Stereochemistry of Dioxovanadium(V) Complexes. II. The Crystal and Molecular Structures of Ammonium (Dihydrogen ethylenediaminetetraacetato)dioxovanadate(V) Trihydrate[1]

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Abstract: The quantitative stereochemical description of the complex anion $[O_2VAH_2]^-$, the product of chelation of the dioxovanadium(V) ion, VO_2^+, by the dihydrogen ethylenediaminetetraacetate ion, AH_2^{2-}, comes from the determination by X-ray analysis of the atomic arrangement in crystalline $NH_4[O_2VAH_2]\cdot 3H_2O$. The VO_2 entity is in the cis configuration with an OVO angle of 107.1°; the V–O distances of 1.623 (2) and 1.657 (2) Å imply substantial double bonding. Long complexing bonds, 2.35 and 2.36 Å, extend from the vanadium to the two nitrogen atoms in positions trans to the oxo oxygen atoms; two carboxylate oxygen atoms at 2.00 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, $P2_1/c$, utilized by the crystalline arrangement. The monoclinic unit cell has $a = 7.600$, $b = 13.607$, $c = 17.400$ Å, and $\beta = 98.1°$. An experimental density of 1.65 g/cm³ compares favorably with a calculated density of 1.66 g/cm³ for a cell content of $4NH_4[O_2VAH_2]\cdot 3H_2O$. The intensities of all independent reflections having $(\sin\theta)/\lambda \lesssim 0.67$ Å^{-1} were measured with Mo Kα radiation by θ–2θ scanning on a computer-controlled four-circle Picker diffractometer; the 3975 data retained as statistically observable were employed for structure determination and refinement by Patterson, Fourier, and anisotropic least-squares techniques to a conventional R of 0.052.

The considerations which led us to undertake the integrated stereochemical studies of dioxovanadium(V) complexes that are reported at this time are detailed in the preceding paper.[2] The determination of the atomic arrangement and the stereochemistry of the complex anion in crystalline ammonium (dihydrogen ethylenediaminetetraacetato)dioxovanadate(V) trihydrate, $NH_4[O_2VAH_2]\cdot 3H_2O$, is described herein. The stereochemical relation of the singly charged $[O_2VAH_2]^-$ complex to the triply charged $[O_2VA]^{3-}$ species of the following paper[3] turns out to be surprisingly close, both qualitatively and quantitatively.

Experimental Section

Crystalline $NH_4[O_2VAH_2]\cdot 3H_2O$ was prepared by the method of Przyborowski, *et al.*[4] Specimens suitable for X-ray analysis were grown by allowing acetone to diffuse slowly into an aqueous solution of the salt. Precession photographs from the crystals displayed the symmetry and the extinctions uniquely demanded by the monoclinic space group[5] $P2_1/c$; this choice was supported by the lack of detectable piezoelectricity and by all subsequent developments during the determination of structure. Accurate lattice constants were obtained by the least-squares refinement[6] of the angular settings for 30 reflections on a Picker computer-controlled four-circle diffractometer, using the automatic centering routine supplied therewith; negative values of 2θ were represented by 11 of the settings. The resolved Mo Kα_1 component (λ 0.70926 Å) was employed. All measurements were made at the ambient laboratory temperature of 20 ± 1°. This procedure gave the lattice constants $a = 7.600$ (1), $b = 13.607$ (2), $c = 17.400$ (4) Å, $\cos\beta = -0.1413$ (2), or $\beta = 98.12°$. The experimental density of 1.65 g/cm³, measured by flotation, compares well with the calculated density of 1.66 g/cm³ for a cell content of $4NH_4[VO_2H_2A]\cdot 3H_2O$.

