is consistent with a single bond [2.22 (4) Å for terminal Ta—CH$_3$ (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989)] as are the Ta—S and Ta—S' distances of 2.418 (9) and 2.517 (17) Å [compared to 2.529 (3) and 2.520 (3) Å for Zr—S in a zirconocene thioaldehyde complex (Buchwald, Nielsen & Dewan, 1987) and 2.452 (1) Å for Ti—S in an analogous titanocene (Park, Henling, Schaefer & Grubbs, 1990)]. Although the disorder precludes a definitive conclusion, these results suggest that the complex is primarily thiotantalacyclopropane in nature.

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Structure of Triaqua(nitrilotriacetato)vanadium(III) Tetrahydrate

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Abstract. [V(C$_6$H$_6$NO$_6$)(H$_2$O)$_3$].4H$_2$O, M_r = 365.17, triclinic, $P\bar{1}$, a = 7.929 (2), b = 8.716 (3), c = 10.914 (3) Å, α = 98.77 (2), β = 90.30 (2), γ = 105.79 (2)°, V = 716.4 (8) Å^3, Z = 2, D_x = 1.693 g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 7.3 cm^{-1}, $F(000)$ = 380, room temperature. R = 0.060 for 3829 independent reflections [$F_o > 3\sigma(F_o)$]. The V atom is surrounded by three O atoms of the water molecules, and one N and three O donor atoms of the title ligand (nta). The geometry is described as a capped octahedral seven-coordinate structure. Two triangular faces consist of three O atoms of the nta ligand and three water molecules respectively, and they are almost parallel. The N donor atom is placed on the triangular face formed by three O atoms of the nta ligand.

Introduction. Recently vanadium(III) chemistry has attracted much attention, especially in relation to the status of vanadium in ascidians (Michibata & Sakurai, 1990). A V^{III} complex with a nitrilo-

triacetate (nta) ligand was first prepared by Podlaha & Petras (1970), and formulated as [V(nta)-(H$_2$O)$_2$].5H$_2$O. They reported that the complex is fairly resistant to air oxidation, though V^{III} complexes, in general, are quite air sensitive. In order to establish the geometry of the air-stable V^{III}–nta complex, we have determined its crystal structure.

Experimental. All procedures in the sample preparation were carried out under an argon atmosphere by using a standard syringe and vacuum-line techniques. The title complex was prepared as follows: V$_2$(SO$_4$)$_3$ (3.9 g) (Claunch & Jones, 1963) was suspended in 50 cm^3 of water. The suspension was stirred at 333 K for 2 d to give a brownish green solution. The mixture of H$_3$nta (3.8 g) and BaCO$_3$ (5.3 g) in 50 cm^3 of water was added to the above V^{III} solution. By stirring at 313 K for 1 d, a green solution with a white precipitate of BaSO$_4$ was obtained. The precipitate was filtered off and the filtrate reduced to half the volume. The solution was allowed to stand in an ice bath for several hours. The green crystals which appeared were collected by filtration, washed with a

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Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for the non-*H *atoms*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
V	0.04843 (8)	0.35835 (7)	0.22604 (6)	1.04 (1)
N	0.3041 (4)	0.2995 (4)	0.2162 (3)	1.20 (5)
O(1)	0.0071 (4)	0.1389 (3)	0.2808 (3)	1.81 (5)
O(2)	0.1109 (5)	−0.0253 (4)	0.3787 (3)	2.65 (7)
O(3)	0.1265 (4)	0.3699 (4)	0.0470 (3)	1.81 (5)
O(4)	0.2670 (5)	0.2753 (5)	−0.1101 (3)	3.09 (7)
O(5)	0.2222 (4)	0.5371 (4)	0.3449 (3)	1.99 (6)
O(6)	0.4970 (4)	0.6850 (4)	0.3959 (4)	2.51 (7)
O(7)	−0.0194 (4)	0.5634 (3)	0.1875 (3)	1.97 (5)
O(8)	−0.1095 (4)	0.3822 (4)	0.3765 (3)	2.26 (6)
O(9)	−0.1884 (5)	0.2283 (5)	0.1291 (3)	2.86 (7)
O(10)	0.1492 (4)	0.3000 (4)	0.6107 (3)	2.23 (6)
O(11)	0.3955 (4)	0.0309 (4)	0.7825 (3)	2.15 (6)
O(12)	0.3142 (4)	0.8759 (4)	0.5374 (3)	2.09 (6)
O(13)	0.2751 (6)	0.8004 (7)	0.1097 (4)	5.0 (1)
C(1)	0.1315 (5)	0.0940 (5)	0.3264 (4)	1.55 (7)
C(2)	0.3134 (5)	0.2002 (5)	0.3136 (4)	1.60 (7)
C(3)	0.2313 (5)	0.2884 (5)	0.0002 (4)	1.70 (7)
C(4)	0.3096 (5)	0.2089 (5)	0.0911 (4)	1.60 (7)
C(5)	0.3882 (5)	0.5681 (5)	0.3346 (4)	1.64 (7)
C(6)	0.4467 (5)	0.4521 (5)	0.2377 (4)	1.76 (7)

