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Molecular Stereochemistry of (α,γ-Dimethyl-α,γ-dihydrooctaethylporphinato)oxotitanium(IV)

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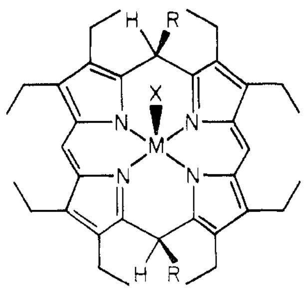
Crystals of (α,γ-dimethyl-α,γ-dihydrooctaethylporphinato)oxotitanium(IV) crystallize in the space group *C*2/*c*; the unit cell has a = 16.005 (9) Å, b = 15.915 (8) Å, c = 14.746 (8) Å, and β = 113.74 (2)° and contains four molecules. The calculated and experimental densities are 1.21 and 1.21 g/cm³, respectively. Intensity data were collected by θ–2θ scanning with Mo Kα radiation and 2721 data were retained as observed and used for the solution and refinement of structure; the conventional and weighted R values are 0.054 and 0.078, respectively. The reduced porphyrin has a folded core; the titanium(IV) ion is displaced 0.58 Å from the mean plane of the four nitrogen atoms. The average Ti–N distance in the square-pyramidal coordination group is 2.110 Å and the Ti–O bond length is 1.619 Å. The short Ti–O bond length of the titanyl ion suggests a multiple bond. The complex has crystallographically required C_2 symmetry; the two methyl groups at C-α and C-γ as well as the oxo ligand are in the syn-axial configuration pointing outward from the exo side of the porphodimethene plane.

Porphodimethenes (α,γ-dihydroporphine derivatives, e.g., **1**) have saturated α- and γ-meso-carbon atoms and have been suggested as intermediates[2-5] in porphyrin syntheses. The porphodimethenes, **1**, rather than the chlorines, are the primary products of the chemical[6,7] and photochemical[8,9] hydrogenation of metalloporphyrins. Recently, the Krasnovskii photoreduction product of chlorophyll a has been shown[10] to be β,δ-dihydrochlorophyll a, a compound closely related to the porphodimethenes. Therefore, we are studying the molecular stereochemistry of porphodimethene derivatives as part of a systematic program of investigation of the structures of dihydroporphyrins.

The saturated α- and γ-meso-carbon atoms of the porphodimethene give the macrocycle an enhanced flexibility compared to the porphyrins. In our first study,[11] we investigated the low-spin four-coordinate nickel(II) chelate **2**. The low-spin nickel(II) ion is relatively small and the porphodimethene macrocycle achieves short Ni–N bond distances by a substantial ruffling of the core. Coordination of a titanium(IV) ion, on the other hand, does not demand the short metal–nitrogen complexing bonds characteristic of the nickel(II) complex, and the conformation of the core should be substantially altered. The core in the titanium(IV) complex **3**[12] is expected to be folded along the line joining the two saturated meso-carbon atoms with essentially planar pyrromethene halves, whereas in the nickel(II) complex the pyrromethene halves are substantially folded. Finally, the structure of (α,γ-dimethyl-α,γ-dihydrooctaethylporphinato)oxotitanium(IV) (to be written as OTi(OEPMe$_2$)) provides accurate stereochemical parameters of the titanyl (TiO^{2+}) cation.[13]



1, R = H; M = Zn; no X
2, R = CH$_3$; M = Ni; no X
3, R = CH$_3$; M = Ti; X = O

Table I. Atomic Coordinates in the Unit Cell[a]