Intensity data were collected using Zr-filtered Mo Kα radiation at a takeoff angle of ~2.5° on a computer-controlled four-circle diffractometer; the specimen crystal was a sphere 0.42 mm in diameter. All independent reflections for which $(\sin\theta)/\lambda < 0.670$ Å^{-1} 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, checked periodically, showed a gradual decrease in intensity over the data collection interval of approximately 7%; the average decrease in their intensities *vs.* reflection number was used to correct for crystal decomposition. With a linear absorption coefficient of the crystal for Mo Kα radiation of only 0.68 mm^{-1} and, consequently, a μR for the spherical specimen of 0.14, no corrections for absorption were deemed necessary. Nor were extinction corrections included in the calculated reflection amplitudes. The intensity data were reduced to a set of relative squared amplitudes, $|F_o|^2$, by application of the standard Lorentz and polarization factor (Lp). Those data for which $|F_o| > 0.67\sigma_F$ were retained as objectively observed, σ_F being the standard deviation computed from $\sigma_F^2 = (Ct + k^2B)/4|F_o|^2(Lp)^2$, Ct the total decacount from the scan, k the ratio of scanning time to total background counting time, and B the total background count, in decacounts; 3975 independent reflections, 90% of the geometrically possible total, were thus retained and used for the determination and least-squares refinement of the structure.

A three-dimensional Patterson synthesis gave the position of the vanadium atom in the asymmetric unit of structure, and the positions of the remaining atoms were developed from Fourier syntheses with initial phasing based on the contribution of the vanadium atom to the structure amplitudes. The structure was then refined by block-diagonal least-squares[7] techniques using all of the data with individual isotropic thermal parameters for all atoms. The convergence of this refinement was followed by a Fourier difference synthesis from which approximate positions for all hydrogen atoms of the chelate were found along with those for many of the hydrogen atoms in the water molecules and in the ammonium ion. These hydrogen atoms were included in the subsequent refinements, in fixed positions, with thermal parameters taken from those of the associated atom. The apparent C–H distances ranged from 0.87 to 1.09 Å. Block-diagonal least-

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(1) This investigation was supported in part by National Science Foundation Grant No. GP-6710X, Grant No. 2-R01-GM09370 from the National Institutes of Health, General Medical Sciences, and by the Advanced Research Projects Agency.

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

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

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

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

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

(7) 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). Our local block-diagonal program REFINE, written by J. J. Park, was employed.

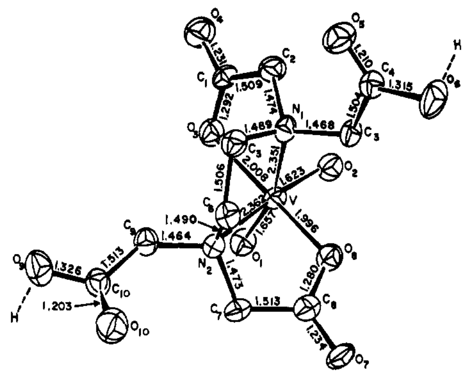

Figure 1. Model in perspective of the complex anion carrying the pertinent bond distances (Å). Atoms are represented as ellipsoids having the shapes and relative sizes concomitant with the data of Table II.

squares minimization was then carried to convergence using individual anisotropic thermal parameters for all atoms (except hydrogen). The final conventional R was 0.052, the weighted R was 0.063, and the estimated standard deviation of an observation of unit weight was 1.223. The final parameter shifts were less than 5% of their estimated standard deviation during the last cycle. Empirical weights ($w = 1/\sigma^2$) were calculated from $\sigma = \Sigma_0^3 a_n|F_o|^n$, the a_n's being the coefficients from the least-squares fitting of the curve, $||F_o| - |F_c|| = \Sigma_0^3 a_n|F_o|^n$; the values of $|F_c|$ came from a sensibly final description of the structure. A final difference Fourier synthesis had no peaks greater than 5% of that observed for a carbon atom.[8]

The parameters thus obtained for the three atoms in the VO_2 entity were then subjected to two further tests. The positional and the anisotropic thermal parameters of these atoms, and the scale factor as well, were allowed to vary in full-matrix least-squares refinement,[9] while the parameters of all other atoms were fixed at the values given by the block-diagonal least-squares refinement. No significant change resulted. The coordinates of these three atoms were then evaluated[10] from the peak positions in the Fourier synthesis of the observed amplitudes with corrections (nearly trivial) for the nonconvergence of the series.[10] No significant shift of an atomic position was to be found.

