but at the present time a detailed assignment of this region is not possible.

Registry No. $K_4Mo(CN)_7\cdot 2H_2O$, 37838-58-7; $K_4Mo(CN)_7$, 37838-59-8; $Cs_4Mo(CN)_7\cdot xH_2O$, 37838-60-1.

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Contribution from the Department of Chemistry, Simon Fraser University, Burnaby 2, British Columbia, Canada

Crystal Structure at −100° of Ammonium Oxoperoxo(pyridine-2,6-dicarboxylato)vanadate(V) Hydrate, $NH_4[VO(O_2)(H_2O)(C_5H_3N(COO)_2)]\cdot xH_2O$ ($x \approx 1.3$)

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The crystal structure at −100° of the compound $NH_4[VO(O_2)(H_2O)(C_5H_3N(COO)_2)]\cdot xH_2O$ ($x \approx 1.3$) has been determined from three-dimensional X-ray intensity data collected by counter methods on a computer-controlled diffractometer using a Joule-Thomson low-temperature device. The compound crystallizes in the monoclinic space group C_2/c with eight formula units in a cell having lattice constants $a = 11.307$ (2) Å, $b = 25.490$ (5) Å, $c = 8.316$ (2) Å, and $\beta = 96.90$ (1)° (at temperature −100 (2)°). The structure was solved by direct methods and refinement by full-matrix least-squares methods has given a conventional R value of 3.1% for the 1331 observed reflections. The structure is comprised of two crystallographically different ammonium ions (one lying on a twofold axis and the other on a center of symmetry) and a vanadium-based anion. These ions are held together by both electrostatic forces and extensive hydrogen bonding. The vanadium atom environment is a seven-coordinate distorted pentagonal bipyramid, with a vanadyl oxygen and a water molecule at the apices and a peroxy group, the nitrogen from the pyridine ring, and one oxygen atom from each carboxylate group forming an approximate pentagonal plane. The vanadium atom is displaced 0.25 Å from the "plane" toward the vanadyl oxygen atom. Interatomic distances within the anion are 1.870 (2) and 1.872 (2) Å for the $V-O_{peroxo}$ bonds, 1.579 (2) Å for the V=O bond, 2.053 (2) and 2.064 (2) Å for the $V-O_{carboxylate}$ distances, 2.211 (2) Å for the $V-O_{water}$ distance, 2.088 (2) Å for the V–N distance, and 1.441 (2) Å for the $O-O_{peroxo}$ bond.

Introduction

Structural data on transition metal-peroxo compounds have recently been extended to include the peroxovanadates with the elucidation of the structures of $NH_4[VO(O_2)_2(NH_3)]$,[1] $(NH_4)_4[O(VO(O_2)_2)_2]$,[2] and $(NH_4)_3[V(O_2)_4]$.[2,3] The mononuclear oxodiperoxoamminevanadate(V) anion was shown[1] to have a distorted pentagonal-pyramidal geometry, analogous to the oxodiperoxopyridinechromium(VI) complex,[4] $CrO(O_2)_2(C_5H_5N)$, while the dinuclear $[O(VO(O_2)_2)_2]^{4-}$ anion was demonstrated[2] to have distorted pentagonal-bipyramidal coordination geometry around each vanadium atom. The tetraperoxovanadate(V) anion[2,3] has a quasidodecahedral structure as does the tetraperoxoniobate(V) compound,[5] $KMg[Nb(O_2)_4]\cdot 7H_2O$, and the tetraperoxochromium(V) compound,[6] $K_3[Cr(O_2)_4]$. It has been proposed[7] that the triperoxovanadates could have eight-coordination of the metal similar to that observed in the peroxoniobate(V) compounds $K[Nb(O_2)_3(C_{12}H_8N_2)]\cdot 3H_2O$,[8] $K[Nb(O_2)_3(C_{12}H_8N_2)]\cdot 3H_2O\cdot H_2O_2$,[8] and $(NH_4)_3[Nb(O_2)_2(C_2O_4)_2]\cdot H_2O$.[9] To continue the structural study of peroxovanadates, the crystal structure of the monoperoxy complex $NH_4[VO(O_2)(H_2O)(C_5H_3N(COO)_2)]\cdot xH_2O$ ($x \approx 1.3$) has been determined and work on the compounds $K_3[VO(O_2)(C_2O_4)_2]$ and $K_3[VO(O_2)_2(C_2O_4)]$ is in progress.

Experimental Section

The preparation of ammonium oxoperoxo(pyridine-2,6-dicarboxylato)vanadate(V) hydrate, $NH_4[VO(O_2)(H_2O)(C_5H_3N(COO)_2)]\cdot xH_2O$ ($x \approx 1.3$), as was first reported by Hartkamp[10,11] was used. This method involved the reaction of ammonium vanadate, pyridine-2,6-dicarboxylic acid, and hydrogen peroxide in the ratio 1:1:1 to give dark red crystals. A crystal fragment of maximum dimensions 0.46 × 0.25 × 0.34 mm in the directions a, b, and c, respectively, was selected and mounted with the longest dimension approximately parallel to the rotation axis. This single crystal yielded the complete diffraction data (obtained over a period of *ca.* 2 weeks); no decomposition was observed.

Weissenberg photographs of the $0kl$–$3kl$ layers and precession photographs of the $hk0$–$hk1$ and $h0l$–$h2l$ layers using Cu Kα radiation showed absences for hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$ ($h = 2n + 1$). This, combined with Laue symmetry ($2/m$), indicated the space group as either Cc or C_2/c. (Our work indicates that the centrosymmetric space group C_2/c provides a satisfactory model.)

Crystal Data

Data are as follows for $NH_4[VO(O_2)(H_2O)(C_5H_3N(COO)_2)]\cdot xH_2O$ ($x = 1.311$ (8)): mol wt 323.6, monoclinic, $a = 11.307$ (2) Å, $b = 25.490$ (5) Å, $c = 8.316$ (2) Å, $\beta = 96.90$ (1)°, $V = 2379.42$ (1) Å^3 (at −100 (2)°), $d_m = 1.74$ (5) g/cm^3 (at 22°), $Z = 8$, $d_c = 1.79$ g/cm^3 (at 22°), $d_c = 1.83$ g/cm^3 (at −100°), $F(000) = 1320$, μ(Mo Kα) 10.0 cm^{-1}, λ(Cu Kα) 1.5418 Å, λ(Mo Kα_1) 0.70926 Å.

