

**Table VIII.** Bond Parameters of the Oxalate Chelates

A. Bond Lengths, Å <sup>a</sup>			
Ring 1		Ring 2	
Bond	Length	Bond	Length
O <sub>3</sub> -C <sub>1</sub>	1.280 (4)	O <sub>4</sub> -C <sub>2</sub>	1.291 (3)
O <sub>7</sub> -C <sub>1</sub>	1.234 (4)	O <sub>8</sub> -C <sub>2</sub>	1.221 (3)
C <sub>1</sub> -C <sub>3</sub>	1.531 (4)	C <sub>2</sub> -C <sub>4</sub>	1.544 (4)
O <sub>5</sub> -C <sub>3</sub>	1.262 (4)	O <sub>6</sub> -C <sub>4</sub>	1.263 (3)
O <sub>9</sub> -C <sub>3</sub>	1.241 (4)	O <sub>10</sub> -C <sub>4</sub>	1.239 (3)

B. Bond Angles, Deg <sup>a</sup>			
Ring 1		Ring 2	
Type	Value	Type	Value
VO <sub>3</sub> C <sub>1</sub>	121.7 (2)	VO <sub>4</sub> C <sub>2</sub>	119.7 (2)
O <sub>3</sub> C <sub>1</sub> O <sub>7</sub>	124.7 (3)	O <sub>4</sub> C <sub>2</sub> O <sub>8</sub>	125.6 (3)
O <sub>3</sub> C <sub>1</sub> C <sub>3</sub>	114.9 (3)	O <sub>4</sub> C <sub>2</sub> H <sub>4</sub>	114.1 (2)
O <sub>7</sub> C <sub>1</sub> C <sub>3</sub>	120.4 (3)	O <sub>8</sub> C <sub>2</sub> H <sub>4</sub>	120.2 (3)
VO <sub>5</sub> C <sub>3</sub>	114.4 (2)	VO <sub>6</sub> C <sub>4</sub>	113.7 (2)
O <sub>5</sub> C <sub>3</sub> O <sub>9</sub>	127.0 (3)	O <sub>6</sub> C <sub>4</sub> O <sub>10</sub>	127.3 (3)
O <sub>5</sub> C <sub>3</sub> C <sub>1</sub>	113.9 (3)	O <sub>6</sub> C <sub>4</sub> C <sub>2</sub>	144.0 (2)
O <sub>9</sub> C <sub>3</sub> C <sub>1</sub>	119.1 (3)	O <sub>10</sub> C <sub>4</sub> C <sub>2</sub>	118.6 (3)

<sup>a</sup> The figures in parentheses are the estimated standard deviations in the last significant figure.

edge of the coordination polyhedron; the sum of the interior ring angles is 538.4°.

The C-O bond lengths in each carboxylate group vary accordingly as the oxygen atom is (O<sub>c</sub>) or is not (O<sub>u</sub>) coordinated to the vanadium atom. In the two carboxylate groups of type A the C-O<sub>c</sub> bond lengths average to 1.286 (6, 4) Å,<sup>33</sup> the C-O<sub>u</sub> distances to 1.228 (7, 4) Å; these data are consistent with rather strong V-O<sub>c</sub> complexing bonds. In the B carboxylate groups, by contrast, the averaged values of the C-O<sub>c</sub> and C-O<sub>u</sub> bonds are 1.262 (1, 4) and 1.240 (1, 4) Å, respectively, both suggestive of rather weaker complexing interactions with the vanadium atom. The data of Table VIII are in generally excellent agreement with the results of earlier precise determinations of structure for oxalic acid,<sup>47</sup> oxalates,<sup>48</sup> and oxalato complexes.<sup>49</sup>

(47) (a) F. F. Iwasaki and Y. Saito, *Acta Crystallogr.*, **23**, 56 (1967); (b) T. M. Sabine, G. W. Cox, and B. M. Craven, *ibid.*, *Sect. B*, **25**, 2437 (1969); (c) R. G. Delaplane and J. A. Ibers, *ibid.*, *Sect. B*, **25**, 2423 (1969).

