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Structure of Dioxo[*N*,*N*,*N*′,*N*′-tetrakis-(2-pyridylmethyl)ethylenediamine]-vanadium(V) Chloride Monohydrate, $[VO_2(tpen)]Cl.H_2O$

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Abstract

In the complex cation of the title compound (1), with site symmetry C_2, the VO_2 group is coordinated by tpen *via* two ethylenediamine N atoms and two pyridyl N atoms. The VO_2 moiety shows *cis* configuration with an O(1)—V—O(1′) angle of 107.90 (2)° and short V—O distances of 1.615 (2) Å.

Comment

Recently the synthesis, magnetism and crystal structure of the first binuclear vanadyl–tpen [tpen = *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine] complex, containing a *syn*-$V_2O_2(\mu\text{-OH})_2^{2+}$ core, was reported (Neves, Wieghardt, Nuber & Weiss, 1988). Here we describe the molecular structure of an octahedral *cis*-dioxo vanadium(V) complex with tpen as tetradentate ligand. $[VO_2(tpen)]^+$ represents the first cationic species of this class of complexes in which the *cis*-VO_2 entity is bonded exclusively by N-donor atoms of a neutral ligand.

The title compound is built up by discrete mononuclear $[VO_2(tpen)]^+$ cations, uncoordinated Cl anions, and water molecules of crystallization. The vanadium(V) ion is in a pseudo-octahedral environment in which the VO_2 moiety is in the expected *cis* configuration and lies *trans* to the N atoms of the ethylenediamine backbone. The coordination sphere around the V atom is completed by two pyridyl N atoms, while two pendant pyridyl groups remain uncoordinated. The molecule has a crystallographically imposed twofold axis which passes through the V-atom centre and the midpoint of the C(3)—C(3′) bond (Fig. 1). The five-membered ring (VN_2C_2) formed by chelation of the ethylenediamine backbone has the usual skew conformation with a torsion angle N(1)—C(3)—C(3′)—N(1′) of 28.1°; the two atoms of the ethylene bridge are displaced by 0.35 (2) Å on opposite sides of the V–N(1)–N(1′) plane. The sum of the interior angles is 514.6°. This value is in excellent agreement with that observed for $[VO_2(edta)]^{3-}$ [515.0° (edta = ethylenediaminetetraacetate) (Scheidt, Countryman & Hoard, 1971)]. The two remaining five-membered rings are formed by the 2-pyridylmethyl groups. An analysis of the planarity of these rings (sum of the interior ring angles = 521.2°) shows the extent of puckering in the inner regions of these rings (Mandel & Douglas, 1989). Similar values have been observed for glycinato five-membered rings in $[VO_2(edtaH_2)]^-$ (Scheidt, Collins & Hoard, 1971) and $[VO_2(edta)]^{3-}$ (Scheidt, Countryman & Hoard, 1971).

The VO_2 entity in the *cis* configuration has an O—V—O obtuse angle of 107.90 (2)°, significantly deviated from the ideal angle of 90°. As expected, the opposite N(1)—V—N(1′) angle is acute, and has a value of 75.52 (1)°. The O—V—O angle of 107.90 (2)° is almost equal to those observed in $[VO_2(edtaH_2)]^-$ (107.1°) and $[VO_2(edta)]^{3-}$ (107.0°), and somewhat larger than in other octahedral *cis*-VO_2 complexes, which have values in the range 104–106° (Drew, Einstein & Gransden, 1974; Neves, Walz, Wieghardt, Nuber & Weiss, 1988).

The short V—O distances of 1.615 (2) Å in (1) indicate strong multiple-bond character as previously discussed by other authors (Scheidt, Tsai & Hoard, 1971). However, it is important to note that these V═O bonds are significantly shorter (by 0.025 Å) than the mean values reported in the above literature for similar *cis*-VO_2 octahedral complexes. This may arise from the presence of a cationic vanadate(V) species in (1). From this point of view it is consistent to consider a decrease of electron density at the metal centre, that determines an increase of the V—O bond order, and consequently the shortening of the V—O bond lengths. This also would be consistent with the slight increase in the observed O—V—O angle in (1).

The V—N(amine) bonds *trans* to the VO_2 group are long [V—N(1) = V—N(1') = 2.349 (2) Å], which is characteristic of the strong *trans* effect of the two oxo ligands. The other two V—N bonds of the pyridyl groups [V—N(11) = V—N(11') = 2.123 (2) Å] are shorter and do not differ significantly from the V—N(pyridine) bond length [2.106 (3) Å] observed in Li[VO_2(*S*-peida)].2CH_3OH (*S*-peida^{2-} = (*S*)-{[1-(2-pyridyl)ethyl]imino}diacetate) (Kojima, Okazaki, Ooi & Saito, 1983).

The Cl anion and the water molecule do not show any interaction with the cationic complex of (1). The remaining structural parameters for the ligand are as expected and will not be discussed in detail.