Atom	10^4x	10^4y	10^4z
O	0	3272 (2)	1/4
N_1	1384 (2)	1911 (2)	2981 (2)
N_2	85 (2)	1875 (2)	3908 (2)
C_{a1}	1896 (2)	1979 (2)	2449 (2)
C_{a2}	1979 (2)	1639 (2)	3927 (2)
C_{a3}	852 (2)	1575 (2)	4705 (2)
C_{a4}	−587 (2)	1934 (2)	4233 (2)
C_{b1}	2820 (2)	1756 (2)	3020 (2)
C_{b2}	2875 (2)	1550 (2)	3956 (2)
C_{b3}	617 (2)	1442 (2)	5534 (2)
C_{b4}	−289 (2)	1678 (2)	5232 (2)
C_{m1}	1513 (2)	2282 (2)	1391 (2)
C_1	1469 (3)	3265 (3)	1353 (3)
C_{m2}	1712 (2)	1490 (2)	4698 (2)
C_{11}	3575 (2)	1732 (3)	2660 (3)
C_{12}	3664 (3)	874 (4)	2229 (4)
C_{21}	3706 (2)	1291 (2)	4846 (2)
C_{22}	3807 (3)	340 (3)	4996 (4)
C_{31}	1232 (2)	1099 (2)	6522 (2)
C_{32}	1142 (4)	158 (3)	6632 (3)
C_{41}	−856 (3)	1673 (3)	5836 (2)
C_{42}	−1435 (3)	878 (4)	5705 (4)
Atom	10^5x	10^5y	10^5z
Ti	0	22551 (5)	1/4

[a] The figures in parentheses are the estimated standard deviations in the last significant figure.

Experimental Section

Crystals of OTi(OEPMe$_2$) were obtained by slow evaporation of a benzene solution. A preliminary X-ray study established a monoclinic four-molecule unit cell with *Cc* or *C*2/*c* as the possible space groups. Lattice constants a = 16.005 (9) Å, b = 15.915 (8) Å, c = 14.746 (8) Å, and β = 113.74 (2)° (λ 0.71069 Å) came from a least-squares refinement that utilized the setting angles of 23 reflections, each collected at ±2θ. These constants led to a calculated density at 20 ± 1° of 1.21 g/cm³ for a cell content of 4 TiON$_4$C$_{38}$H$_{50}$; the observed density (by flotation) is 1.21 g/cm³.

Intensity data were measured on a Syntex *P*1̄ diffractometer using the θ–2θ scanning technique with graphite-monochromated Mo Kα radiation. Data collection techniques were essentially the same as described previously.[14] Four standard reflections were measured periodically (every 50 reflections) and no crystal decomposition was noted. The dimensions of the crystal used in data collection were 0.30 × 0.34 × 0.50 mm. All independent data having $(\sin\theta)/\lambda < 0.648$ Å^{-1} were measured. With a linear absorption coefficient of 0.296 mm^{-1}, no absorption correction was deemed necessary.

The net intensities were reduced to a set of relative squared amplitudes as described previously.[14] Standard deviations were calculated and all data having $F_o < 3\sigma(F_o)$ were taken to be unobserved; 2721 independent data were considered observed (70% of the theoretical number possible). Only the observed data were used for the determination and refinement of structure.

With four molecules per unit cell, the choice of *C*2/*c* as the space group requires that the molecule have C_2 symmetry; the choice of space group *Cc* leads to no required symmetry for the molecule. The initial choice of *C*2/*c* as the space group was fully confirmed by all subsequent developments during the determination of structure. The