It was decided that the data be collected at low temperature because of the rapid falloff in the average reflection's intensity with increasing 2θ. To measure the reflection intensities for the unique set of data at −100°, an Air Products and Chemicals

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Cryo-Tip refrigerator was adapted for use with the Picker four-circle diffractometer, automated with the FACS-I system, using niobium-filtered Mo Kα radiation, $\lambda\bar{\alpha}$ 0.71069 Å, and a scintillation detector with pulse-height analysis. (The Cryo-Tip refrigerator is a subminiature single-fluid, open-cycle Joule-Thomson cooler specifically designed for use in single-crystal X-ray diffraction studies.) Cell dimensions were determined by least-squares refinement of 17 reflections whose 2θ values were greater than 38° and accurately measured at -100 (2)° on the diffractometer using an automatic centering routine with a takeoff angle of 1.0°. In order to eliminate intrinsic multiple reflections, the crystal was deliberately misaligned so that it had a general orientation. During data collection, the takeoff angle was 3.1° and the detector with an aperature 5.0 mm high and 4.0 mm wide was positioned 28 cm from the crystal. Measurements for the set of data with $2\theta \leqslant 45°$ were made at a scan rate of 2°/min in 2θ with a symmetrical θ–2θ scan width of $1.3° + (180/\pi)(2 \tan \theta)(\delta\lambda/\lambda)°$ (to account for the α_1–α_2 splitting). The background intensity was determined by the normalization of two stationary background counts of 10 sec measured at both scan limits. Of the 1562 intensities measured, 1331 were above 1.8σ and were considered as observed reflections ($\sigma = \sqrt{N}$ where N is the scan count plus the total normalized background count). Two standard reflections were measured every 60 reflections and retained a constancy within 2% over the entire data collection. Lorentz and polarization factors were applied to give the structure factors in the usual manner. No absorption corrections were considered necessary since the absorption coefficient for Mo Kα radiation was low (10.0 cm^{-1}).

Structure Determination

The symbolic addition procedure[12,13] was used to initiate the solution of the structure in space group C_2/c. E values were determined and four reflections were assigned phases (0,12,0, $E = +4.71$; 352, $E = +3.39$; 1,23,3, $E = -3.32$; 606, $E = -2.67$); all signs could be deduced in terms of one variable. Of the two F_o Fourier maps using those reflections with $E \geqslant 2.5$, one gave reasonable positions for the vanadium atom and the majority of the nonhydrogen atoms and, when the coordinates and isotropic temperature factors for those atoms were refined by full-matrix least-squares techniques, the R value[14] was 0.32. A second electron density map revealed the remaining nonhydrogen atoms, and further refinement followed by electron density difference syntheses located most of the hydrogen atoms and indicated anisotropic thermal motion for all (nonhydrogen) atoms. Refinement was carried out using the data with $(\sin \theta)/\lambda < 0.40$, and the agreement at this point was $R = 0.039$. A close examination of electron density difference maps indicated that the water molecule on the twofold position had only partial occupancy (see below) and that some of the atomic scattering curves might require adjustment to compensate for atomic charge (as was the case for $NH_4[VO(O_2)_2(NH_3)]$[1]). The occupancy for atom O(10) was allowed to vary and curves corresponding to V^{3+} (for the vanadium atom), O^- (for the peroxo and coordinated carboxylato oxygen atoms), and N^+ (for the ammonium nitrogen atoms) were introduced to give an R value of 0.033. The remaining hydrogen atom positions (around N(3)) were calculated on the basis of sensible hydrogen bonding, given appropriate occupancies, and allowed to refine (on all of the data) with fixed isotropic temperature factors giving a final unweighted R value of 0.031 and a weighted R_w value[14] of 0.041.

Since our model involved two features which needed careful justification, *viz.*, partial occupancy of a water molecule and disorder of a half-multiplicity ammonium ion, it was considered prudent to examine the evidence fully. On the basis of residual electron density in the difference map, it was not clear whether there was a water molecule on the twofold position and an ammonium ion on the center of symmetry, or *vice versa*. It was decided that the former resulted in the more satisfactory model for the following reasons. First, disorder on a center of symmetry is more chemically reasonable for an ammonium ion than it is for a water molecule. (Though phase changes at low temperature commonly remove this feature.[15a]) Second, two peaks which could correspond to the hydrogen atoms were located near the twofold axis position whereas numerous appropriate peaks were observed about the center of symmetry position. Third, the hydrogen bonding to the twofold position does not appear to be as strong as the hydrogen bonding to the center of symmetry position (on the basis of contact distances and angles). This could explain the nonstoichiometry of the water of crystallization. Finally, since this model gave the better agreement ($R = 0.031$ as opposed to 0.033), then on the basis of Hamilton's criterion[15b] it is the better model.

The data were initially given unit weights, but refinement to convergence was carried out with $\sigma = \sqrt{AB/F}$ ($w = 1/\sigma^2$, $A = 0.34$, $B = 10.0$) for $F \leqslant 10.0$ and $\sigma = \sqrt{AF/B}$ for $F > 10.0$. A was adjusted such that $[\Sigma w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$ (where (NO – NV) is the number of observations minus the number of variables) was 1.00. The unobserved reflections were excluded from the refinement. It was observed that the I_o value for the $20\bar{2}$ reflection was underestimated by approximately 40%. This may be due to coincidence losses and/or extinction; the reflection was arbitrarily increased to bring it to good agreement with F_c.

A final electron density difference synthesis showed, as its major positive feature, a pair of peaks of heights 0.40 and 0.36 e/Å^3 (at 1.20 and 1.25 Å, respectively), positioned nearly linearly around the vanadium atom and making an angle of approximately 12° to the O(4)–O(1) vector. These peaks are attributed to uncorrected anisotropic motion of the vanadium atom. The largest negative feature of the final difference map was a trough of depth -0.25 e/Å^3 located at the center of the pyridine ring.

