Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3181.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1994). C**50**, 1417–1419

[*N*,*N'*-Bis(2-hydroxybenzyl)-*N*-methyl-*N'*-(2-pyridylmethyl)-1,3-propanediamine]oxovanadium(IV) Hemihydrate, [VO(bbmppn)].0.5H$_2$O

ADEMIR NEVES

Departamento Química UFSC,
88040-900 Florianópolis SC, Brazil

IVO VENCATO

Departamento Física UFSC,
88040-900 Florianópolis SC, Brazil

YVONNE P. MASCARENHAS

Instituto de Física e Química de São Carlos USP,
13560-970 São Carlos SP, Brazil

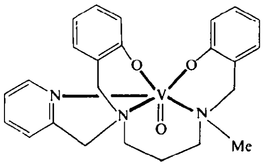
(*Received* 7 *January* 1994; *accepted* 10 *March* 1994)

Abstract

The novel title complex, {2,2'-[*N*-methyl-*N'*-(2-pyridylmethyl-κN)-1,3-propanediyldinitrilo-$\kappa^2 N,N'$-methylene]diphenolato-$\kappa^2 O,O'$}oxovanadium(IV) hemihydrate, [VO(bbmppn)], [VO(C$_{24}$H$_{27}$N$_3$O$_2$)].0.5H$_2$O, has been synthesized and its structure determined. The coordination environment around the VO^{2+} group is defined by two phenolate O and two amine N atoms in the equatorial plane, where atoms of the same type occupy *cis* positions with respect to one another. The pyridyl N atom of the pentadentate ligand, in a *trans* position with respect to the terminal oxo group, completes the coordination sphere.

Comment

As a result of the reported binding of vanadium to tyrosinate residues in vanadium-modified transferrin (Harris & Carrano, 1984) and its interaction with the characterized polyphenol tunichrome in the vandocytes of the tunicates (Bruening, Olttz, Furukawa, Nakanishi & Kustin, 1985), vanadium phenolate chemistry is receiving considerable attention from inorganic chemists (Riley, Pecoraro, Carrano, Bonadies & Raymond, 1986; Neves, Ceccato, Erasmus-Buhr, Gehring, Haase, Paulus, Nascimento & Batista, 1993). Here we report the synthesis and crystal structure of a vanadyl(IV) complex containing a new N$_3$O$_2$-donor ligand (H$_2$bbmppn) which contains phenolate and pyridine as pendant arms.



(I)

The V ion lies in a highly distorted octahedral environment with the V centre being displaced above the equatorial plane by 0.245 (1) Å towards the oxo ligand. The V=O distance is short [1.602 (5) Å], indicating the considerable double-bond character typical of vanadyl(IV) complexes (Neves, Walz, Wieghardt, Nuber & Weiss, 1988; Neves *et al.*, 1993). Consequently, the V—N(pyridine) bond *trans* to the V=O group is long [V—N(1) = 2.259 (5) Å], which is characteristic of the strong *trans* influence of the V=O group. The V—O(phenolate) [average 1.916 (5) Å] and V—N(amine) [average 2.209 (6) Å] bond distances in the equatorial plane are identical to those found in the closely related [VO$^{\rm IV}$(bbpen)] complex [1.923 (2) and 2.208 (3) Å, respectively], where H$_2$bbpen = *N*,*N'*-bis(2-hydroxybenzyl)-*N*,*N'*-bis(2-pyridylmethyl)ethylenediamine (Neves *et al.*, 1993).

However, despite the similarities between the title structure and [VO(bbpen)], it is worth noting that the V—N bond lengths *trans* to the V=O group are significantly different in the two complexes {2.259 (5) Å in the title structure and 2.307 (2) Å in [VO(bbpen)]}. This fact reflects the smaller displacement (0.245 Å) of the V centre from the N$_2$O$_2$ plane in the present complex compared with that (0.345 Å) in [VO(bbpen)]. In the title complex, the six-membered chelate ring formed by the 1,3-propanediamine group, which requires a larger bite angle [N(2)—V—N(3) = 93.2 (2)°], is in the equatorial plane. On the other hand, in the [VO(bbpen)] complex, one of the amine N atoms of the ethylenediamine backbone which forms the more rigid five-membered ring is coordinated *trans* rather than *cis* to the V=O bond. As a consequence, the higher flexibility of the six-membered ring in the title structure allows coordination of the pyridyl arm *trans* to the V=O group. From this information we must conclude that, despite the similarities between the H$_2$bbmppn and H$_2$bbpen ligands, it is possible to observe significant structural differences in their corresponding vanadyl(IV) complexes.

Finally, the structure shows two hydrogen bonds involving the O(*W*) water molecule, placed in a special position, as a donor to the O(1) and O(1$^{\rm i}$) atoms [symmetry code: (i) $1-x$, y, $\frac{3}{2}-z$], characterized by symmetrical distances of 2.752 Å for O(*W*)···O(1) and O(*W*)···O(1$^{\rm i}$), and an O(1)···O(*W*)···O(1$^{\rm i}$) angle of 131.3° [H(*W*)—O(*W*)—H(*W*$^{\rm i}$) = 116.1°].