Table II. Thermal Parameters ($Å^2$)[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B[b]
Ti	2.31 (3)	2.55 (3)	1.78 (3)	0.0	0.49 (2)	0.0	2.28
O	4.4 (2)	2.8 (1)	3.4 (1)	0.0	1.0 (1)	0.0	3.60
N_1	2.51 (9)	3.2 (1)	2.09 (9)	−0.10 (8)	0.71 (7)	0.14 (7)	2.63
N_2	2.56 (9)	3.1 (1)	1.94 (8)	0.06 (8)	0.74 (7)	0.03 (7)	2.53
C_{a1}	2.7 (1)	3.1 (1)	2.4 (1)	−0.43 (9)	0.77 (9)	0.09 (9)	2.74
C_{a2}	2.4 (1)	2.8 (1)	2.3 (1)	0.04 (9)	0.51 (9)	0.05 (9)	2.58
C_{a3}	3.1 (1)	2.7 (1)	1.95 (9)	−0.08 (9)	0.63 (9)	−0.05 (9)	2.61
C_{a4}	3.0 (1)	3.1 (1)	2.2 (1)	0.0 (1)	1.01 (9)	−0.49 (9)	2.72
C_{b1}	2.4 (1)	3.3 (1)	3.0 (1)	−0.35 (9)	1.07 (9)	−0.0 (1)	2.88
C_{b2}	2.5 (1)	2.7 (1)	2.9 (6)	−0.17 (9)	0.67 (9)	0.03 (9)	2.81
C_{b3}	3.6 (1)	3.0 (1)	1.9 (1)	−0.1 (1)	0.90 (9)	−0.19 (9)	2.80
C_{b4}	3.4 (1)	3.6 (1)	2.2 (1)	−0.1 (1)	1.2 (1)	−0.48 (9)	2.91
C_{m1}	3.0 (1)	4.2 (1)	2.6 (1)	−0.6 (1)	1.04 (9)	0.6 (1)	3.09
C_1	4.7 (2)	4.8 (2)	4.0 (2)	−1.7 (1)	0.5 (1)	1.4 (1)	4.28
C_{m2}	2.6 (1)	2.8 (1)	2.1 (1)	0.1 (1)	0.4 (1)	0.1 (1)	2.61
C_{11}	2.6 (1)	5.8 (2)	3.7 (1)	−0.5 (1)	1.3 (1)	−0.2 (11)	3.78
C_{12}	5.1 (2)	8.4 (3)	8.1 (3)	0.3 (2)	3.4 (2)	−3.0 (3)	6.18
C_{21}	2.6 (1)	3.7 (1)	3.3 (1)	−0.1 (1)	0.4 (1)	0.4 (1)	3.33
C_{22}	5.3 (2)	4.0 (2)	7.0 (3)	1.1 (2)	0.8 (2)	1.6 (2)	5.32
C_{31}	4.2 (2)	4.2 (2)	2.0 (1)	0.1 (1)	0.9 (1)	0.3 (1)	3.37
C_{32}	9.7 (3)	3.8 (2)	4.4 (2)	1.2 (2)	1.1 (2)	0.8 (2)	5.61
C_{41}	4.5 (2)	5.8 (2)	2.6 (1)	0.2 (1)	2.0 (1)	−0.5 (1)	3.73
C_{42}	6.4 (2)	8.3 (3)	5.4 (2)	−2.7 (2)	3.8 (2)	−1.1 (2)	5.53

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

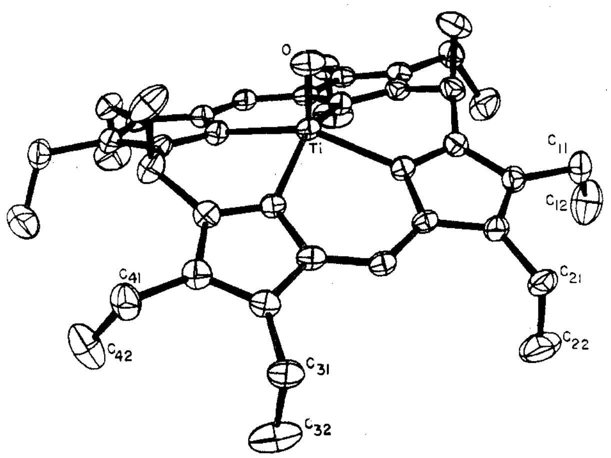


Figure 1. Computer-drawn model in perspective of the OTi($(OEPMe_2)$) molecule as it exists in the crystal. The peripheral ethyl groups are identified with the symbol used in the paper.

structure was solved by the standard heavy-atom method. Full-matrix least-squares refinement[15] was followed by a difference Fourier synthesis which revealed electron density concentrations appropriately located for the hydrogen atoms bonded directly to the ring and the methylene carbon hydrogen atoms. The hydrogen atoms of the methyl groups could not be reliably located. The positions of the hydrogen atoms that could be found in the difference Fourier synthesis were idealized (CCH = 109.5°, C-H = 0.95 Å) and included in the subsequent refinement cycles as fixed contributors. The refinement was then carried to convergence[16] using anisotropic thermal parameters for all heavy atoms. The final value of $R_1 = \sum[|F_o| - |F_c|]/\sum|F_o|$ was 0.054; that of $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ was 0.078. The estimated standard deviation of an observation of unit weight was 1.21. The final parameter shifts were less than 10% of the estimated standard deviations during the last cycle. A final difference Fourier was judged to be significantly free of features with no peaks greater than 0.2 e $Å^{-3}$.