The scattering factors for the nonhydrogen atoms, including anomolous scattering for the vanadium atom, were taken from ref 16a; the scattering factors for the hydrogen atom were taken from a table of Stewart, *et al.*[16b] The N^+ scattering curve was obtained by averaging the scattering curves for C and O^{2+}; this curve has been used previously[1] and differs from the nitrogen curve by no more than 0.05 above $(\sin \theta)/\lambda = 0.35$.

Results

The positional and thermal parameters obtained in the final least-squares refinement cycle are listed in Table I, while the interatomic distances and angles are given in Table II. Errors in interatomic distances and angles were calculated from the inverse matrix and include correlation between atomic parameters and errors in the cell dimensions. The equations of the various planes within the anion and deviations of the atoms comprising those planes are given in Table III. Table IV gives the angles between the planes. Measured and calculated structure factors are available.[17]

Analysis of the thermal motion[18] of the atoms in the anion (excluding O(4), O(6), and O(8), which are bound to only one other atom within the anion) indicate that their motion can best be described in terms of a rigid body. This motion, however, does not have a significant effect on the bond lengths since the corrected values were in no case greater than one standard deviation. Table V indicates the principal axes of T and ω, and the rms ΔU_{ij} is 0.002 (2) Å^2.

Figure 1 shows the anion with the nonhydrogen atoms as 50% probability thermal ellipsoids, while Figure 2 is a projection down the c axis of the unit cell with hydrogen bonding shown as dashed lines.

Discussion

The compound $NH_4[VO(O_2)(H_2O)(C_5H_3N(COO)_2)]\cdot$

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(14) R is defined as $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. R_w is defined as $[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

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(17) A listing of measured and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-829.

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Table I. Final Positional and Thermal Parameters for $(NH_4)[VO(O_2)(H_2O)(C_5H_3N(COO)_2)] \cdot xH_2O$ ($x \approx 1.3$)

Atom	x/a	y/b	z/c	U, Å^2
V	0.2230 (1)[a]	0.0763 (1)	0.1915 (1)	b
O(1)	0.1433 (2)	0.0704 (1)	0.3339 (3)	b
O(2)	0.3036 (2)	0.0121 (1)	0.1985 (3)	b
O(3)	0.1974 (2)	0.0122 (1)	0.0839 (3)	b
O(4)	0.3286 (2)	0.0963 (1)	−0.0072 (3)	b
O(5)	0.3759 (2)	0.0980 (1)	0.3345 (3)	b
O(6)	0.4827 (2)	0.1626 (1)	0.4616 (3)	b
O(7)	0.0842 (2)	0.0989 (1)	0.0213 (3)	b
O(8)	−0.0456 (2)	0.1626 (1)	−0.0597 (3)	b
O(9)	0.2598 (2)	0.3959 (1)	0.3244 (3)	b
O(10)[c]	0	0.4209 (2)	$^1/_4$	b
N(1)	0.2173 (2)	0.1581 (1)	0.2030 (3)	b
N(2)[d]	$^1/_2$	0.4671 (2)	$^1/_4$	b
N(3)[d]	0	$^1/_2$	0	b
C(1)	0.3953 (3)	0.1461 (1)	0.3731 (4)	b
C(2)	0.3027 (3)	0.1833 (1)	0.2960 (4)	b
C(3)	0.3002 (3)	0.2373 (1)	0.3109 (4)	b
C(4)	0.2054 (3)	0.2641 (1)	0.2264 (4)	b
C(5)	0.1181 (3)	0.2372 (1)	0.1293 (4)	b
C(6)	0.1275 (3)	0.1834 (1)	0.1200 (4)	b
C(7)	0.0460 (3)	0.1465 (1)	0.0180 (4)	b
H(1)	0.394 (4)	0.114 (2)	0.000 (5)	0.044
H(2)	0.291 (4)	0.100 (2)	−0.092 (5)	0.044
H(3)	0.363 (3)	0.255 (2)	0.381 (4)	0.038
H(4)	0.199 (3)	0.301 (2)	0.239 (4)	0.044
H(5)	0.052 (3)	0.254 (2)	0.068 (4)	0.038
H(6)	0.327 (4)	0.380 (2)	0.355 (4)	0.038
H(7)	0.264 (4)	0.417 (2)	0.368 (5)	0.038
H(8)	0.051 (3)	−0.018 (2)	0.221 (5)	0.038
H(9)	0.479 (3)	0.451 (2)	0.168 (4)	0.038
H(10)[e]	0.051 (6)	0.404 (3)	0.289 (7)	0.038
H(11)[d]	0.010 (13)	0.479 (5)	0.069 (12)	0.038
H(12)[d]	−0.047 (8)	0.526 (5)	−0.002 (16)	0.038
H(13)[d]	0.038 (7)	0.524 (4)	0.052 (9)	0.038
H(14)[d]	0.044 (10)	0.498 (6)	−0.071 (18)	0.038

