It should be noted that there is one aδ ring in the ten-coordinate acid species and the mean plane of the four oxygen atoms is some 0.78 Å below the metal ion.[3a] In the nine-coordinate anionic species there are two eλ-aδ type rings. The four oxygen atoms are still below the metal ion but the separation decreases to 0.62 and 0.49 Å in the lanthanum and the terbium complexes, respectively. Concomitant with this change in conformational type is the shrinkage of the free space (*i.e.*, free from the chelating agent) around the metal ion and the resulting ejection of one water molecule out of the coordination sphere. An interesting possibility may be noted here in connection with this kind of discrete change in the conformational types. The lanthanide ions have closely similar chemical properties and have ionic sizes that vary in a systematic and successive manner. The EDTA chelate of, say, the largest ion will belong to a certain conformational type. As successively smaller ions along the series are substituted, the complexing bond lengths will decrease and the complex will become more and more compact. It is possible that at a certain point along the series, overcrowding of ligands will force a change in conformational type. Just before such a change, the ligands of the EDTA moiety will be in a most compact state so as to provide enough space for a maximum number of water molecules. After the change, the EDTA moiety will adopt a more spacious conformation and the space available to the water ligands will shrink, resulting in an ejection of one or more of the water molecules from the coordinate sphere. The reported thermodynamic behavior of lanthanide–EDTA complexes[2] is in qualitative agreement with that expected from this type of transition occurring in the region of Sm–Gd. A fuller discussion relating to this possibility will be presented in a report currently under preparation.[3b]

The conformational types δ-δλ-λλ and δ-δλ-δδ contain three of the eλ-aδ type rings. These types are therefore probably not very suitable for forming complexes with high coordination number. For complexes with coordination numbers of 8 or less, on the other hand, the types δ-λλ-λλ and δ-δδ-δδ will be preferable because of their symmetric nature.[20] The types δ-λλ-λδ and δ-λλ-δδ contain one or two eλ-aδ type rings and each contains one short contact. Plausibility of occurrence of these types is difficult to assess because of their highly unsymmetric character.

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(20) It should, however, be noted that the ϕ_1 angles of one of the axial rings of the species $[CoEDTA]^-$ and $[Fe(OH_2)EDTA]^-$ are essentially 0° (Table III). These species may thus be regarded as an intermediate of the types δ-λλ-λλ and δ-δλ-λλ. Whether the dissymmetry between the two axial rings is an inherent property of this type of complexes or is a result of packing forces in the solid state is a difficult question to settle unambiguously. There is no *a priori* reason that the system should be unsymmetrical and hence the latter possibility is assumed throughout this discussion. The fact that this phenomenon occurs in all three complexes which crystallize in very different space groups and also in the $Ni(OH_2)H_2EDTA$ species would, however, favor the former possibility. If it is indeed the case that the ϕ_1 angle of one of the aλ rings of the δ-λλ-λλ type must remain near zero, then it becomes fairly certain that the diaquo eight-coordinate dodecahedral complex based on the δ-λλ-λλ type will never be realized since this geometry requires large ruffling of both of the axial rings and thus an increase in ϕ_2 angle to 25–30° if the ϕ_1 angle is to remain 0°.

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The Crystal Structure of Ammonium Oxodiperoxoamminevanadate(V)

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The crystal structure of the compound $NH_4[VO(O_2)_2(NH_3)]$ has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the orthorhombic space group *Pnma* with four formula units in a cell of dimensions a = 8.370 (2) Å, b = 6.877 (1) Å, and c = 9.244 (2) Å. Refinement by full-matrix least-squares methods has given a conventional R value of 3.1% for the 566 observed reflections. The coordination of the vanadium atom can best be described in terms of a pentagonal pyramid, the four oxygens of the two peroxo groups and the ammonia nitrogen atom forming the distorted base of the pyramid, while the vanadyl oxygen occupies the apical position. Each ion has crystallographic mirror symmetry, the peroxy groups being the only nonhydrogen atoms lying off the mirror plane. Analysis of the motion of the anion as a rigid body yields interatomic distances of 1.883 (3) and 1.882 (3) Å for the V—O peroxo bonds, 1.606 (3) Å for the V═O bond, 2.110 (4) Å for the V—NH_3 distance, and 1.472 (4) Å for the O—O peroxo bond.