Table 2. *Selected bond distances* (Å) *and angles* (°)

V—N	2.222 (3)	V—O(7)	2.101 (3)
V—O(1)	2.033 (3)	V—O(8)	2.090 (3)
V—O(3)	2.062 (3)	V—O(9)	2.094 (3)
V—O(5)	2.051 (3)		
N—V—O(1)	73.7 (1)	O(3)—V—O(5)	108.9 (1)
N—V—O(3)	73.3 (1)	O(3)—V—O(7)	77.8 (1)
N—V—O(5)	73.4 (1)	O(3)—V—O(8)	156.3 (1)
N—V—O(7)	130.4 (1)	O(3)—V—O(9)	80.7 (1)
N—V—O(8)	130.2 (1)	O(5)—V—O(7)	79.2 (1)
N—V—O(9)	127.6 (1)	O(5)—V—O(8)	79.9 (1)
O(1)—V—O(3)	115.7 (1)	O(5)—V—O(9)	159.0 (1)
O(1)—V—O(5)	112.1 (1)	O(7)—V—O(8)	82.7 (1)
O(1)—V—O(7)	156.0 (1)	O(7)—V—O(9)	85.0 (1)
O(1)—V—O(8)	78.8 (1)	O(8)—V—O(9)	84.4 (1)
O(1)—V—O(9)	78.2 (1)		

small amount of cold water, and then dried. Yield: 4.7 g.

Green crystal 0.23 × 0.48 × 0.50 mm; Enraf–Nonius CAD-4 diffractometer, 50 kV and 26 mA; unit-cell dimensions by least-squares refinement from 25 reflections with $24 < 2\theta < 28°$; ω–2θ scan, scan rate varied from 1 to 5° min^{-1} (in ω), scan width (0.7 + 0.350tanθ)°; three intensity standards were monitored every 2 h of X-ray exposure time and a linear decay correction was applied (correction factor on I, 0.996–1.000); orientation (for the same three reflections) was monitored after every 200 scans; 4152 unique reflections of 4357 measured reflections, $2\theta \le$ 60° ($-11 \le h \le 11$, $-12 \le k \le 12$, $0 \le l \le 15$); 3829 reflections with $F_o > 3\sigma(F_o)$ were used for structure determination; intensities were corrected for Lorentz and polarization; and an empirical absorption correction based on a series of ψ scans was applied (maximum and minimum transmission factors 1.00 and 0.92, respectively). The V-atom position was determined from direct methods and the other non-

H-atom positions were determined from successive difference Fourier maps. No H atoms were included in the calculation. The structure was refined by full-matrix least squares on F using anisotropic thermal parameters for non-H atoms; 190 refined parameters; $R = 0.060$ and $wR = 0.086$, $w = 4F_o^2/\sigma^2(F_o)^2$, $S = 1.45$, $\Delta_{max} = 0.02\sigma$; $\Delta\rho_{max}$ in final difference Fourier map = $0.84\,\text{e}\,\text{Å}^{-3}$. All calculations were performed on a VAX computer using *MOLEN* (Fair, 1990). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. The final atomic parameters are given in Table 1. The molecular structure and numbering scheme are depicted in the *ORTEP* (Johnson, 1965) diagram given in Fig. 1. Selected bond distances and angles are summarized in Table 2.*

Figs. 1 and 2 clearly indicate that the complex is a seven-coordinate structure, although the earlier study (Podlaha & Petras, 1970) suggested a six-coordinate
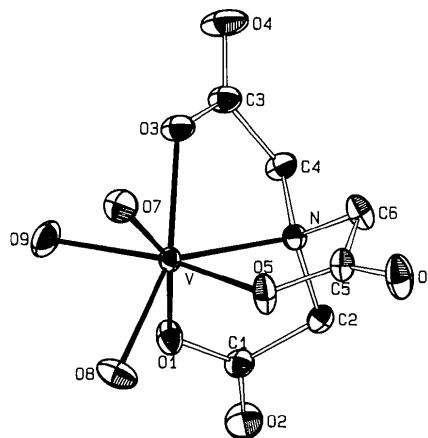
Fig. 1. *ORTEP* (Johnson, 1965) drawing of the [V(nta)(H₂O)₃] complex (50% probability thermal ellipsoids) with the atom-numbering scheme.
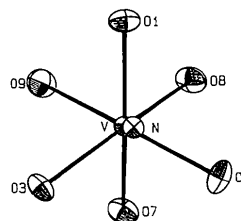