The atomic coordinates within the asymmetric unit are given in Table I and the associated thermal parameters in Table II. The positions of the hydrogen atoms are listed in Table III. All atoms are placed in the general positions[5] of $P2_1/c$: $\pm(x, y, z)$; $\pm(x, {}^1/_2 - y, {}^1/_2 + z)$.

Discussion of the Structural Results

The vanadium atom of the complex anion (Figure 1)[11] is octahedrally complexed to two oxo ligands, two nitrogen atoms, and two oxygen atoms from the two (unprotonated) glycinate arms of the chelating agent. Although a twofold axis cannot be required in the space group $P2_1/c$, the complex anion exhibits little departure from C_2 symmetry. The unique axis passes through the midpoint of the C–C bond (C_5–C_6 in Figure 1) in the ethylenediamine ring and the central atom.

Table I. Atomic Coordinates in Crystalline $NH_4[VO_2AH_2]\cdot 3H_2O^a$

Atom	10^4x	10^4y	10^4z
O_1	−413 (3)	1468 (1)	1446 (1)
O_2	2432 (3)	1823 (2)	2466 (1)
O_3	−604 (2)	1024 (1)	2949 (1)
O_4	−618 (3)	1266 (2)	4215 (1)
O_5	4609 (3)	−1176 (2)	4314 (1)
O_6	6804 (3)	−977 (2)	3608 (1)
O_7	2951 (3)	−267 (2)	3438 (1)
O_8	2730 (2)	413 (1)	1478 (1)
O_9	4603 (3)	−1591 (2)	1528 (1)
O_{10}	−2340 (3)	−2104 (2)	954 (1)
N_1	2232 (3)	−98 (2)	3141 (1)
N_2	−74 (3)	−598 (2)	1733 (1)
C_1	83 (3)	948 (2)	3670 (2)
C_2	1865 (4)	444 (2)	3835 (2)
C_3	4142 (3)	229 (2)	3120 (2)
C_4	5169 (3)	840 (2)	3752 (2)
C_5	1223 (3)	−1038 (2)	3064 (2)
C_6	921 (4)	−1364 (2)	2229 (2)
C_7	390 (4)	−651 (2)	940 (2)
C_8	2155 (3)	−150 (2)	908 (2)
C_9	−1990 (3)	−648 (2)	1758 (2)
C_{10}	−2949 (4)	−1532 (2)	1372 (2)
NH_4	5116 (4)	+1538 (2)	569 (2)
$W_1{}^b$	3916 (3)	−3013 (2)	2848 (1)
$W_2{}^b$	−1359 (3)	−2255 (2)	4444 (1)
$W_3{}^b$	6098 (4)	1888 (2)	4218 (2)
	10^5x	10^5y	10^5z
V	10317 (6)	9685 (3)	21393 (3)

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

Table IV details the parameters[12] of the coordination octahedron and Table V those of the chelation framework. Chelation gives rise to three five-membered rings, the ethylenediamine and two glycinato rings; the two carboxylic acid (or glycine) arms remain uncoordinated. The quasi-planar glycinato rings are each nearly perpendicular to the plane formed by the metal and the two nitrogen atoms. Carboxylate oxygen–vanadium lengths are 2.008 and 1.996 Å, while vanadium–nitrogen bond lengths are 2.351 and 2.362 Å; the difference between the mean of the V–O and the V–N distances is 0.35 Å. Since a difference of only ~0.04 Å in M–N and M–O distances is predicted from consideration of the covalent radii of oxygen and nitrogen,[13] and is found in the $[CoA]^-$ ion[14] and in the $[Ni(OH_2)AH_2]$ complex,[15] the V–O bond can be taken as much stronger than the V–N bond. This difference in the M–N and M–O bond lengths parallels that observed in the seven-coordinate complex,[16] $[H_2OFeA]^-$, formed by the high-spin ferric ion. Indeed, the V–N bond length is close to the maximum value, the 2.377 Å recorded for the seven-coordinate $[H_2O$-

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(8) A table of observed and calculated structure amplitudes from this analysis has been deposited as Document No. NAPS-01308 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.

(9) 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.

(10) 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. See also D. M. Collins and J. L. Hoard, *ibid.*, 92, 3761 (1970).