Introduction

An extensive investigation of the chemistry of the transition metal–peroxy complexes has been carried out,[1] but relatively little structural chemistry of peroxo complexes which do not involve chromium, molybdenum, and cobalt has been elucidated. The only previous structural work known to us on peroxovanadates was the demonstration of the isomorphism of the compounds $K_3[M^V(O_2)_4]$ (M^V = V, Cr, Nb, or Ta) by X-ray powder photographic methods,[2] the chromium compound having been shown to have a quasidodecahe-

(1) J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, **6**, 279 (1964).

(2) J. E. Fergusson, C. J. Wilkins, and J. F. Young, *J. Chem. Soc.*, 2136 (1962).

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $NH_4[VO(O_2)_2(NH_3)]$

Atom	x/a	y/b	z/c	U, Å^2
V	0.2304 (1)[a]	$^1/_4$	0.2248 (1)	*b*
O(1)	0.4061 (3)	$^1/_4$	0.1569 (4)	*b*
O(2)	0.2340 (3)	0.4405 (4)	0.3692 (3)	*b*
O(3)	0.1662 (3)	0.5105 (3)	0.2329 (3)	*b*
N(1)	0.1026 (5)	$^1/_4$	0.0295 (4)	*b*
N(2)	0.0685 (5)	$^1/_4$	0.6269 (5)	0.030 (1)
H(1)	0.059 (10)	$^1/_4$	0.539 (10)	0.100 (30)
H(2)	0.152 (11)	$^1/_4$	0.650 (10)	0.099 (30)
H(3)	0.038 (4)	0.162 (6)	0.644 (4)	0.039 (11)
H(4)	0.006 (9)	$^1/_4$	0.050 (8)	0.080 (25)
H(5)	0.124 (5)	0.155 (6)	−0.017 (4)	0.044 (11)

Atom	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	0.0202 (4)	0.0266 (2)	0.0203 (4)	0.0	0.0039 (4)	0.0
O(1)	0.0248 (14)	0.0484 (19)	0.0350 (17)	0.0	0.0082 (12)	0.0
O(2)	0.0426 (14)	0.0670 (19)	0.0389 (13)	−0.0143 (15)	0.0071 (12)	−0.0277 (13)
O(3)	0.0457 (14)	0.0273 (10)	0.0541 (13)	−0.0035 (9)	0.0168 (12)	−0.0077 (13)
N(1)	0.0326 (21)	0.0385 (24)	0.0264 (22)	0.0	−0.0008 (16)	0.0

[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 $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}\cdot hla^*c^* + 2U_{23}klb^*c^*)]$.

dral structure.[3] The analogy between these tetraperoxo complexes has prompted recent work[4] on the synthesis of triperoxovanadates with possible eight-coordination of the metal, similar to that in the peroxoniobates and peroxotantalates.[5] Thus, it is quite apparent that structural data on peroxovanadate(V) complexes will not only be useful in directing future synthetic work but will also provide a unique opportunity for comparison with the known stereochemistry of the analogous peroxochromium(VI) complexes. To initiate the structural study of peroxovanadates, the crystal structure of $NH_4[VO(O_2)_2(NH_3)]$ has been determined, and the structure of the monoperoxy complex $(NH_4)[VO(O_2)(H_2O)(C_5H_3N(COO)_2)]$ is under investigation.