Atom	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	0.0202 (3)	0.0103 (3)	0.0222 (3)	−0.0008 (2)	−0.0022 (2)	−0.0008 (2)
O(1)	0.0270 (11)	0.0186 (11)	0.0241 (11)	0.0027 (9)	−0.0025 (9)	−0.0010 (8)
O(2)	0.0306 (12)	0.0141 (11)	0.0387 (12)	0.0034 (9)	0.0040 (10)	0.0003 (10)
O(3)	0.0364 (13)	0.0168 (11)	0.0333 (12)	−0.0056 (9)	0.0015 (10)	−0.0082 (9)
O(4)	0.0250 (12)	0.0314 (13)	0.0258 (12)	−0.0119 (10)	−0.0049 (9)	0.0029 (10)
O(5)	0.0227 (11)	0.0122 (12)	0.0302 (11)	0.0034 (8)	−0.0065 (9)	−0.0010 (9)
O(6)	0.0211 (11)	0.0219 (12)	0.0431 (13)	0.0029 (10)	−0.0182 (10)	−0.0062 (10)
O(7)	0.0222 (10)	0.0162 (12)	0.0255 (11)	−0.0043 (9)	−0.0051 (8)	−0.0017 (8)
O(8)	0.0268 (12)	0.0265 (13)	0.0466 (14)	−0.0010 (10)	−0.0211 (11)	0.0067 (11)
O(9)	0.0339 (13)	0.0247 (14)	0.0300 (13)	0.0060 (11)	−0.0092 (10)	−0.0066 (10)
O(10)	0.0235 (33)	0.0290 (35)	0.0273 (32)	0	0.0029 (22)	0
N(1)	0.0185 (13)	0.0145 (13)	0.0242 (13)	0.0006 (11)	−0.0074 (10)	−0.0012 (10)
N(2)	0.0238 (21)	0.0191 (22)	0.0315 (23)	0	−0.0062 (18)	0
N(3)	0.0458 (35)	0.0285 (27)	0.0299 (29)	0.0101 (25)	0.0135 (23)	0.0055 (23)
C(1)	0.0235 (17)	0.0202 (18)	0.0244 (16)	0.0025 (13)	−0.0035 (14)	−0.0003 (13)
C(2)	0.0204 (15)	0.0165 (17)	0.0272 (16)	−0.0008 (13)	−0.0060 (13)	−0.0004 (12)
C(3)	0.0261 (17)	0.0185 (19)	0.0383 (19)	−0.0023 (14)	−0.0099 (15)	−0.0051 (14)
C(4)	0.0337 (19)	0.0122 (18)	0.0497 (21)	0.0031 (14)	−0.0080 (16)	−0.0023 (15)
C(5)	0.0264 (17)	0.0192 (18)	0.0386 (19)	0.0056 (14)	−0.0092 (15)	0.0024 (14)
C(6)	0.0179 (15)	0.0176 (16)	0.0266 (17)	0.0004 (12)	−0.0045 (13)	0.0013 (13)
C(7)	0.0237 (17)	0.0210 (18)	0.0234 (16)	−0.0035 (14)	−0.0036 (14)	0.0025 (13)

[a] Estimated standard deviations of the least significant figures are given in parentheses here and in subsequent tables. [b] Anisotropic thermal parameters. The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [c] Occupancy 0.311 (8). [d] Multiplicity $^1/_2$. [e] Occupancy 0.622.

xH_2O ($x \approx 1.3$) consists of eight formula units in a *c*-centered monoclinic unit cell (Figure 2). The structure is comprised of two crystallographically different ammonium ions (one lying on a twofold axis and the other on a center of symmetry, both having half-multiplicity) and a vanadium-based anion which are held together by both electrostatic forces and extensive hydrogen bonding. The vanadium atom environment is a seven-coordinate distorted pentagonal bipyramid, with a vanadyl oxygen and a water molecule at the apices and the peroxy group, the nitrogen from the pyridine ring, and one oxygen atom from each carboxylate group forming an approximate pentagonal plane. Thus, the coordination geometry in the $[VO(O_2)(H_2O)(C_5H_3N(COO)_2)]^-$ anion is similar to that observed in the $[O(Ti(O_2)(H_2O)(C_5H_3N(COO)_2))_2]^{2-}$ anion[19a] and is comparable to the seven-coordination observed in other vanadium complexes, *e.g.*, $(NH_4)_4[O(VO(O_2)_2)_2]$[2] and $[VO(NO_3)_3 \cdot CH_3CN]$.[19b]

The vanadium atom is displaced 0.25 Å out of the pentag-

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Table II. Interatomic Distances (Å) and Angles (deg)

(a) Bond Distances

V-O(1)	1.579 (2)	O(4)-H(1)	0.78 (4)
V-O(2)	1.870 (2)	O(4)-H(2)	0.87 (4)
V-O(3)	1.872 (2)	C(3)-H(3)	0.97 (4)
V-O(4)	2.211 (2)	C(4)-H(4)	0.96 (4)
V-O(5)	2.053 (2)	C(5)-H(5)	0.95 (4)
V-O(7)	2.064 (2)	O(9)-H(6)	0.65 (4)
V-N(1)	2.088 (2)	O(9)-H(7)	0.87 (4)
O(2)-O(3)	1.441 (3)	N(2)-H(8)	0.76 (4)
N(1)-C(2)	1.327 (4)	N(2)-H(9)	0.81 (4)
N(1)-C(6)	1.325 (4)	O(10)-H(10)	0.76 (7)
C(1)-O(5)	1.280 (4)	N(3)-H(11)	0.78 (12)
C(1)-O(6)	1.233 (4)	N(3)-H(12)	0.85 (10)
C(1)-C(2)	1.498 (4)	N(3)-H(13)	0.84 (8)
C(2)-C(3)	1.384 (5)	N(3)-H(14)	0.82 (11)
C(3)-C(4)	1.388 (5)		
C(4)-C(5)	1.380 (5)		
C(5)-C(6)	1.378 (5)		
C(6)-C(7)	1.505 (4)		
C(7)-O(7)	1.288 (4)		
C(7)-O(8)	1.223 (4)		

(b) Bond Angles[a]