(11) C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," 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) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(14) H. A. Weakliem and J. L. Hoard, *J. Amer. Chem. Soc.*, **81**, 549 (1959).

(15) G. S. Smith and J. L. Hoard, *ibid.*, **81**, 556 (1959).

(16) J. L. Hoard, M. D. Lind, and J. V. Silverton, *ibid.*, **83**, 2770 (1961); M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, **3**, 34 (1964).

Table II. Thermal Parameters[a]

Atom type	Anisotropic parameters, Å² B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B, Å² [b]
V	2.09 (2)	1.49 (1)	2.14 (1)	−0.02 (1)	0.71 (1)	0.06 (1)	1.82
O_1	2.89 (8)	2.59 (8)	2.95 (8)	0.38 (7)	0.40 (7)	0.53 (7)	2.76
O_2	3.12 (9)	2.35 (8)	3.52 (9)	−0.51 (7)	0.92 (9)	−0.40 (7)	2.86
O_3	2.10 (7)	2.40 (7)	2.45 (7)	0.40 (6)	0.55 (6)	−0.02 (6)	2.26
O_4	2.90 (9)	5.07 (12)	2.95 (9)	1.06 (8)	0.91 (7)	−0.87 (8)	3.19
O_5	3.03 (9)	4.65 (11)	3.01 (9)	0.85 (8)	0.90 (7)	1.17 (8)	3.27
O_6	2.16 (8)	5.58 (13)	4.23 (11)	1.12 (8)	0.96 (7)	1.87 (10)	3.35
O_7	3.15 (9)	4.12 (10)	2.59 (8)	0.29 (8)	1.31 (7)	−0.07 (8)	2.99
O_8	2.38 (7)	2.48 (8)	2.56 (8)	−0.14 (6)	0.87 (6)	−0.11 (6)	2.38
O_9	2.13 (8)	3.37 (9)	4.09 (10)	−0.11 (7)	0.32 (7)	−0.48 (8)	3.08
O_{10}	3.79 (10)	3.22 (9)	4.07 (10)	−0.91 (8)	1.38 (8)	−1.27 (8)	3.36
N_1	1.76 (7)	1.86 (8)	2.16 (8)	0.19 (6)	0.53 (6)	−0.03 (6)	1.88
N_2	1.89 (8)	1.92 (8)	2.03 (8)	0.00 (6)	0.48 (6)	0.08 (6)	1.92
C_1	2.13 (10)	2.55 (10)	2.27 (10)	0.16 (8)	0.71 (8)	−0.29 (8)	2.22
C_2	2.33 (10)	2.67 (11)	2.25 (10)	0.37 (8)	0.67 (8)	−0.32 (9)	2.31
C_3	1.77 (9)	2.37 (10)	2.52 (10)	0.17 (8)	0.73 (8)	0.27 (8)	2.11
C_4	2.03 (10)	2.60 (11)	2.52 (10)	0.02 (8)	0.38 (8)	−0.04 (9)	2.36
C_5	2.16 (9)	1.82 (9)	2.32 (10)	0.00 (8)	0.46 (8)	0.45 (8)	2.04
C_6	2.41 (10)	1.48 (8)	2.70 (11)	0.18 (8)	0.30 (8)	−0.03 (8)	2.12
C_7	2.62 (11)	3.07 (12)	2.01 (10)	−0.25 (9)	0.61 (8)	−0.19 (9)	2.47
C_8	2.44 (10)	2.26 (10)	2.21 (10)	0.42 (8)	0.55 (8)	0.27 (8)	2.24
C_9	1.92 (9)	2.16 (10)	2.55 (10)	0.12 (8)	0.39 (8)	−0.05 (8)	2.19
C_{10}	2.29 (10)	2.29 (10)	2.40 (10)	−0.21 (8)	0.34 (8)	0.30 (8)	2.31
NH_4	4.6 (1)	3.2 (1)	3.8 (1)	−0.3 (1)	1.5 (1)	−0.1 (1)	3.4
W_1	3.3 (1)	4.9 (1)	4.1 (1)	0.6 (1)	0.9 (1)	0.4 (1)	4.0
W_2	4.4 (1)	5.1 (1)	3.1 (1)	2.1 (1)	0.5 (1)	0.2 (1)	3.8
W_3	4.0 (1)	6.7 (2)	5.4 (1)	2.7 (1)	1.8 (1)	2.6 (1)	4.4