Experimental Section

The preparation of ammonium oxodiperoxoamminevanadate(V), $NH_4[VO(O_2)_2(NH_3)]$, was based on previous equilibria studies[6] involving the formation of the $VO(O_2)_2^-$ anion and was carried out as follows. Divanadium pentoxide, V_2O_5 (1.82 g, 0.01 mol), was dissolved in 30% hydrogen peroxide (50 ml). To the deep red solution obtained, ammonium nitrate (1.60 g, 0.02 mol) was added, immediately followed by concentrated ammonium hydroxide, which was added dropwise until a bright yellow solution was obtained. This solution was allowed to stand for *ca.* 12 hr, after which the mother liquor was decanted from the bright yellow crystals. From these a needle-shaped crystal was selected and cleaved to maximum dimensions 0.13 × 0.40 × 0.13 mm in the directions *a*, *b*, and *c*, respectively. This single crystal was mounted with the longest dimension parallel to the rotation axis and yielded the complete diffraction data (obtained over a period of 2 weeks); during this time no decomposition was observed.

Weissenberg photographs of the *h*0*l*–*h*3*l* zones and precession photographs of the *hk*0 and 0*kl* zones, using Cu Kα radiation, showed absences for 0*kl*, $k + l = 2n + 1$, and for *hk*0, $h = 2n + 1$. This, combined with the Laue group *mmm*, indicated either the space group *Pnma* or *Pn*2$_1$*a*. (Our work indicates that the former can provide an adequate model.)

Crystal Data

Data are as follows for $NH_4[VO(O_2)_2(NH_3)]$: mol wt 166.0, orthorhombic, $a = 8.370$ (2) Å, $b = 6.877$ (1) Å, $c = 9.244$ (2) Å, $V = 532.07$ (1) Å^3, $d_m = 2.03$ g/cm^3, $Z = 4$, $d_c = 2.08$ g/cm^3, $F(000) = 336$, μ(Mo Kα) = 19.2 cm^{-1}, λ(Cu Kα) 1.5418 Å, λ(Mo Kα_1) 0.70926 Å.

Cell dimensions were determined by least-squares refinement of ten reflections whose 2θ values (>50°) were accurately measured at 21° 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. Reflection intensities for the unique set of data were measured on a Picker four-circle diffractometer, automated with the FACS-I system, using niobium-filtered Mo Kα radiation, λ_α 0.71069 Å, and a scintillation detector with pulse height analysis. The takeoff angle was 3.0°, 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 inner set of data with $2\theta \leq 40°$ were made at a scan rate of 2°/min with a symmetrical θ–2θ scan width of 1.3° + (2 tan θ)($\delta\lambda/\lambda$) radians (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. An outer set of data for the range $40° < 2\theta \leq 60°$ was measured in an analogous manner except that the base width was reduced to 1.1° since the earlier work indicated it was a little too wide. The two sets of data were initially combined using two scale factors, but this was later considered to be unnecessary as the refined scales differed by less than 1σ. Of the 831 intensities measured, 566 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 50 reflections and retained a constancy within 2% over the entire data collection. Several reflections which had a high count rate were remeasured at lower beam intensity and provided no evidence for coincidence losses. No absorption corrections were considered necessary since the μr was 0.12 and the crystal had a regular shape. Lorentz and polarization factors were applied to give structure factors.[7]

Structure Determination

A three-dimensional Patterson function showed that the vanadium atom occupied a special position of the type x, $^1/_4$, z. A three-dimensional electron density map was computed from the structure factors phased by the vanadium atom ($R = 0.353$) and yielded the remaining nonhydrogen atom positions. Least-squares refinement on these atomic positional and isotropic temperature parameters brought the R value[8] down to 0.079. At this point an electron density difference map revealed the hydrogen atoms and anisotropic thermal motion of the nonhydrogen

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(3) R. Stomberg, *Acta Chem. Scand.*, **17**, 1563 (1963).

(4) J. Sala-Pala and J. E. Guerchais, *J. Chem. Soc. A*, 1132 (1971).

(5) C. Djordjevic and N. Vuletic, *Inorg. Chem.*, **7**, 1864 (1968).

(6) (a) K. F. Jahr, L. Schoepp, and J. Fuchs, *Z. Naturforsch. B*, **14**, 469 (1959); (b) M. Orhanovic and R. G. Wilkins, *J. Amer. Chem. Soc.*, **89**, 278 (1967).