We conclude that, despite the stereochemical similarities between (1) and other related octahedral anionic complexes which are dominated by the *cis* configuration of the VO_2 group, it is possible to observe structural differences that may be attributed to the positive charge of the $[VO_2(tpen)]^+$ cation.

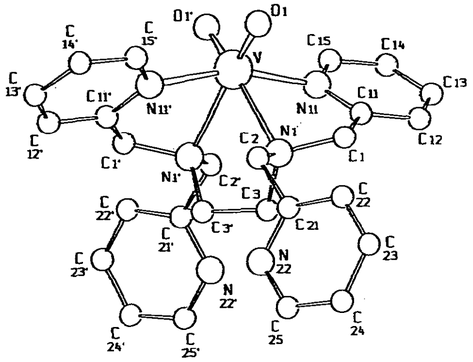

Fig. 1. A perspective view of the cation of (1) with atomic numbering.

Experimental

Crystal data

$[VO_2(C_{26}H_{28}N_6)]Cl.H_2O$
M_r = 560.96
Monoclinic
$P2/n$
a = 13.010 (3) Å
b = 7.687 (1) Å
c = 13.412 (2) Å
β = 103.63 (2)°
V = 1303.6 (5) Å^3
Z = 2

D_x = 1.429 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 9–14°
μ = 0.5091 mm^{-1}
T = 293 K
Lozenge
1.35 × 0.60 × 0.10 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.7343, T_{max} = 1.1351, T_{av} = 0.9805
5399 measured reflections
4147 independent reflections
3987 observed reflections [$I > 3\sigma(I)$]

R_{int} = 0.017
θ_{max} = 33°
h = 0 → 19
k = 0 → 11
l = −20 → 20
3 standard reflections ($\bar{1}07$, 621 and $7\bar{2}2$)
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
Final R = 0.048
wR = 0.052
S = 0.844
3827 reflections
174 parameters
H-atom parameters not refined
$w = 1/\sigma^2$
$(\Delta/\sigma)_{max}$ = 0.001

$\Delta\rho_{max}$ = 0.878 e Å^{-3}
$\Delta\rho_{min}$ = −0.913 e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: 1.5591 × 10^{-8}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2A)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

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

	x	y	z	B_{eq}
V	0.750	0.39021 (7)	0.250	2.122 (8)
Cl	0.750	0.3323 (1)	0.750	4.13 (2)
O(1)	0.7132 (1)	0.5139 (2)	0.3326 (1)	3.29 (3)
O(2)	0.9538 (2)	0.1370 (3)	0.7056 (2)	5.30 (5)
N(1)	0.7432 (1)	0.1486 (2)	0.3555 (1)	2.01 (3)
N(11)	0.9071 (1)	0.3477 (2)	0.3361 (1)	2.29 (3)
N(22)	0.5933 (2)	−0.1667 (3)	0.4097 (2)	3.05 (4)
C(1)	0.8229 (2)	0.1911 (3)	0.4512 (1)	2.39 (3)
C(2)	0.6364 (1)	0.1305 (3)	0.3785 (2)	2.33 (3)
C(3)	0.7749 (2)	−0.0098 (3)	0.3070 (1)	2.16 (3)
C(11)	0.9208 (2)	0.2621 (3)	0.4254 (1)	2.18 (3)
C(12)	1.0196 (2)	0.2471 (2)	0.4921 (2)	2.78 (4)
C(13)	1.1059 (2)	0.3202 (4)	0.4646 (2)	3.22 (4)
C(14)	1.0926 (2)	0.4058 (4)	0.3724 (2)	3.16 (4)
C(15)	0.9916 (2)	0.4192 (3)	0.3104 (2)	2.79 (4)
C(21)	0.6270 (1)	−0.0133 (3)	0.4521 (2)	2.33 (3)
C(22)	0.6514 (2)	0.0123 (4)	0.5574 (2)	3.43 (5)
C(23)	0.6444 (2)	−0.1267 (5)	0.6207 (2)	4.30 (6)
C(24)	0.6139 (2)	−0.2860 (4)	0.5780 (2)	4.37 (5)
C(25)	0.5877 (2)	−0.2993 (4)	0.4728 (2)	4.02 (5)

Table 2. *Geometric parameters* (Å, °)

V—O(1)	1.615 (2)	C(2)—C(21)	1.507 (3)
V—N(1)	2.349 (2)	C(11)—C(12)	1.387 (3)
V—N(11)	2.123 (2)	C(12)—C(13)	1.381 (3)
N(1)—C(1)	1.484 (3)	C(13)—C(14)	1.375 (4)
N(1)—C(2)	1.499 (3)	C(14)—C(15)	1.384 (3)
N(1)—C(3)	1.485 (3)	C(21)—C(22)	1.387 (3)
N(11)—C(11)	1.342 (3)	C(22)—C(23)	1.381 (4)
N(11)—C(15)	1.344 (3)	C(23)—C(24)	1.371 (5)
N(22)—C(21)	1.338 (3)	C(24)—C(25)	1.375 (5)
N(22)—C(25)	1.338 (4)	C(3)—C(3^i)	1.513 (4)
C(1)—C(11)	1.499 (3)		