[a] The number in parentheses that follows each B_{ij} value is the estimated standard deviation in the last significant figure. The B_{ij} (Å²) are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [b] Isotropic thermal parameter calculated from $B = 4\cdot[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Fractional Coordinates of the Hydrogen Atoms

Atom[a]	10^3x	10^3y	10^3z
HO_9	−510	−208	117
HO_6	733	−140	400
H_1C_2	173	2	420
H_2C_2	250	98	382
H_1C_3	463	42	306
H_2C_3	432	−45	272
H_1C_5	−3	−82	324
H_2C_5	184	−158	341
H_1C_6	38	−197	217
H_2C_6	217	−152	204
H_1C_7	−42	−29	67
H_2C_7	38	−138	66
H_1C_9	−253	−15	150
H_2C_9	−213	−59	228
H_1NH_4	594	158	20
H_2NH_4	446	95	48
H_1W_1	499	−310	260
H_1W_2	−44	−272	420
W_1W_3	743	166	421
H_2W_3	578	163	471

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

Table IV. Parameters of the Coordination Octahedron

A. Bond and Edge Lengths[a]

Type	Length, Å	Type	Length, Å
$O_1{-}O_2$	2.640 (3)	$N_1{-}N_2$	2.885 (3)
$O_1{-}O_3$	2.707 (3)	$O_8{-}N_1$	3.051 (3)
$O_1{-}O_8$	2.782 (3)	$O_8{-}N_2$	2.627 (3)
$O_1{-}N_2$	2.861 (3)	$V{-}O_2$	1.623 (2)
$O_2{-}O_3$	2.786 (3)	$V{-}O_1$	1.657 (2)
$O_2{-}O_8$	2.607 (3)	$V{-}O_8$	1.996 (2)
$O_2{-}N_1$	2.878 (3)	$V{-}O_3$	2.008 (2)
$O_3{-}N_1$	2.624 (3)	$V{-}N_1$	2.351 (2)
$O_3{-}N_2$	3.123 (3)	$V{-}N_2$	2.362 (3)

B. Bond Angles Subtended at the V(V) Atom

Type	Angle, deg	Type	Angle, deg
O_2VO_1	107.14 (10)	O_1VN_2	88.95 (9)
O_2VO_8	91.57 (9)	O_8VO_3	159.07 (9)
O_2VO_3	99.66 (9)	O_8VN_1	88.79 (8)
O_2VN_1	90.90 (8)	O_8VN_2	73.59 (8)
O_2VN_2	159.81 (10)	O_3VN_1	73.53 (7)
O_1VO_8	98.77 (9)	O_3VN_2	90.83 (8)
O_1VO_3	94.74 (8)	N_1VN_2	75.49 (7)
O_1VN_1	160.11 (8)		

[a] The estimated standard deviations are given in parentheses.

MnA]$^{2-}$ chelate of high-spin manganese(II),[17] that is observed in EDTA complexes of the first transition series. The averaged Mn–O bond distance in the manganese chelate is only 0.13 Å below the Mn–N value, thus suggesting the retention of a quasispherical behavior on the part of the Mn^{2+} ion that is notably absent in the VO_2^+ species. In view of the strong trans effect exerted by the bonding to the two oxo ligands of the VO_2 group in the $[O_2V(ox)_2]^{3-}$ complex,[2] it appears that ~0.20 Å of the 0.35 Å difference between the bond distances to nitrogen and carboxylate oxygen in the $[O_2VAH_2]^-$ ion should be ascribed to this same source. The substantial remainder of ~0.15 Å is indicative of the low affinity of the VO_2^+ ion for amino nitrogen relative to that for carboxylate oxygen; shorter V–N bonds, indeed, would give some reduction of strain within the glycinato rings of the chelate (*vide infra*).

Averaged distances for standard types of bonds in the complex anion are C–N = 1.476 (3) Å,[18] C–C = 1.510 (4) Å in glycinato rings, and 1.506 (4) Å in the

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(17) S. Richards, B. Pederson, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, 3, 27 (1964).