(7) A table of measured and calculated structure factors 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, by referring to code number INORG-72-1079. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(8) R is defined as $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

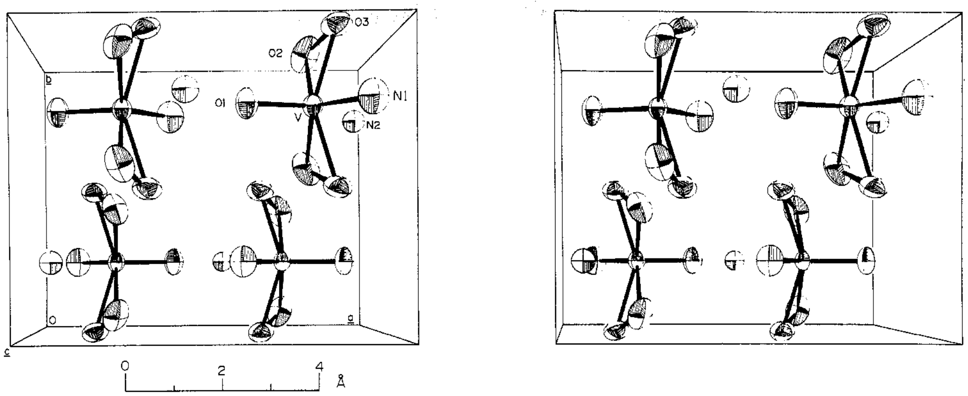

Figure 1.—Stereoscopic crystal packing diagram for $NH_4[VO(O_2)_2(NH_3)]$, with 50% probability thermal ellipsoids.

atoms in the anion. The agreement improved to $R = 0.035$. A close analysis of the variation of agreement between $|F_o|$ and $|F_c|$ as a function of $|F_o|$, of $(\sin\theta)/\lambda$, and also of an electron density difference map suggested that some of the atomic scattering curves might require adjustment to compensate for atomic charge. Curves corresponding to V^{3+} (for the vanadium atom), O^- (for the peroxo oxygens), and N^+ (for the ammonium nitrogen) were introduced giving a final unweighted R value of 0.031 and a weighted R_w value[9] of 0.039.

The data were given unit weights in the refinement until an R value of 0.035 had been achieved. Refinement to convergence was carried out with $\sigma = \sqrt{AB/F}$ ($w = 1/\sigma^2$, $A = 0.21$, $B = 12.5$) for $F \leqslant 12.5$ and $\sigma = \sqrt{AF/B}$ for $F > 12.5$. A was adjusted such that $[\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ (where $(NO - NV)$ is the number of observations minus the number of variables) was 1.00. The unobserved reflections (which have a magnitude of $\sigma/2$ and appear with negative values of F_o in the structure factor table[7]) were excluded from the refinement.

A final electron density difference synthesis showed, as its major feature, a peak of height 0.48 e/Å^3 at the position (0.32, $^1/_4$, 0.22). This position is almost centrally located between the vanadium and vanadyl oxygen atoms and we attribute this peak to increased electron density arising from the V═O double bond. Such a feature is in accordance with previously found electron density distributions.[10]

The scattering factors for the nonhydrogen atoms, including anomalous scattering for the vanadium atom, were taken from ref 11a; the scattering factors for the hydrogen atoms were taken from a table of Stewart, *et al.*[11b] The N^+ scattering curve was obtained by averaging the scattering curves for C and O^{2+}; this curve differed from the nitrogen scattering curve by no more than 0.05 electron 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 tabulated in Table II. Errors in interatomic distances and angles were calculated from the inverse matrix and include correlation between atomic parameters and the errors in the cell dimensions. The basal atoms of the anion (O(2), O(3), N(1), and the mirror-related oxygen atoms of the second peroxo group) are distorted out of a plane; the equation of this plane and the deviations of the atoms from it are given in Table III. The packing of molecules in the unit cell is presented as a stereoscopic diagram (Figure 1) with 50% probability thermal ellipsoids.