Atomic coordinates and the associated anisotropic thermal parameters in the asymmetric unit of structure are listed in Tables I and II, respectively. Primed and unprimed symbols, e.g., C_i and C_i', denote a pair of atoms related by the twofold axis of symmetry.

Table III. Bond Lengths in the Coordination Group and the Macrocycle Skeleton[a,b]

Bond	Value, Å	Bond	Value, Å	Bond	Value, Å
Ti-O	1.619 (4)	C_{a2}-C_{b2}	1.425 (4)	C_{b3}-C_{b4}	1.385 (5)
Ti-N_1	2.108 (3)	C_{a2}-C_{m2}	1.386 (4)	C_{b3}-C_{31}	1.495 (4)
Ti-N_2	2.113 (3)	C_{a3}-C_{b3}	1.432 (4)	C_{b4}-C_{41}	1.507 (4)
N_1-C_{a1}	1.347 (4)	C_{a3}-C_{m2}	1.387 (4)	C_{m1}-C_1	1.567 (5)
N_1-C_{a2}	1.405 (4)	C_{a4}-C_{b4}	1.413 (4)	C_{11}-C_{12}	1.536 (6)
N_2-C_{a3}	1.398 (4)	C_{a4}-C_{m1}'	1.501 (4)	C_{21}-C_{22}	1.529 (6)
N_2-C_{a4}	1.347 (4)	C_{b1}-C_{b2}	1.386 (4)	C_{31}-C_{32}	1.520 (6)
C_{a1}-C_{b1}	1.420 (4)	C_{b1}-C_{11}	1.504 (4)	C_{41}-C_{42}	1.533 (6)
C_{a1}-C_{m1}	1.507 (4)	C_{b2}-C_{21}	1.502 (4)		

[a] The number in parentheses following each datum is the estimated standard deviation in the last significant figure. [b] Primed and unprimed symbols denote a pair of atoms related by the twofold axis.

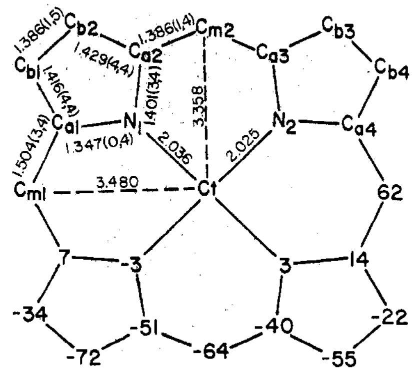


Figure 2. A formal diagram of the porphodimethene core displaying, on the upper half, the special symbols identifying each atom. On the lower half of the diagram, the special symbol identifying each atom is replaced by the perpendicular displacement of the atom, in units of 0.01 Å, from the mean plane of the four nitrogen atoms of the core. Displayed in the upper left of the diagram are selected bond distances, averaged in agreement with C_{2v} symmetry. The numbers in parentheses following each averaged value are, respectively, the mean deviation from the average and the estimated standard deviation of an individual length. Distances from the center of the four nitrogen atoms (Ct) to selected atoms are also shown.

Discussion

The numbering system employed in Tables I–IV for the carbon and nitrogen atoms in the asymmetric unit of structure is displayed in Figures 1 and 2. Figure 1 is a computer-drawn[17] model in perspective of the OTi(OEPMe2) molecule

Table IV. Bond Angles in the Coordination Group and the Macrocycle Skeleton[a,b]