(18) The figure in parentheses is the root-mean-square value of the individual standard deviations.

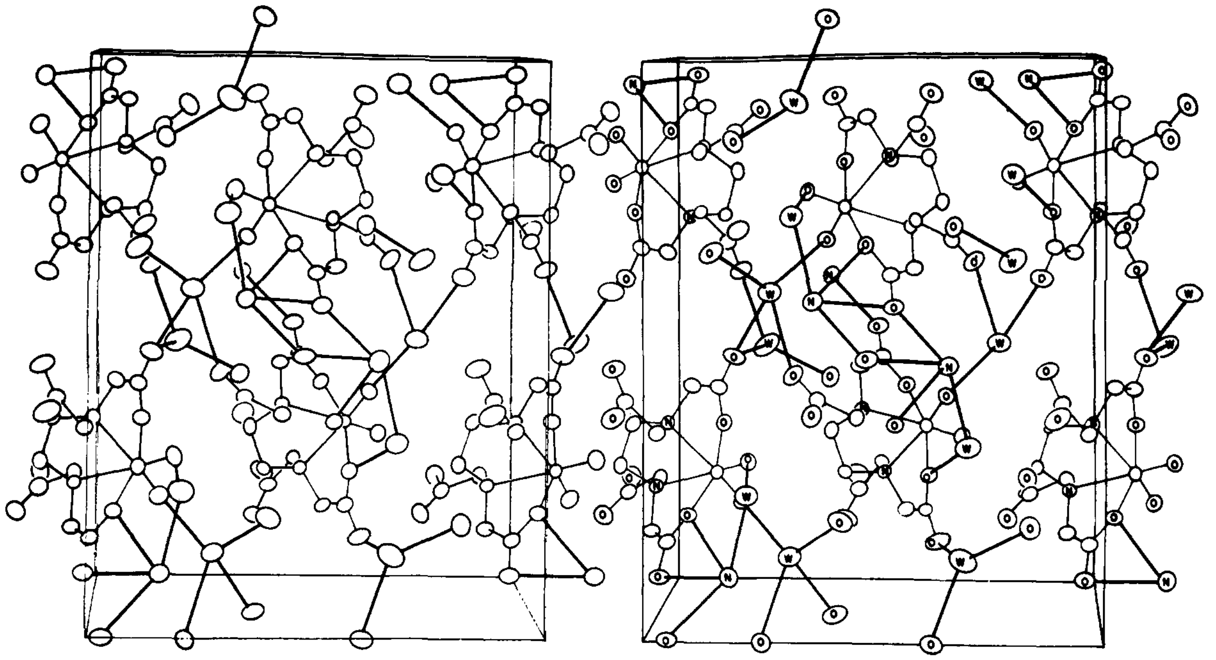

Figure 2. Stereoscopic representation of the contents of the unit cell. (The cheapest sort of 3D viewer suffices to bring out the three-dimensional detail.)

ethylenediamine ring. These values are typical of those found in other EDTA complexes. The C–O bond lengths within the carboxylate groups vary accordingly as the oxygen atoms, O_c and O_u, are or are not coordinated to the metal atom; the averaged distances, $C-O_c$ = 1.286 (3), $C-O_u$ = 1.232 (2) Å, in this complex correspond to strong $M-O_c$ interaction. Similarly, the two pairings of averaged C–O bond lengths in the uncoordinated carboxylic acid groups, 1.321 (3) and 1.207 (3) Å, correspond to the protonated and unprotonated oxygens of the CH_2COOH arms, respectively. The approximate positions of the protons attached to O_9 and O_6, clearly indicated in the difference Fourier synthesis, confirm this assignment. Both the carboxylate and the carboxylic acid groups are essentially planar; the sum of the bond angles subtended at the central carbon atom is 360 ± 0.1° for every such group.