Analysis of the thermal motion[12] of the atoms in the

TABLE II

INTERATOMIC DISTANCES (Å) AND ANGLES (DEG) WITH THEIR ESTIMATED STANDARD DEVIATIONS

(a) Bonded Contacts

V–O(1)	1.599 (3) [1.606][a]	N(1)–H(4)	0.81 (4)
V–O(2)	1.871 (3) [1.882]	N(1)–H(5)	0.83 (8)
V–O(3)	1.872 (3) [1.883]	N(2)–H(1)	0.82 (9)
V–N(1)	2.098 (4) [2.110]	N(2)–H(2)	0.73 (10)
O(2)–O(3)	1.463 (4) [1.472]	N(2)–H(3)	0.67 (4)

(b) Interionic Contacts (between Nonhydrogen Atoms) Shorter Than 3.0 Å

V···O(1) $(-^1/_2 + x, ^1/_2 - y, ^1/_2 - z)$[b]	2.926 (3)
O(1)···N(2) $(^1/_2 + x, ^1/_2 - y, ^1/_2 - z)$	2.955 (6)[c]
O(2)···N(1) $(^1/_2 - x, 1 - y, ^1/_2 + z)$	2.932 (4)[c]
O(3)···O(1) $(-^1/_2 + x, ^1/_2 - y, ^1/_2 - z)$	2.997 (3)
O(3)···N(2) $(-x, ^1/_2 + y, 1 - z)$	2.872 (4)[c]
O(3)···N(2) $(^1/_2 - x, 1 - y, -^1/_2 + z)$	2.933 (4)[c]

(c) Interionic Contacts (Involving Hydrogen Atoms) Shorter Than 2.5 Å

O(1)···H(1) $(^1/_2 + x, ^1/_2 - y, ^1/_2 - z)$	2.22 (9)[c]
O(3)···H(2) $(^1/_2 - x, 1 - y, -^1/_2 + z)$	2.37 (7)[c]
O(3)···H(3) $(-x, ^1/_2 + y, 1 - z)$	2.31 (4)[c]

(d) Bond Angles

O(1)–V–O(2)	105.4 (1)	V–N(1)–H(4)	108 (5)
O(1)–V–O(3)	106.3 (1)	V–N(1)–H(5)	111 (3)
O(1)–V–N(1)	97.5 (2)	H(4)–N(1)–H(5)	110 (4)
O(2)–V–O(3)	46.0 (1)	H(1)–N(2)–H(2)	113 (8)
O(2)–V–N(1)	128.5 (1)	H(1)–N(2)–H(3)	101 (4)
O(2)–V–O(2)′	88.9 (1)	H(2)–N(2)–H(3)	107 (4)
O(3)–V–N(1)	83.6 (1)		
O(3)–V–O(3)′	146.3 (1)		

(e) Interionic Contact Angles

O(1)–V···O(1) $(-^1/_2 + x, ^1/_2 - y, ^1/_2 - z)$	178.8 (4)
V–O(1)···V $(^1/_2 + x, ^1/_2 - y, ^1/_2 - z)$	135.0 (2)
N(2)–H(1)···O(1) $(-^1/_2 + x, ^1/_2 - y, ^1/_2 - z)$	150 (8)[c]
N(2)–H(2)···O(3) $(^1/_2 - x, 1 - y, ^1/_2 + z)$	130 (3)[c]
N(2)–H(3)···O(3) $(-x, -^1/_2 + y, 1 - z)$	140 (5)[c]
N(1)–H(4)···O(2) $(-^1/_2 + x, ^1/_2 - y, ^1/_2 - z)$	151 (1)[c]

[a] Corrected for rigid-body motion. [b] Symmetry transformation applies to coordinates of the last atom. [c] Possible hydrogen bonds.