O(1)-V-O(2)	102.3 (1)	O(5)-C(1)-O(6)	125.4 (3)
O(1)-V-O(3)	101.9 (1)	O(5)-C(1)-C(2)	114.1 (3)
O(1)-V-O(4)	172.1 (1)	O(6)-C(1)-C(2)	120.5 (3)
O(1)-V-O(5)	96.2 (1)	C(1)-C(2)-N(1)	111.5 (3)
O(1)-V-O(7)	94.9 (1)	C(1)-C(2)-C(3)	127.7 (3)
O(1)-V-N(1)	92.2 (1)	N(1)-C(2)-C(3)	120.8 (3)
O(2)-V-O(3)	45.3 (1)	C(2)-C(3)-C(4)	117.8 (3)
O(2)-V-O(4)	85.4 (1)	C(2)-C(3)-H(3)	119 (2)
O(2)-V-O(5)	81.0 (1)	C(4)-C(3)-H(3)	123 (2)
O(2)-V-O(7)	126.3 (1)	C(3)-C(4)-C(5)	120.4 (3)
O(2)-V-N(1)	152.8 (1)	C(3)-C(4)-H(4)	120 (2)
O(3)-V-O(4)	84.8 (1)	C(5)-C(4)-H(4)	120 (2)
O(3)-V-O(5)	125.7 (1)	C(4)-C(5)-C(6)	118.2 (3)
O(3)-V-O(7)	81.6 (1)	C(4)-C(5)-H(5)	123 (2)
O(3)-V-N(1)	153.0 (1)	C(6)-C(5)-H(5)	118 (2)
O(4)-V-O(5)	83.0 (1)	C(5)-C(6)-C(7)	127.4 (3)
O(4)-V-O(7)	81.8 (1)	C(5)-C(6)-N(1)	120.9 (3)
O(4)-V-N(1)	80.0 (1)	N(1)-C(6)-C(7)	111.7 (3)
O(5)-V-O(7)	147.2 (1)	C(6)-C(7)-O(7)	113.3 (3)
O(5)-V-N(1)	74.5 (1)	C(6)-C(7)-O(8)	120.7 (3)
O(7)-V-N(1)	74.3 (1)	O(7)-C(7)-O(8)	126.0 (3)
V-O(2)-O(3)	67.3 (1)	H(6)-O(9)-H(7)	103 (4)
V-O(3)-O(2)	67.4 (1)	H(10)-O(10)-H(10)$^{\mathrm{I}}$	111 (3)
V-O(4)-H(1)	127 (3)	H(8)-N(2)-H(8)$^{\mathrm{I}}$	121 (3)
V-O(4)-H(2)	114 (3)	H(8)-N(2)-H(9)	98 (3)
H(1)-O(4)-H(2)	111 (4)	H(8)-N(2)-H(9)$^{\mathrm{I}}$	111 (3)
V-O(5)-C(1)	120.7 (2)	H(9)-N(2)-H(9)$^{\mathrm{I}}$	118 (3)
V-O(7)-C(7)	120.2 (2)	H(11)-N(3)-H(12)	126 (8)
V-N(1)-C(2)	119.0 (2)	H(11)-N(3)-H(13)	96 (8)
V-N(1)-C(6)	119.2 (2)	H(11)-N(3)-H(14)	116 (9)
C(2)-N(1)-C(6)	121.8 (3)	H(12)-N(3)-H(13)	106 (8)
		H(12)-N(3)-H(14)	118 (9)
		H(13)-N(3)-H(14)	96 (8)

(c) Interionic or Intermolecular Contacts Less Than 3.2 Å[a]

O(4)···O(6)$^{\mathrm{I}}$	2.714 (4)	H(1)···O(6)$^{\mathrm{I}}$	1.86 (4)
O(4)···O(9)$^{\mathrm{II}}$	2.714 (4)	H(2)···O(9)$^{\mathrm{II}}$	1.95 (4)
O(4)···N(3)$^{\mathrm{V}}$	3.123 (4)	O(4)···H(12)$^{\mathrm{V}}$	2.27 (8)
C(3)···O(8)$^{\mathrm{III}}$	3.202 (4)	H(3)···O(8)$^{\mathrm{III}}$	2.38 (4)
C(5)···O(6)$^{\mathrm{III}}$	3.209 (4)	H(5)···O(6)$^{\mathrm{III}}$	2.40 (4)
O(9)···O(8)$^{\mathrm{III}}$	2.737 (4)	H(6)···O(8)$^{\mathrm{III}}$	1.87 (4)
O(9)···O(3)$^{\mathrm{IV}}$	3.083 (4)	H(7)···O(3)$^{\mathrm{IV}}$	2.48 (4)
O(9)···O(10)$^{\mathrm{VI}}$	2.996 (4)	O(9)···H(10)$^{\mathrm{VI}}$	2.35 (7)
N(2)···O(3)$^{\mathrm{V}}$	2.992 (4)	H(8)···O(3)$^{\mathrm{V}}$	2.25 (4)
N(2)···O(7)$^{\mathrm{II}}$	2.882 (4)	H(9)···O(7)$^{\mathrm{II}}$	2.08 (4)
O(10)···N(3)$^{\mathrm{VI}}$	2.897 (4)	O(10)···H(11)$^{\mathrm{VI}}$	2.13 (12)
N(3)···O(5)$^{\mathrm{IV}}$	3.104 (4)	H(13)···O(5)$^{\mathrm{IV}}$	2.27 (8)
N(3)···O(2)$^{\mathrm{II}}$	2.938 (4)	H(14)···O(2)$^{\mathrm{II}}$	2.14 (11)

Table II (*Continued*)

(d) Interionic or Intermolecular Contact Angles[a]