Angle	Value, deg	Angle	Value, deg	Angle	Value, deg
$OTiN_1$	105.05 (8)	$N_1C_{a2}C_{b2}$	109.3 (2)	$C_{a3}C_{b3}C_{b4}$	106.7 (3)
$OTiN_2$	106.65 (7)	$N_1C_{a2}C_{m2}$	124.0 (3)	$C_{a3}C_{b3}C_{31}$	126.0 (3)
N_1TiN_1'	149.9 (1)	$C_{b2}C_{a2}C_{m2}$	126.7 (3)	$C_{b4}C_{b3}C_{31}$	127.3 (3)
N_2TiN_2'	146.7 (1)	$N_2C_{a3}C_{b3}$	108.9 (3)	$C_{a4}C_{b4}C_{b3}$	106.4 (3)
N_1TiN_2	87.2 (1)	$N_2C_{a3}C_{m2}$	124.4 (3)	$C_{a4}C_{b4}C_{41}$	125.9 (3)
N_1TiN_2'	84.2 (1)	$C_{b3}C_{a3}C_{m2}$	126.5 (3)	$C_{b3}C_{b4}C_{41}$	127.7 (3)
$C_{a1}N_1C_{a2}$	106.0 (2)	$N_2C_{a4}C_{b4}$	111.6 (3)	$C_{a1}C_{m1}C_{a4}'$	114.1 (2)
$C_{a1}N_1Ti$	125.9 (2)	$N_2C_{a4}C_{m1}'$	122.7 (3)	$C_{a1}C_{m1}C_1$	110.5 (3)
$C_{a2}N_1Ti$	127.8 (2)	$C_{b4}C_{a4}C_{m1}'$	125.6 (3)	$C_{a4}'C_{m1}C_1$	109.1 (3)
$C_{a3}N_2C_{a4}$	106.3 (2)	$C_{a1}C_{b1}C_{b2}$	106.4 (3)	$C_{a2}C_{m2}C_{a3}$	128.6 (3)
$C_{a3}N_2Ti$	127.7 (2)	$C_{a1}C_{b1}C_{11}$	126.1 (3)	$C_{b1}C_{11}C_{12}$	113.0 (3)
$C_{a4}N_2Ti$	125.8 (2)	$C_{b2}C_{b1}C_{11}$	127.4 (3)	$C_{b2}C_{21}C_{22}$	113.7 (3)
$N_1C_{a1}C_{b1}$	111.5 (3)	$C_{a2}C_{b2}C_{b1}$	106.7 (3)	$C_{b3}C_{31}C_{32}$	114.2 (3)
$N_1C_{a1}C_{m1}$	122.6 (3)	$C_{a2}C_{b2}C_{21}$	125.4 (3)	$C_{b4}C_{41}C_{42}$	114.0 (3)
$C_{b1}C_{a1}C_{m1}$	125.9 (3)	$C_{b1}C_{b2}C_{21}$	127.9 (3)		

[a] The number in parentheses following each datum is the estimated standard deviation in the last significant figure. [b] Primed and unprimed symbols denote a pair of atoms related by the twofold axis.

(**3**) as it exists in the crystal. Bond parameters (with estimated standard deviations)[18] are listed in Tables III and IV. The crystallographically imposed twofold axis of symmetry passes through the titanium and oxygen atoms (Figure 1) of the titanyl cation. Although not required of the molecule in the crystal, the core of the molecule has approximate C_{2v} symmetry. Figure 2 displays average values of the bond lengths (C_{2v} symmetry) and radii of the core.

The displacement of the skeletal carbon atoms from the mean plane of the four nitrogen atoms is given in Figure 2. In the lower half of the diagram, the symbol identifying each atom is replaced by the perpendicular displacement (in units of 0.01 Å) of this atom from the mean plane of the four nitrogen atoms. The twofold related atoms in the upper half of the diagram have displacements of the same magnitude and sign. As is usual, local flatness is preserved for each pyrrole ring with the maximum deviation from exact planarity being less than 0.006 Å. As expected, the core is folded along the line joining the two saturated meso-carbon atoms (C_{m1} and C_{m1}' of Figure 2). The 38.2° angle between the normals to the pyrromethene halves (the mean plane of a pyrromethene half is defined by atom C_{m2} and the two unique pyrrole rings) specifies the folding. The two pyrrole rings of a pyrromethene half are almost coplanar; the angle between the normals to the two pyrrole ring mean planes is 4.6°. The comparable values for the ruffled core of the nickel(II) chelate, **2**,[11] are 52 and ~23°, respectively.