TABLE III

Mean Plane as $Ax + By + Cz + D = 0$[a]

Distorted Basal Plane[b] (Excluding the Vanadium Atom):

$(0.9420)x + (0.0000)y + (-0.3355)z - 0.6587 = 0$

Atom	Dev from plane, Å	Atom	Dev from plane, Å
V	0.461 (1)	O(3)	−0.071 (3)
O(2)	0.042 (3)	N(1)	0.059 (4)

[a] The normal equation of a plane, expressed in ångströms, refers to the set of axes x, y, z (corresponding to a, b, and c, respectively). [b] This plane provides only an approximate description of the structure; there are highly significant departures from planarity.

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

[10] A. M. O'Connell, A. I. M. Rae, and E. N. Maslen, *Acta Crystallogr.*, **21**, 208 (1966).

[11] (a) "International Tables of X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1965, Section 3.3; (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[12] V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **24**, 63 (1968).

anion indicate that their motion can well be approximated to that of a rigid body (appropriate constraints were maintained to preserve the mirror symmetry). This motion has a significant effect on the bond lengths, and the corrected values are given in Table II and are used throughout the discussion. Table IV indicates the principal axes of **T** and **ω**. The rms $\Delta U_{i,j}$ is 0.003 (4) Å^2.

TABLE IV

T (Å^2) AND **ω** (DEG^2) EIGENVECTORS AND DIRECTION COSINES FROM RIGID-BODY ANALYSIS

Eigenvectors of **T**	Direction cosines^a		
0.0290	0.0000	1.0000	0.0000
0.0264	0.6651	0.0000	0.7467
0.0184	0.7467	0.0000	−0.6651
Eigenvectors of **ω**	Direction cosines^a		
39.8	0.8007	0.0000	−0.5991
15.2	0.5991	0.0000	0.8007
13.1	0.0000	−1.0000	0.0000

^{a} Relative to orthogonal axes parallel to *a*, *b*, and *c*.

Discussion

The compound $NH_4[VO(O_2)_2(NH_3)]$ consists of four formula units in the primitive orthorhombic unit cell (Figure 1). Both the cation and the anion lie on the mirror plane, with half of each ion comprising the asymmetric unit. The vanadium atom is bonded to five oxygen atoms and one nitrogen atom in what can best be described as a pentagonal pyramid, the four oxygens of the two peroxo groups (which are related by the mirror plane) and the ammonia nitrogen atom forming the base of the distorted pyramid and the vanadyl oxygen occupying the apical position. Thus, the coordination geometries in the $[VO(O_2)_2(NH_3)]^-$ anion and in the oxodiperoxopyridinechromium(VI) complex,[13] $[CrO(O_2)_2py]$, are not significantly different.

The vanadium atom is not coplanar with the basal pentagon but is displaced 0.46 Å toward the vanadyl oxygen O(1). Distortions of this type are commonly found in oxovanadium(V) complexes[14] and are attributed to vanadium–oxygen π bonding (*i.e.*, "double bond–single bond repulsions"[15]). In the complex $[CrO(O_2)_2py]$,[13] the chromium was similarly displaced by 0.51 Å, while in the pentagonal-bipyramidal complexes $[VO(NO_3)_3\cdot CH_3CN]$,[16a] $[CrO(O_2)_2bipy]$,[16b] and $[CrO(O_2)phen]$,[16c] the metal atoms were observed to be displaced 0.27, 0.31, and 0.27 Å, respectively, out of the equatorial plane toward the oxide oxygen. These complexes of V^V and Cr^{VI} suggest that the observed displacements of the metal atoms from the plane are significantly greater in the pentagonal-pyramidal complexes than in the pentagonal-bipyramidal complexes, as might be expected.