V–O(2)···N(3)$^{\rm II}$	118.2 (1)	$^{\rm VI}$O(9)···O(10)···O(9)$^{\rm I}$	155.5 (3)
O(3)–O(2)···N(3)$^{\rm II}$	104.7 (3)	$^{\rm VI}$O(9)···O(10)···N(3)$^{\rm VI}$	102.2 (3)
V–O(3)···O(9)$^{\rm IV}$	135.3 (1)	$^{\rm VI}$O(9)···O(10)···N(3)$^{\rm VII}$	94.8 (3)
V–O(3)···N(2)$^{\rm V}$	101.3 (1)	$^{\rm I}$O(9)···O(10)···N(3)$^{\rm VI}$	94.8 (3)
O(2)–O(3)···O(9)$^{\rm IV}$	75.0 (3)	$^{\rm I}$O(9)···O(10)···N(3)$^{\rm VII}$	102.2 (3)
O(2)–O(3)···N(2)$^{\rm V}$	107.6 (3)	$^{\rm VI}$N(3)···O(10)···N(3)$^{\rm VII}$	91.7 (3)
$^{\rm VI}$O(9)···O(3)···N(2)$^{\rm V}$	67.7 (3)	$^{\rm V}$O(3)···N(2)···O(3)$^{\rm IV}$	134.8 (3)
V–O(4)···O(6)$^{\rm I}$	121.7 (1)	$^{\rm IV}$O(3)···N(2)···O(3)$^{\rm II}$	113.0 (3)
V–O(4)···O(9)$^{\rm II}$	125.1 (1)	$^{\rm IV}$O(3)···N(2)···O(3)$^{\rm III}$	93.3 (3)
V–O(4)···N(3)$^{\rm V}$	101.2 (1)	$^{\rm V}$O(3)···N(2)···O(7)$^{\rm II}$	93.3 (3)
$^{\rm I}$O(6)···O(4)···O(9)$^{\rm II}$	106.4 (3)	$^{\rm V}$O(3)···N(2)···O(7)$^{\rm III}$	113.0 (3)
$^{\rm I}$O(6)···O(4)···N(3)$^{\rm V}$	90.7 (3)	$^{\rm II}$O(7)···N(2)···O(7)$^{\rm III}$	108.7 (3)
$^{\rm II}$O(9)···O(4)···N(3)$^{\rm V}$	103.4 (3)	$^{\rm II}$O(2)···N(3)···O(4)$^{\rm V}$	125.5 (3)
V–O(5)···N(3)$^{\rm IV}$	110.2 (1)	$^{\rm II}$O(2)···N(3)···O(5)$^{\rm IV}$	90.1 (3)
C(1)–O(5)···N(3)$^{\rm IV}$	127.2 (3)	$^{\rm II}$O(2)···N(3)···O(10)$^{\rm VI}$	113.3 (3)
C(1)–O(6)···C(5)$^{\rm III}$	146.9 (3)	$^{\rm V}$O(4)···N(3)···O(5)$^{\rm IV}$	67.9 (3)
C(1)–O(6)···O(4)$^{\rm I}$	115.5 (3)	$^{\rm V}$O(4)···N(3)···O(10)$^{\rm VI}$	120.5 (3)
$^{\rm I}$O(4)···O(6)···C(5)$^{\rm III}$	96.3 (3)	$^{\rm IV}$O(5)···N(3)···O(10)$^{\rm VI}$	106.3 (3)
V–O(7)···N(2)$^{\rm II}$	121.8 (1)	O(4)–H(1)···O(6)$^{\rm I}$	168 (3)
C(7)–O(7)···N(2)$^{\rm II}$	117.0 (3)	O(4)–H(2)···O(9)$^{\rm II}$	163 (3)
C(7)–O(8)···C(3)$^{\rm III}$	146.8 (3)	C(3)–H(3)···O(8)$^{\rm III}$	143 (3)
C(7)–O(8)···O(9)$^{\rm III}$	126.6 (3)	C(5)–H(5)···O(6)$^{\rm III}$	143 (3)
$^{\rm III}$C(3)···O(8)···O(9)$^{\rm III}$	86.2 (3)	O(9)–H(6)···O(8)$^{\rm III}$	170 (3)
$^{\rm IV}$O(3)···O(9)···O(8)$^{\rm III}$	110.0 (3)	O(9)–H(7)···O(3)$^{\rm IV}$	155 (4)
$^{\rm IV}$O(3)···O(9)···O(4)$^{\rm II}$	101.5 (3)	N(2)–H(8)···O(3)$^{\rm V}$	166 (3)
$^{\rm IV}$O(3)···O(9)···O(10)$^{\rm VI}$	88.2 (3)	N(2)–H(9)···O(7)$^{\rm II}$	172 (3)
$^{\rm II}$O(4)···O(9)···O(8)$^{\rm III}$	124.7 (3)	O(10)–H(10)···O(9)$^{\rm VI}$	143 (6)
$^{\rm II}$O(4)···O(9)···O(10)$^{\rm VI}$	63.0 (3)	N(3)–H(11)···O(10)$^{\rm VI}$	168 (6)
$^{\rm III}$O(8)···O(9)···O(10)$^{\rm VI}$	156.2 (3)	N(3)–H(12)···O(4)$^{\rm V}$	180 (6)
		N(3)–H(13)···O(5)$^{\rm IV}$	171 (6)
		N(3)–H(14)···O(2)$^{\rm II}$	163 (6)

[a] Superscripts indicate the symmetry operation to be applied: (I) $-x, y, \frac{1}{2}-z$; (II) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (III) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (IV) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (V) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (VI) x, y, z; (VII) $x, -y, \frac{1}{2}+z$.

Table III. Least-Squares Mean Planes

Plane	χ^2	Coefficients[a]	Atoms comprising the plane	Displacements of the atoms from the plane, Å
1	15.8	0.6452	O(2)	0.000 (2)
		0.1784	O(3)	0.003 (2)
		−0.7429	O(5)	−0.004 (2)
		−0.9239	O(7)	−0.005 (2)
			N(1)	0.005 (2)
2	3.1	0.6138	O(5)	0.002 (2)
		0.1090	C(1)	−0.003 (3)
		−0.7819	C(2)	0.003 (3)
		−0.5142	N(1)	−0.002 (2)
3	239.9	0.6335	O(7)	0.015 (2)
		0.1741	C(6)	0.024 (3)
		−0.7539	C(7)	−0.025 (3)
		−0.8808	N(1)	−0.014 (2)
4	744.2	−0.7573	V	−0.012 (1)
		0.0055	O(1)	0.009 (2)
		−0.6530	O(4)	0.007 (2)
		2.7734	C(4)	0.002 (3)
			N(1)	−0.006 (2)
5	13.8	0.6230	N(1)	−0.006 (2)
		0.0922	C(2)	0.000 (3)
		−0.7767	C(3)	0.005 (3)
		−0.4799	C(4)	−0.005 (4)
			C(5)	0.000 (3)
			C(6)	0.005 (3)
6	19.5	0.6062	O(5)	0.003 (2)
		0.1045	O(6)	0.004 (2)
		−0.7884	C(1)	−0.010 (3)
		−0.4535	C(2)	0.003 (3)
7	4.8	0.5958	O(7)	0.002 (2)
		0.1869	O(8)	0.002 (2)
		−0.7811	C(6)	0.001 (3)
		−0.8861	C(7)	−0.005 (3)

[a] These are coefficients for the normal equation of a plane in the form $Ax + By + Cz + D = 0$, expressed in angstroms, referring to the set of axes x, y, z (corresponding to a, b, and c^*, respectively).