The mean plane of the porphodimethene skeleton is parallel to the mean plane of the four nitrogen atoms but is displaced by 0.21 Å. Consequently, the displacement of individual atoms from the mean plane of the core can be obtained by adding 0.21 Å to the cited displacements given in Figure 2. The titanium(IV) ion is displaced 0.79 Å out of the mean plane of the porphodimethene core and 0.58 Å out of the plane of the four nitrogen atoms. The conformation of the macrocycle can thus be described as "roof-like" with the two saturated meso-carbon atoms (C_{m1} and C_{m1}') and the titanium(IV) ion along the ridge of the roof (Figures 1 and 3). The methyl groups of the saturated meso-carbon atoms thus have the syn-axial configuration and, along with the oxygen atom of the titanyl group, are ~1.5 Å above the ridge of the roof occupying what could be termed the chimney positions. A remarkable feature of the molecular conformation as found in the crystal is the all-syn orientation of the ethyl groups which gives the molecule a spider-like shape (Figure 1). Such an orientation is rather rare in crystals of metallooctaalkylporphyrins.

The Ti–N bond distances of 2.113 (3) and 2.108 (3) Å are relatively long bond distances for metal ions coordinated to porphyrin type ligands and are concomitant with the large out-of-plane displacement of the titanium(IV) ion. The Ti–N bond distances are nonetheless quite short relative to those observed in other titanium(IV) complexes. Ti–N distances vary from 2.172 Å in a titanium(IV) complex of 2,6-pyridinedicarboxylate[19] to ~2.22 Å in 8-hydroxyquinoline complexes[20] and 2.24 Å in a Schiff base complex.[21]

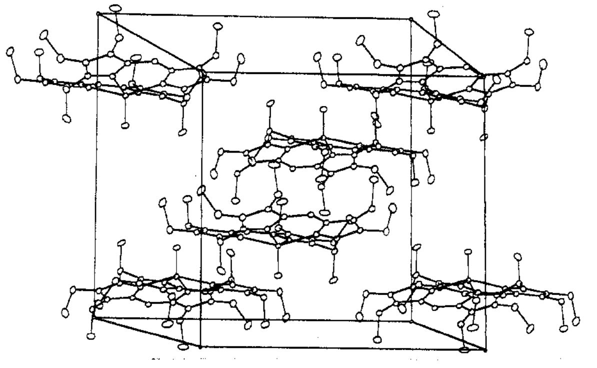


Figure 3. A diagram illustrating the packing of the $OTi(OEPMe_2)$ molecules in the unit cell. The origin is at the lower left front corner; the *b* axis is vertical and the *a* axis is horizontal.

The Ti–O distance of the titanyl moiety is quite short (1.619 (4) Å), not unexpectedly about 0.2 Å shorter than the Ti–O bond distance in oxo-bridged binuclear complexes of titanium(IV) (1.825 Å[19] in $K_2[Ti_2O_5(C_7H_3O_4N)]$ and 1.80 Å[22] in $[TiCl(acac)_2]_2O$). The 1.62-Å bond distance is comparable to the M–O distances reported for the vanadyl (VO^{2+}) ion (1.57–1.62 Å)[23] and for the dioxovanadium(V) (VO_2^+) cation (1.60–1.64 Å)[24] and it is likely that π bonding plays the same important role in stabilizing all these metal–oxygen entities. By contrast to these results, the Ti–O bond distance of 1.79 Å reported[25] for $[(C_2H_5)_4N]_2TiCl_4O$ appears to be long.

Average bond distances of the core are displayed in Figure 2. The numbers in parentheses following each averaged value are, respectively, the mean deviation from the average and the estimated standard deviation of an individual bond length in the last significant figure of the datum. Differences in the values for the two symmetry-unique C_a–N bonds and deviations of the C–C bond lengths from values found for porphyrin derivatives have been previously discussed in terms of limiting Kekule structures for π-electron delocalization in the porphodimethene core.[11]

Figure 3 displays the packing of the molecules in the unit cell. There are no unusually short intermolecular contacts. Of the 15 nonbonded intermolecular contacts less than 4.0 Å, in which at least one atom is from the porphodimethene core, 12 involve contacts between atoms of the peripheral ethyl groups and core atoms with distances ranging from 3.5 Å upward. The intramolecular contacts between the titanyl oxygen atom and the methyl carbon atoms on the saturated meso-carbon atoms ($O\cdots C_1$) are 3.41 Å.