The short V—O(1) bond length of 1.606 (3) Å is indicative of a vanadium–oxygen double bond. It is slightly longer than V═O bond lengths in some other vanadium(V) compounds (*e.g.*, $[VO(NO_3)_3\cdot CH_3CN]$,[16a] 1.55 (2) Å; $VO(OCH_3)_3$,[14] 1.51 (5) and 1.58 (4) Å; $VOCl_3$,[17] 1.56 (4) Å) and slightly shorter than in the vanadium(IV) compound $VO(bzac)_2$[18] (1.612 (10) Å). The $V–NH_3$ distance of 2.110 (4) Å is not representative of a strong coordination of the ammonia, but it is much stronger than the $V–NCCH_3$ coordination distance of 2.24 (3) Å in the complex $[VO(NO_3)_3\cdot CH_3CN]$.[16a]

The O(2)–O(3) bond length of 1.472 (4) Å in the peroxo groups is slightly shorter than the 1.49 Å accepted[1,19] for the O_2^{2-} entity but significantly longer than the mean O–O distance of 1.404 (16) Å observed in $[CrO(O_2)_2py]$[13] and 1.40 (2) Å observed in $[CrO(O_2)_2bipy]$[16b] and $[CrO(O)_2phen]$.[16c] This shortening of the peroxo bond has been observed[1,19] in most transition metal–peroxo complexes and is attributed to the mode of coordination of the peroxo group,[1,19,20] *i.e.*, partial withdrawal of electron density from the antibonding π^*2p_y orbitals of the peroxo group to the empty d_{xy} and $d_{x^2-y^2}$ orbitals of the metal. The vibrational spectra of the complexes $[VO(O_2)_2(NH_3)]^-$ and $[CrO(O_2)_2py]$[13] both show stretching frequencies for the peroxo group[20–22] at 880 cm^{-1}, a somewhat surprising observation considering how significantly different the peroxo bond lengths appear to be in these two complexes.

The V–O(2) and V–O(3) bond lengths of 1.882 (3) and 1.883 (3) Å, respectively, show that the peroxo group is truly symmetrically π bonded to the vanadium atom. These bonds are significantly shorter than the mean V–O bond lengths of 2.05 (4) Å for the bidentate nitrates and 1.92 (2) Å for the monodentate nitrate in $[VO(NO_3)_3\cdot CH_3CN]$[16a] but slightly longer than the mean $Cr–O_{peroxo}$ bond length of 1.82 (4) Å in $[CrO(O_2)_2py]$,[13] as might be expected from the O–O bond lengths. This is consistent also with the expectation that V^V has a larger covalent radius than Cr^{VI}, which is further supported by the fact that the V═O and V—N bonds are slightly longer than the corresponding Cr═O and Cr—N bonds.

One of the shortest intermolecular contacts involving nonhydrogen atoms is between the vanadium atom and the vanadyl oxygen of a second anion. The V···O(1) distance is 2.926 (3) Å, while the O(1)–V···O(1) and V–O(1)···V angles are 178.8 (1) and 135.0 (2)°, respectively (see Table II). This distance is shorter than the sum of the van der Waals radii (but still too long to be considered a formal bond) and is most likely an electrostatic interaction which results in a more satisfactory charge distribution. Such a contact might allow one to consider the environment around the vanadium atom as very weakly tending toward a distorted pentagonal bipyramid. Indeed the slightly lengthened V═O bond and smaller displacement of the vanadium out of the plane (compared to the chromium analog $[CrO(O_2)_2py]$) may reflect this long interaction. Of the remaining intermolecular contacts between nonhydrogen atoms which are less than 3.0 Å, the majority appear to be weak hydrogen bonds. The details of these are presented in Table II.

The observed mean N–H bond length of 0.80 (10) Å is comparable to the mean N–H bond length of 0.88 (4) Å

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observed in the compound $Cr(CO_2CH_2NH_2)_3 \cdot H_2O$.[23] Considering the distortion in the electron density distribution normally encountered in X-ray studies[24] for hydrogen atoms, the observed bond distances are close to the expected values.