Table V. Bond Parameters of the EDTA Chelate

	A. Bond Lengths,[a] Å		
Bond	Length	Bond	Length
O_3–C_1	1.292 (3)	N_2–C_6	1.490 (3)
O_4–C_1	1.231 (3)	N_2–C_7	1.473 (3)
C_1–C_2	1.509 (4)	N_2–C_9	1.464 (3)
N_1–C_2	1.474 (3)	C_7–C_8	1.513 (4)
N_1–C_3	1.468 (3)	C_8–O_8	1.280 (3)
N_1–C_5	1.489 (3)	C_8–O_7	1.234 (3)
C_3–C_4	1.504 (4)	C_9–C_{10}	1.513 (4)
C_4–O_6	1.315 (3)	C_{10}–O_9	1.326 (3)
C_4–O_5	1.210 (4)	C_{10}–O_{10}	1.203 (4)
C_5–C_6	1.506 (4)		

	B. Bond Angles,[a] Deg		
Type	Value	Type	Value
$N_2C_6H_5$	110.4 (2)	$N_1C_3C_4$	117.5 (2)
$N_1C_5C_6$	110.3 (2)	$O_5C_4O_6$	123.3 (3)
$N_2C_7C_8$	110.1 (2)	$O_5C_4C_3$	126.4 (2)
$O_7C_8O_8$	122.8 (3)	$O_6C_4C_3$	110.2 (2)
$O_7C_8C_7$	120.6 (2)	$C_3N_1C_2$	112.5 (2)
$O_8C_8C_7$	116.6 (2)	$C_3N_1C_5$	113.0 (2)
C_8O_8V	119.7 (2)	C_3N_1V	109.8 (1)
$N_2C_9C_{10}$	116.2 (2)	$C_2N_1C_5$	110.4 (2)
$O_{10}C_{10}O_9$	122.8 (3)	C_2N_1V	101.6 (1)
$O_{10}C_{10}C_9$	125.5 (2)	C_5N_1V	108.8 (1)
$O_9C_{10}C_9$	111.7 (2)	$C_9N_2C_7$	113.3 (2)
VO_3C_1	118.2 (2)	$C_9N_2C_6$	112.1 (2)
$O_4C_1O_3$	124.1 (2)	C_9N_2V	110.2 (2)
$O_4C_1C_2$	119.2 (2)	$C_7N_2C_6$	109.8 (2)
$O_3C_1C_2$	116.7 (2)	C_7N_2V	101.7 (2)
$N_1C_2C_1$	109.9 (2)	C_6N_2V	109.2 (2)

[a] The estimated standard deviations are given in parentheses.

The chelated framework employs glycinato rings of the R type,[19] meaning that the complexing bonds ($V-O_3$ and $V-O_8$) effect closure of these rings roughly along the normal to the plane defined by the central metal and the two nitrogen atoms. Closure effected by a complexing bond that lies nearly or exactly within the VNN plane gives a ring of the G type that, in an EDTA complex, generally carries significantly more strain than the R alternative. Assuming octahedral coordination to be preserved, just two geometric isomers of the $[O_2VAH_2]^-$ complex are both chemically and stereochemically plausible on an *a priori* basis: a trans configuration for the VO_2 group requires the two glycinato rings to be of the G type, whereas the observed cis geometry of the VO_2 group calls for R rings. It is clear, nonetheless, that the R rings in the $[O_2VAH_2]^-$ ion are quite as strained as are the G rings in several other EDTA chelates. A gross measure of the combined folding and kinking in a five-membered glycinato ring is provided by the departure of the sum of the interior angles from the 540° corresponding to planarity. Values for this sum in the $[O_2VAH_2]^-$ complex are 519.9 and 521.7°, as compared with averaged values for G rings of 524.7° in $[H_2OFeA]^-$, 518.2° in $[H_2OMnA]^{2-}$, and 524.7° in $[CoA]^-$, and with values for R rings that run 11–13° higher in these same chelates.[14,16,17]

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(19) See especially ref 14 and also ref 15 and 16.

Angular strain is particularly apparent in the O_cVN angles (73.5, 73.6°) and the VNC angles (101.6, 101.7°) within the glycinato rings, and, of course, in the NVN angle (75.5°) of the ethylenediamine ring. The larger part of the strain in the chelation framework is the stereochemical consequence of the very long V–N bonds that are thus extended for reasons noted above. There is, however, a further direct contribution to strain from the geometry of the VO_2 entity, inasmuch as this necessarily leads to tight packing relations with the neighboring O_c atoms that must be relieved by having the O_cVO_c angle decrease to 159.1°; this atypically small angle at the junction of two R rings is partially responsible for the small O_cVN ring angles.