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Registry No. $OTi(OEPMe_2)$, 54161-69-2.

Supplementary Material Available. A listing of structure factor amplitudes (×10) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $2.50 for photocopy or $4.50 for microfiche, referring to code number AIC50063K.

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An Asymmetrically Coordinated Diperoxo Compound. Crystal Structure of $K_3[VO(O_2)_2(C_2O_4)]\cdot H_2O$

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Crystals of $K_3[VO(O_2)_2(C_2O_4)]\cdot H_2O$ are monoclinic with $a = 7.100$ (2) Å, $b = 7.857$ (2) Å, $c = 17.421$ (4) Å, $\beta = 98.45$ (2)°, $Z = 4$, and space group $P2_1/c$. A total of 2205 counter intensities were measured of which 1900 ($>2.3\sigma$) were used to refine the structure by least-squares methods to $R = 5.6\%$. The anion is pentagonal bipyramidal in shape, the vanadyl oxygen atom (1.622 (4) Å) at one apex. Two asymmetrically coordinated (1.861 (4) and 1.923 (4) Å) peroxy groups are related by an approximate anionic mirror plane. The two oxygen atoms involved in the shorter bonds are adjacent ($O\cdots O$ = 2.56 Å). The coordinated oxalate group has V–O distances 2.060 (4) and 2.251 (4) Å (apical). The vanadium atom is 0.28 Å above the approximate pentagonal plane comprising the two peroxo groups and one of the oxalate oxygen atoms. The water molecule is weakly involved in hydrogen bonds to oxalate and peroxo groups.

Introduction

Structural data on mononuclear transition metal–diperoxo compounds include determinations of structure for V(V),[1] Nb(V),[2] Cr(IV),[3-5] Cr(VI),[6-8] and Mo(VI)[9] complexes. The seven-coordinate species[10] have pentagonal-bipyramidal coordination geometries while the two examples of six-coordination, the $CrO(O_2)_2(C_5H_5N)$ molecule[8] and the $[VO(O_2)_2NH_3]^-$ anion,[1] have distorted pentagonal-pyramidal geometries. The eight-coordinate $[Nb(O_2)_2(C_2O_4)_2]^{3-}$ anion[2] has a quasidodecahedral structure similar to that reported for the triperoxoniobate(V) anion $[Nb(O_2)_3(C_{12}H_8N_2)]^-$,[12] the tetraperoxoniobate(V) compound $KMg[Nb(O_2)_4]\cdot 7H_2O$,[13] and the tetraperoxochromium(V) compound $K_3[Cr(O_2)_4]$.[14,15] The peroxo groups in the $[Cr(O_2)_4]^{3-}$ anion are asymmetrically π bonded to the chromium ion; i.e., the chromium ion is nearer to one oxygen of the peroxo group than to the other. A ligand field calculation, based on the optical and electron paramagnetic resonance spectra for this unusual d[1] system, has accounted for the significant difference in Cr–O peroxo bond lengths.[15] To continue the structural study of mononuclear transition metal–diperoxo compounds, the crystal structure of the seven-coordinate $K_3[VO(O_2)_2(C_2O_4)]\cdot H_2O$ compound has been determined.

Experimental Section

Large orange crystals of $K_3[VO(O_2)_2(C_2O_4)]\cdot H_2O$ were prepared using the method reported by Vuletic and Djordjevic.[16] The crystal chosen to collect the complete diffraction data (obtained over a period of ca. 3 weeks) had dimensions 0.40 × 0.12 × 0.06 mm with the *a* axis along the longest dimension; no decomposition was observed.

On the basis of Weissenberg and precession photographs the crystals were assigned to the monoclinic system. The observed systematic absences are $h0l$ for l odd and $0k0$ for k odd, confirming space group