(48) (a) R. Beagley and R. W. H. Small, *ibid.*, **17**, 783 (1964);

**Table IX.** Hydrogen-Bonding Parameters<sup>a</sup>

Bond	Length, Å	Bond	Length, Å
W <sub>1</sub> -O <sub>5</sub>	2.808 (3)	N <sub>2</sub> -O <sub>1</sub>	2.815 (4)
W <sub>1</sub> -O <sub>7</sub>	2.894 (4)	N <sub>2</sub> -O <sub>7</sub>	2.852 (4)
W <sub>1</sub> -O <sub>9</sub>	2.912 (4)	N <sub>2</sub> -O <sub>2</sub>	2.890 (4)
W <sub>2</sub> -O <sub>6</sub>	2.838 (3)	N <sub>7</sub> -O <sub>9</sub>	2.897 (4)
W <sub>2</sub> -O <sub>4</sub>	2.931 (3)	N <sub>8</sub> -O <sub>1</sub>	2.809 (4)
N <sub>1</sub> -O <sub>3</sub>	2.804 (3)	N <sub>8</sub> -W <sub>2</sub>	2.854 (4)
N <sub>1</sub> -W <sub>1</sub>	2.828 (4)	N <sub>8</sub> -W <sub>1</sub>	2.932 (4)
N <sub>1</sub> -O <sub>10</sub>	2.875 (4)	N <sub>8</sub> -O <sub>10</sub>	2.989 (4)
N <sub>1</sub> -O <sub>8</sub>	2.945 (3)		

Bond angle	Value, deg	Bond angle	Value, deg
O <sub>5</sub> W <sub>1</sub> O <sub>7</sub>	127.1 (1)	O <sub>3</sub> N <sub>1</sub> W <sub>1</sub>	111.0 (1)
O <sub>5</sub> W <sub>1</sub> O <sub>9</sub>	89.3 (1)	O <sub>3</sub> N <sub>1</sub> O <sub>10</sub>	125.6 (1)
O <sub>5</sub> W <sub>1</sub> N <sub>1</sub>	115.7 (1)	O <sub>3</sub> N <sub>1</sub> O <sub>8</sub>	68.4 (1)
O <sub>6</sub> W <sub>1</sub> N <sub>3</sub>	109.4 (1)	W <sub>1</sub> N <sub>1</sub> O <sub>10</sub>	93.8 (1)
O <sub>7</sub> W <sub>1</sub> O <sub>9</sub>	56.7 (1)	W <sub>1</sub> N <sub>1</sub> O <sub>8</sub>	130.6 (1)
O <sub>7</sub> W <sub>1</sub> N <sub>1</sub>	110.7 (1)	O <sub>10</sub> N <sub>1</sub> O <sub>8</sub>	128.0 (1)
O <sub>7</sub> W <sub>1</sub> N <sub>3</sub>	94.8 (1)	O <sub>1</sub> N <sub>2</sub> O <sub>7</sub>	108.6 (1)
O <sub>9</sub> W <sub>1</sub> N <sub>1</sub>	151.2 (1)	O <sub>1</sub> N <sub>2</sub> O <sub>2</sub>	95.5 (1)
O <sub>9</sub> W <sub>1</sub> N <sub>3</sub>	68.0 (1)	O <sub>1</sub> N <sub>2</sub> O <sub>9</sub>	105.8 (1)
N <sub>1</sub> W <sub>1</sub> N <sub>3</sub>	89.3 (1)	O <sub>7</sub> N <sub>2</sub> O <sub>2</sub>	107.7 (1)
		O <sub>7</sub> N <sub>2</sub> O <sub>9</sub>	105.0 (1)
O <sub>6</sub> W <sub>2</sub> O <sub>4</sub>	138.8 (1)	O <sub>2</sub> N <sub>2</sub> O <sub>9</sub>	132.4 (1)
O <sub>4</sub> W <sub>2</sub> N <sub>3</sub>	92.0 (1)	O <sub>1</sub> N <sub>3</sub> W <sub>2</sub>	123.9 (1)
O <sub>6</sub> W <sub>2</sub> N <sub>3</sub>	106.5 (1)	O <sub>1</sub> N <sub>3</sub> W <sub>1</sub>	112.6 (1)
		O <sub>1</sub> N <sub>3</sub> O <sub>10</sub>	110.6 (1)
		W <sub>2</sub> N <sub>3</sub> O <sub>1</sub>	95.3 (1)
		W <sub>2</sub> N <sub>3</sub> O <sub>10</sub>	117.7 (1)
		W <sub>1</sub> N <sub>3</sub> O <sub>10</sub>	89.4 (1)

<sup>a</sup> The figures in parentheses are the estimated standard deviations in the last significant figure. W<sub>i</sub> is the symbol used for the i<sup>th</sup> water molecule.

Distances pertinent to the hydrogen bonding in crystalline (NH<sub>4</sub>)<sub>3</sub>[O<sub>2</sub>V(ox)<sub>2</sub>]·2H<sub>2</sub>O are given in Table IX. NH<sub>4</sub><sup>+</sup>-NH<sub>4</sub><sup>+</sup> separations range upward from 3.55 Å. All oxygen atoms of every structural type in the crystal are involved to some degree in the pattern of hydrogen bonding. There are otherwise no unusually short intermolecular contacts.

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