It seems that the alternative stereoisomer containing a linear VO_2 group and glycinato rings of the G type might well have significantly shorter V–N bonds, a less strained chelation framework, and generally easier packing relations than does the observed stereoisomeric form. We must conclude that the stereochemistry of the EDTA chelates, as of the oxalato complex,[2] is dominated by the preference of the VO_2 group for a cis configuration that displays little variation in either bond angle or bond distances from one complex to another. The refinement of the $NH_4[O_2VAH_2]\cdot 3H_2O$ structure (*vide supra*) yields a VO_2 group having an OVO angle of 107.14 (10)° and the respective $V–O_1$ and $V–O_2$ bond lengths of 1.657 (2) and 1.623 (2) Å. The difference of 0.034 Å in the V–O distances, small though it be, is significant according to the standard statistical tests,[20] and it is not obviously attributable to specific interactions with any part of the asymmetric environment nor to the packing relations within the $[O_2VAH_2]^-$ complex. Similar, though somewhat smaller, apparent differences in these V–O distances are observed also in the $[O_2V(ox)_2]^{3-}$ and $[O_2VA]^{3-}$ ions.[2,3] The physical reality of such minor asymmetry in the unconstrained anions is certainly open to question in the absence of any obvious electronic basis for anticipating nonequivalence of the bonds. The probable source of most, if not all, of the observed differences is discussed in paper III following presentation of the structural data for the $[O_2VA]^{3-}$ anion.[3]

Table VI lists data for the observed pattern of hydrogen bonding in crystalline $NH_4[O_2VAH_2]\cdot 3H_2O$. A diagram of the contents of the unit cell is given in Figure 2. The bulky anions are bound into a three-dimensional framework by hydrogen bonds utilizing the ammonium ion, the carboxylic acid groups, and the water molecules (W_1, W_2, and W_3). The ammonium ion coordinates three carboxylate oxygen atoms and a water molecule. 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.

Table VI. Hydrogen-Bonding Parameters[a]

Bond	Length, Å	Bond	Length, Å
$NH_4–W_1$	2.815 (4)	$W_2–O_1$	2.797 (3)
$NH_4–O_7'$	2.887 (4)	$W_2–O_4$	2.919 (3)
$NH_4–O_7$	2.952 (4)	$W_2–O_{10}$	2.961 (3)
$NH_4–O_8$	2.991 (4)	$W_3–O_9H$	2.616 (4)
$W_1–O_2$	2.912 (4)	$W_3–O_4$	2.636 (3)
$W_1–O_3$	2.998 (3)	$W_3–O_5$	2.853 (4)
$W_2–O_6H$	2.553 (3)		

Bond angle	Value, deg	Bond angle	Value, deg
$W_1NH_4O_7'$	125.8 (1)	$O_6W_2O_1$	112.0 (1)
$W_1NH_4O_7$	112.0 (1)	$O_6W_2O_4$	108.6 (1)
$W_1NH_4O_8$	71.8 (1)	$O_6W_2O_{10}$	121.3 (1)
$O_7'NH_4O_7$	75.3 (1)	$O_1W_2O_4$	119.7 (1)
$O_7'NH_4O_8$	112.2 (1)	$O_1W_2O_{10}$	120.7 (1)
$O_7NH_4O_8$	43.6 (1)	$O_4W_2O_{10}$	66.0 (1)
$NH_4W_1O_2$	92.4 (1)	$O_9W_3O_4$	126.7 (1)
$NH_4W_1O_3$	116.4 (1)	$O_9W_3O_5$	126.1 (1)
$O_2W_1O_3$	129.8 (1)	$O_4W_3O_5$	101.0 (1)

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

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(20) H. Lipson and W. Cochran, "The Crystalline State," Vol. III, "The Determination of Crystal Structures," G. Bell and Sons, Ltd., London, 1966, p 356.