Fig. 2. Geometry around the V atom.

structure. The V atom is bonded to three O atoms of the water molecules, and one N and three O donor atoms of the nta ligand, which acts as a tetradentate ligand. The geometry around the V atom can be described as a capped octahedral seven-coordinate structure rather than a capped trigonal prismatic structure as adopted by V^{III} complexes with a capped water molecule and a hexadentate ligand, $[V(L)(H_2O)]^{n-}$ [L: ethylenediaminetetraacetato, edta (Shimoi, Saito & Ogino, 1989); N'-(2-hydroxy-ethyl)ethylenediamine-N,N,N'-triacetato, hedtra (Ogino, Shimoi & Saito, 1989); and trans-1,2-cyclohexanediamine-N,N,N',N'-tetraacetato, cydta (Shimoi, Miyamoto & Ogino, 1991)]. The triangular faces are the O(1)—O(3)—O(5) and O(7)—O(8)—O(9) planes, and they almost form equilateral triangles [each angle is 58.4 (1)–62.0 (1)°; average 60.0°], although the O(1)—O(3)—O(5) plane [bond distance of O(m)—O(n): m,n = 1,3, 3.466 (5); 1,5, 3.387 (4); and 3,5, 3.346 (4) Å] is larger than the O(7)—O(8)—O(9) plane [m,n = 7,8, 2.767 (5); 7,9, 2.833 (5); and 8,9, 2.811 (4) Å]. The N donor atom is placed on the O(1)—O(3)—O(5) triangular face. Furthermore, two triangular faces are almost parallel [dihedral angles: 2 (1)° for the O(1)—O(3)—O(5) and O(7)—O(8)—O(9) planes], and rotate about 60° around the V—N axis, to which two faces are perpendicular [dihedral angles between the V—N—O(m)—O(n) (m,n = 1,7; 3,8; and 5,9) planes are 57.1 (1), 60.0 (1) and 62.8 (1)° respectively], as shown in Fig. 2. The distances from the O(1)—O(3)—O(5) plane to the V and N atoms are 0.5829 (6) and 1.639 (3) Å, respectively, and that from the V atom to the O(7)—O(8)—O(9) plane is 1.3292 (6) Å. This indicates that the V atom is pulled from the centre of the octahedron toward the capping N atom. These structural characteristics differ from those of V^{III} complexes with a capped water molecule and a hexadentate ligand, $[V(L)(H_2O)]^{n-}$ (L = hedtra, edta and cydta), in which two triangular faces are formed by two O atoms and one N atom in the hexadentate ligand, and are twisted. The V—O(aqua) distances [average 2.095 (3) Å] are somewhat longer than the V—O(nta) distances [average 2.052 (3) Å]. The V—O(nta), V—O(aqua), and V—N distances are in the range of the corresponding distances which have been found in $[V(L)(H_2O)]^{n-}$. The geometry in the nta complex, however, seems to be more symmetrical than the hedtra, edta and cydta complexes, since the nta complex has a C_3 axis through the N—V axis (Fig. 2).

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cis-Di[bis(dimethylphosphino)methane P-oxide-P']dichloropalladium(II) Monohydrate

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Abstract. $[Pd(C_5H_{14}OP_2)_2Cl_2].H_2O$, $M_r = 499.55$, orthorhombic, Pbca, a = 14.332 (3), b = 16.592 (3), c = 17.420 (3) Å, V = 4142.3 (2.5) Å^3, Z = 8, D_x = 1.60 g cm^{-3}, λ(Mo $K\alpha$) = 0.70930 Å, μ = 14.5 cm^{-1}, F(000) = 2032, T = 294 (1) K, R = 0.031 for 3004 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ of 4541 total data. The molecule is a cis-dichlorobisphosphine complex of Pd^{II}. The phosphine is unusual in being a bisphosphine monoxide, the oxide function being nonbonding to palladium. Principal bond lengths and angles are: Pd—Cl 2.357 (1), 2.387 (1); Pd—P 2.254 (1), 2.248 (1); P=O 1.476 (3), 1.467 (4); P—C 1.768 (6)–1.819 (4) Å; P—Pd—P 99.27 (4); cis-P—Pd—Cl 85.31 (4), 86.55 (4); trans-P—Pd—Cl 174.06 (4), 175.23 (4); Cl—Pd—Cl 88.85 (4); P—C—P 114.3 (2), 115.7 (2)°.

Introduction. It is well known (Pringle & Shaw, 1982) that monodentate diphosphine complexes can be used as intermediates in the synthesis of homo- or