O(1)—V—N(1)	89.61 (8)	N(22)—C(21)—C(22)	122.1 (2)
O(1)—V—N(11)	96.92 (8)	C(2)—C(21)—C(22)	121.9 (2)
N(1)—V—N(11)	73.68 (7)	C(21)—C(22)—C(23)	119.0 (3)
V—N(1)—C(1)	103.2 (1)	C(22)—C(23)—C(24)	119.3 (3)
V—N(1)—C(2)	111.4 (1)	C(23)—C(24)—C(25)	118.1 (3)
V—N(1)—C(3)	109.3 (1)	N(22)—C(25)—C(24)	123.8 (3)
C(1)—N(1)—C(2)	109.6 (2)	N(1)—C(1)—C(11)	109.9 (2)
C(1)—N(1)—C(3)	110.5 (2)	N(1)—C(2)—C(21)	115.1 (2)
C(2)—N(1)—C(3)	112.5 (2)	N(11)—C(11)—C(1)	116.3 (2)
V—N(11)—C(11)	118.1 (1)	N(11)—C(11)—C(12)	121.6 (3)
V—N(11)—C(15)	122.6 (2)	C(1)—C(11)—C(12)	122.0 (2)
C(11)—N(11)—C(15)	119.0 (2)	O(1)—V—O(1^{i})	107.90 (2)
C(21)—N(22)—C(25)	117.7 (2)	O(1)—V—N(1^{i})	159.67 (1)
C(11)—C(12)—C(13)	118.8 (2)	O(1)—V—N(11^{i})	93.48 (1)
C(12)—C(13)—C(14)	119.8 (2)	N(1)—V—N(1^{i})	75.52 (1)
C(13)—C(14)—C(15)	118.4 (2)	N(1)—V—N(11^{i})	92.16 (7)
N(11)—C(15)—C(14)	122.3 (2)	N(11)—V—N(11^{i})	162.3 (1)
N(22)—C(21)—C(2)	116.0 (2)	N(1)—C(3)—C(3^{i})	110.2 (2)

Symmetry code: (i) $\frac{3}{2} - x, y, \frac{1}{2} - z$.

The title complex (1) was obtained from the reaction of $[V_2^{III}Cl_6(tpen)].2H_2O$ (Neves, Wieghardt, Nuber & Weiss, 1988) with tpen in a mixture of tetrahydrofuran and dimethylformamide at room temperature, whereby V^{III} is oxidized to V^{V} by air. The structure was solved by direct methods (Sheldrick, 1986) and subsequent difference Fourier synthesis. The least-squares refinement used anisotropic thermal parameters for the non-H atoms. The H atoms were not located on the ΔF map. The positions of the H atoms in phenyl groups were calculated and only included in the structure-factor calculations. Programs used were *VAXSDP* (version 3.0, 1986; Frenz, 1978) and *SHELXS*86 (*VMS* version; Sheldrick, 1986).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete bond distances, as well as packing diagrams, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71207 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1042]

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Tetramethylarsonium Pentachlorodicuprate(II)

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Abstract

The crystal structure of $(Me_4As)Cu_2Cl_5$ consists of two-dimensional $(Cu_2Cl_5^-)_\infty$ networks, lying parallel to the (101) plane of the monoclinic unit, separated by the Me_4As^+ cations. Each independent Cu^{II} ion has a distorted square-pyramidal geometry. The *anti*-apical site for Cu(2) is occupied by a Cl atom, Cl(4*a*), at a distance of 3.374 (1) Å, while the *anti*-apical site for Cu(1) is blocked by C(3) of the Me_4As^+ cation.

Comment

In an attempt to prepare an analog of the Jahn–Teller distorted $CsNiCl_3$ type structures found in $(Me_4N)CuCl_3$ (Bond, Willett, Haije & Maaskant, 1988), dilute HCl solutions containing 1:1, 1:1.5 or 1:2 mole ratios of Me_4AsCl and $CuCl_2$ were prepared. Slow evaporation yielded identical deep-red crystals from all three solutions.

The two-dimensional network (Fig. 1) can be envisioned as composed of undulating bibridged $(CuCl_2)_\infty$ chains running parallel to the [101] direction [defined by the Cu atoms Cu(2), Cu(1), Cu(2*b*), Cu(1*b*), Cu(2*d*), Cu(1*d*)]. These chains are linked by the Cl(3) atoms. The undulation of the chains is such that the apical Cu(1)—Cl(3) type bonds are external to the $(CuCl_2)_\infty$ chains, while the apical Cu(2)—Cl(5) type bonds lie in the chain. The undulations also lead to the existence of holes through the layer; each hole is capped by two Me_4As^+ ions in which the C(3) atoms point into the hole. More fundamentally, the structure can be related to the parent hexagonal CdI_2