Finally, returning to the coordination geometry of the vanadium, an alternative view[16a,25] can be proposed in which the metal is formally four-coordinate in a distorted tetrahedral arrangement, each peroxo group bonding with one coordination site (*e.g.*, a vacant sd^3 hybrid) by means of a three-center bond. Such a proposal is not unreasonable, especially when the bond angles to the midpoints of the peroxo groups are examined: O(1)–V–(O_2), 107.2 (1)°; O(1)–V–N(1), 97.5 (1)°; N(1)–V–(O_2), 106.1 (1)°; (O_2)–V–(O_2), 128.5 (1)°. The largest angle is attributed[19] to repulsion between the two peroxo groups, and the smallest angle is a response to this repulsion by the less strongly bound ammonia. This angle of 128.5 (1)° is not as large as corresponding angles observed[19] in diperoxochromium complexes.

Calculations

All calculations were performed on an IBM 360/50 computer. Programs used were as follows: FORDAP, crystallographic Fourier summation and peak searching (A. Zalkin); BUCILS, crystallographic structure factors and full-matrix least squares (University of Canterbury); 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 calculated translational, librational, and screw tensors for a molecule (K. N. Trueblood).

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Two Isostructural Actinide π Complexes. The Crystal and Molecular Structure of Bis(cyclooctatetraenyl)uranium(IV), $U(C_8H_8)_2$, and Bis(cyclooctatetraenyl)thorium(IV), $Th(C_8H_8)_2$

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Crystal and molecular structures of the two isostructural cyclooctatetraene dianion π complexes "uranocene" and "thorocene," $U(C_8H_8)_2$ and $Th(C_8H_8)_2$, have been determined from three-dimensional X-ray diffraction data. The molecules both have D_{8h} molecular symmetry. The heavy atom in each case is symmetrically π bonded to two aromatic cyclooctatetraene dianion rings related by a crystallographic inversion center. The mean uranium–carbon bond length is 2.647 (4) Å and the mean Th–C bond length is 2.701 (4) Å. The cyclooctatetraene dianion rings are planar with average C–C bond lengths of 1.392 (13) and 1.386 (9) Å for $U(C_8H_8)_2$ and $Th(C_8H_8)_2$, respectively. Differences in the metal–carbon bond lengths in $U(C_8H_8)_2$ and $Th(C_8H_8)_2$ can be calculated from the corresponding change in ionic radii. Deep green plates of $U(C_8H_8)_2$ have the following crystal data: monoclinic space group $P2_1/n$, cell constants $a = 7.084$ (3), $b = 8.710$ (3), $c = 10.631$ (5) Å, and $\beta = 98.75$ (3)°. For two fomula units in the cell, the calculated density is 2.29 g/cm³. Bright yellow plates of $Th(C_8H_8)_2$ have the same crystal structure with cell constants $a = 7.0581$ (11), $b = 8.8192$ (17), $c = 10.7042$ (18) Å, and $\beta = 98.44$ (3)°. The calculated density is 2.22 g/cm³. Both structures have been refined using full-matrix least-squares methods to unweighted R factors of 2.09 and 2.07% for $U(C_8H_8)_2$ and $Th(C_8H_8)_2$, respectively.

Introduction

Following the initial characterization of bis(cyclooctatetraenyl)uranium(IV), "uranocene," by Streitwieser and Müller-Westerhoff[1] the synthesis and chemical properties for a number of 4f and 5f transition series π complexes containing cyclooctatetraene dianion have been reported.[2–6] It was originaly postulated that $U(C_8H_8)_2$ has a π-sandwich structure and that symmetry-allowed overlap of the 5f orbitals with the ligand molecular orbitals could contribute to the bonding.[1] Our preliminary report[7] showed the structure of $U(C_8H_8)_2$ to be a true π-sandwich complex with D_{8h} molecular symmetry. The question of f-orbital participation in bonding has since become the subject of much renewed interest and speculation. Mössbauer studies on bis(cyclooctatetraenyl)neptunium(IV)[3] and proton magnetic resonance studies of $U(C_8H_8)_2$[8] and the substituted analog bis(1,3,5,7-tetramethylcyclooctatetraene)uranium(IV)[6] appear to confirm the presence of at least some π interaction between

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