Table IV. Angles between Least-Squares Mean Planes

Planes	Angle, deg	Planes	Angle, deg
1–2	4.9	3–4	89.2
1–3	1.0	3–5	4.9
1–4	90.2	3–6	4.7
1–5	5.5	3–7	2.8
1–6	5.5	4–5	88.0
1–7	3.6	4–6	86.8
2–3	4.2	4–7	86.6
2–4	87.3	5–6	1.4
2–5	1.1	5–7	5.7
2–6	1.4	6–7	4.8
2–7	5.7		

Table V. T (Å^2) and ω (deg^2) Eigenvectors and Direction Cosines from Rigid-Body Analysis

Eigenvectors of T	Direction Cosines[a]		
0.0279	−0.6891	−0.0738	0.7209
0.0156	−0.7156	0.2260	−0.6610
0.0133	−0.1139	−0.9714	−0.2082
Eigenvectors of ω	**Direction Cosines[a]**		
6.3	−0.9530	−0.2496	−0.1719
4.3	−0.0326	−0.4628	0.8859
2.4	−0.3010	0.8470	0.4381

[a] Relative to orthogonalized axes parallel to a, b, and c^*.

onal plane toward the vanadyl oxygen O(1). This type of distortion from coplanarity is commonly found in oxovanadium(V) complexes[20a] and can be attributed[20b] to the

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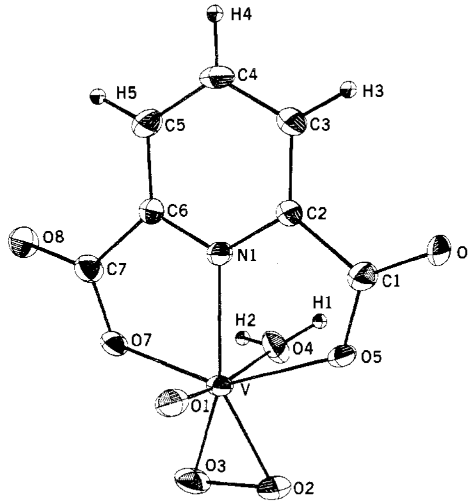

Figure 1. The $[VO(O_2)(H_2O)(C_5H_3N(COO)_2)]^-$ anion with the nonhydrogen atoms as 50% probability thermal ellipsoids.

repulsions which result between the vanadium-oxygen π bonding and the σ bonds of the equatorial plane. In the $[O(Ti(O_2)(H_2O)(C_5H_3N(COO)_2))_2]^{2-}$ anion,[19a] the titanium atom is coplanar with the pentagonal plane; as one might expect, since there are no titanium-oxygen π bonds to cause a repulsion of the type described for the vanadium compound. For the compounds $NH_4[VO(O_2)_2(NH_3)]$,[1] $(NH_4)_4[O(VO(O_2)_2)_2]$,[2] and $[VO(NO_3)_3 \cdot CH_3CN]$,[19b] the vanadium atoms were observed to be displaced 0.46, 0.43, and 0.27 Å, respectively, out of the equatorial plane toward the apical vanadyl oxygen atom.

The V-O(1) bond length is significantly shorter than the V=O bond length of 1.606 (3) Å observed in the compound $NH_4[VO(O_2)_2(NH_3)]$.[1] Similarly, the V–O$_{\text{peroxo}}$ bonds and V–N(1) distance are also significantly shorter than the respective bond lengths of 1.882 (3), 1.883 (3), and 2.110 (4) Å observed in $NH_4[VO(O_2)_2(NH_3)]$.[1] The effect expected in going from pentagonal-pyramidal to pentagonal-bipyramidal coordination geometry would be a decrease in the corresponding nonbonded contact distances *and* an increase in the corresponding bonded distances to relieve steric crowding around the central vanadium atom. Instead of this, however, both the bond lengths and nonbonded contacts were observed to decrease. This systematic difference in the bond lengths might therefore be attributed to other factors. First, interatomic bonded distances which have not been corrected for anisotropic thermal motion will appear slightly shorter. In the $[VO(O_2)_2(NH_3)]^-$ anion[1] such effects were observed to be significant, and therefore the above quoted bond lengths are those corrected for thermal motion; whereas in this low-temperature study the effects of anisotropic thermal motion were found to be minimal (as one might expect) and the bond lengths quoted are therefore uncorrected. Second, it has been suggested[21] that collection of a limited sphere of data will result in a systematic shortening of bond lengths. The evidence for this appears to us to be exceedingly weak and is certainly of a smaller magnitude than that due to thermal motion. In addition, since the smallest *d* spacing in this structure is 0.93 Å, then one might expect that any bond lengths longer than this value would show random rather than systematic variation. Finally, the vanadyl oxygen in the $[VO(O_2)_2(NH_3)]^-$ anion[1] is involved in a hydrogen bond (whereas O(1) in this structure has no hydrogen bonds) which could possibly account for the differences in the V=O bond lengths. On the other hand, the peroxo oxygens of both structures are involved in hydrogen bonding to the same extent. It is therefore apparent that the observed shortening of the bonded (and nonbonded) distances in going from the six- to the seven-coordinate species cannot be simply explained. (The V=O bond lengths of 1.58 (2) and 1.64 (2) Å and the mean V–O$_{\text{peroxo}}$ bond length of 1.87 Å, which were observed in $(NH_4)_4[O(VO(O_2)_2)_2]$,[2] are of a much lower accuracy and therefore not comparable to those of this structure, as is the case for the mean V–O$_{\text{peroxo}}$ bond length of 1.89 Å observed in $(NH_4)_3[V(O_2)_4]$.[2,3])

The O(2)-O(3) bond length of 1.441 (3) Å is significantly shorter than the peroxo bond length of 1.472 (4) Å observed in $NH_4[VO(O_2)_2(NH_3)]$[1] and is consistent with the stronger V-O$_{\text{peroxo}}$ bonds in this structure. (The mean O-O distance of 1.44 (3) Å observed for the compound $(NH_4)_4[O(VO(O_2)_2)_2]$[2] is again comparable.) As was the case for $NH_4[VO(O_2)_2(NH_3)]$,[1] shortening of the O-O bond can be attributed[22-24] to the symmetrical coordination of the peroxo group and the resultant withdrawal of electron density from the antibonding π^* $2p_y$ orbitals on the peroxo group to the empty d_{xy} and $d_{x^2-y^2}$ orbitals on the metal atom; *i.e.*, the more strongly the peroxo group is coordinated to the metal atom, the shorter the O-O bond length. An alternative description[22-27] of the peroxo group as a π-bonded monodentate ligand and the coordination geometry around the metal atom as that of a distorted octahedron[18] would also explain these conclusions. In this latter description, the large deviations of the angles O(5)-V-N(1) (74.5 (1)°) and O(7)-V-N(1) (74.3 (1)°) from 90° would be expected as a result of steric interaction with the peroxo group.

Comparison of the pyridine-2,6-dicarboxylate ligand geometry in this structure to that observed in the $[O(Ti(O_2)(H_2O)(C_5H_3N(COO)_2))_2]^{2-}$ anion[18] shows as a major difference the torsion angles that the carboxylate groups make with the pyridine ring. (In this structure the carboxylate groups are out of the plane of the pyridine ring by 1.4 and 5.7°, compared with 3.8 and 9.6°.) Except for the inward bending distortion of the angles C(1)-C(2)-N(1) (111.5 (3)°), C(7)-C(6)-N(1) (111.7 (3)°), C(2)-C(1)-O(5) (114.1 (3)°), and C(6)-C(7)-O(7) (113.3 (3)°), and the corresponding outward bending angles, from 120°, the dimensions of the pyridine-2,6-dicarboxylate ligand are what might be expected for the isolated moiety; no significant differences between chemically equivalent bonds have been found. Examination of the bond distances involving the titanium atom in the $[O(Ti(O_2)(H_2O)(C_5H_3N(COO)_2))_2]^{2-}$ anion[19a] indicate that on the average they are slightly longer than the corresponding bond distances in this structure. This would be consistent with the expectation that Ti(IV) has a larger covalent radius than V(V) (since the latter has a higher nuclear charge, but the same electronic configuration), and from this one might predict a slightly longer peroxo bond length in the $[O(Ti(O_2)(H_2O)$-

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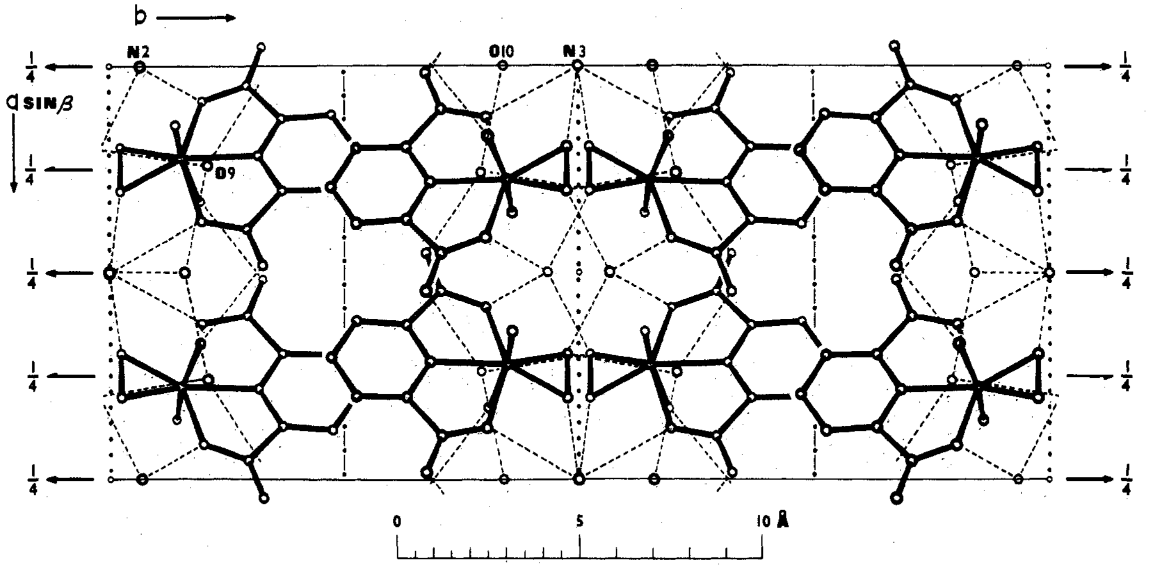

Figure 2. A projection down the *c* axis of the unit cell. The hydrogen bonds are shown as dashed lines.

$(C_5H_3N(COO)_2))_2]^{2-}$ anion,[18] which in fact is the case (1.45 (1) Å is slightly, but not significantly, longer).

The mean C-H, N-H, and O-H bond lengths observed in this structure are comparable to those observed for the compounds $NH_4[VO(O_2)_2(NH_3)]$[1] and $Cr(CO_2CH_2NH_2)_3\cdot H_2O$.[28] (The latter compound has mean C-H, N-H, and O-H distances of 0.96 (5), 0.88 (4), and 0.88 (4) Å, respectively.)

Similar to what was observed in the compound $K_2[OTi(O_2)(H_2O)(C_5H_3N(COO)_2))_2]\cdot 3H_2O$,[19a] the constituent ions and water molecules of this complex are arranged in alternating organic and inorganic "layers" normal to *b*; *i.e.*, the anions are arranged such that the peroxo groups are always adjacent to one another as are the pyridine rings (see Figure 2). The ammonium ions are located in holes in the inorganic layers, with all nearest neighbors oxygen atoms, and are involved, along with the water molecules, in extensive hydrogen bonding. (The organic layers have only van der Waals forces to hold the structure together.) Almost all of the contacts (less than 3.2 Å) between nonhydrogen atoms represent hydrogen bonds, as indicated by the interionic or intermolecular distances and angles given in Table II.

Calculations

All calculations were performed on an IBM 370/155 computer. Programs used were as follows: SAP (III-IV) and DP (I-II), a set of direct phasing programs (S. Hall and F. R. Ahmed); FORDAP, crystallographic Fourier summation and peak searching (A. Zalkin); BUCILS, crystallographic structure factors and full-matrix least squares (University of Canterbury, N. Z.); ORFFE, Fortran crystallographic function and error program (W. R. Busing, K. O. Martin, and H. A. Levy); ORTEP, Fortran thermal ellipsoid plot program for crystal structure illustrations (C. K. Johnson); MEANPLANE, calculation of weighted mean planes through atom groups with esd's (M. E. Pippy and F. R. Ahmed); MGTLS, a program to calculate translational, librational, and screw tensors for a molecule (K. N. Trueblood).

Registry No. $NH_4[VO(O_2)(H_2O)(C_5H_3N(COO)_2)]$, 38162-88-8.

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