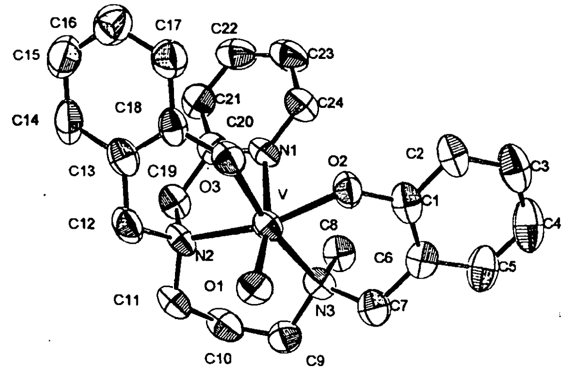


Fig. 1. Perspective view of the title molecule with the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

The reaction of *N*,*N*′-bis(2-hydroxybenzyl)-*N*-methyl-*N*′-(2-pyridylmethyl)-1,3-propanediamine (Neves *et al.*, 1994) with $VOSO_4.5H_2O$ in methanol afforded a violet microcrystalline precipitate which was filtered off and washed with ethanol and ether. Single crystals were obtained by recrystallization from a methanolic solution of the title complex. All attempts to obtain crystals more suitable for X-ray analysis were unsuccessful.

Crystal data

[VO($C_{24}H_{27}N_3O_2$)].0.5H_2O
M_r = 465.4
Monoclinic
$C2/c$
a = 36.520 (3) Å
b = 6.840 (2) Å
c = 18.241 (2) Å
β = 108.03 (2)°
V = 4333 (3) Å^3
Z = 8
D_x = 1.427 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 17.2–29.7°
μ = 4.0 mm^{-1}
T = 296 K
Rectangular
0.10 × 0.08 × 0.05 mm
Pink

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.626, T_{max} = 1.604
3632 measured reflections
2825 independent reflections

2153 observed reflections [$F > 6.0\sigma(F)$]
R_{int} = 0.098
θ_{max} = 60.1°
$h = -40 \rightarrow 38$
$k = -0 \rightarrow 7$
$l = 0 \rightarrow 20$
2 standard reflections
frequency: 30 min
intensity variation: 1.0%

Refinement

Refinement on F
R = 0.0747
wR = 0.0823
S = 5.09
2153 reflections
287 parameters
H-atom parameters not refined
$w = 5.834/[\sigma^2(F) + 0.000818F^2]$
$(\Delta/\sigma)_{max}$ = 0.09

$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}
Extinction correction: $F = F(1-\chi F^2/\sin\theta)$
Extinction coefficient: χ = 7.4 (3) × 10^{-8}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
V	0.3962 (1)	0.1801 (2)	0.6019 (1)	3.51 (4)
O(1)	0.4305 (1)	0.2751 (7)	0.6698 (2)	4.4 (2)
O(2)	0.3798 (1)	0.3678 (7)	0.5212 (2)	4.3 (1)
O(3)	0.3523 (1)	0.2642 (6)	0.6312 (2)	4.0 (1)
N(1)	0.3519 (1)	−0.0222 (8)	0.5247 (3)	3.9 (2)
N(2)	0.4002 (2)	−0.0938 (8)	0.6676 (3)	4.0 (2)
N(3)	0.4393 (2)	0.0833 (8)	0.5469 (3)	3.9 (2)
C(1)	0.3920 (2)	0.422 (1)	0.4627 (3)	4.6 (2)
C(2)	0.3669 (2)	0.522 (1)	0.4007 (4)	5.1 (2)
C(3)	0.3795 (3)	0.584 (1)	0.3406 (4)	6.1 (3)
C(4)	0.4160 (3)	0.544 (1)	0.3396 (5)	6.8 (3)
C(5)	0.4401 (3)	0.442 (1)	0.3993 (4)	5.7 (3)
C(6)	0.4293 (2)	0.376 (1)	0.4608 (4)	4.3 (2)
C(7)	0.4561 (2)	0.266 (1)	0.5257 (4)	4.6 (2)
C(8)	0.4246 (2)	−0.039 (1)	0.4768 (4)	4.7 (2)
C(9)	0.4719 (2)	−0.016 (1)	0.6036 (4)	4.7 (2)
C(10)	0.4620 (2)	−0.197 (1)	0.6421 (4)	5.4 (3)
C(11)	0.4409 (2)	−0.160 (1)	0.7001 (4)	4.8 (2)
C(12)	0.3860 (2)	−0.043 (1)	0.7334 (3)	4.7 (2)
C(13)	0.3439 (2)	0.001 (1)	0.7095 (3)	4.4 (2)
C(14)	0.3188 (3)	−0.111 (1)	0.7376 (4)	5.5 (3)
C(15)	0.2806 (2)	−0.063 (1)	0.7177 (4)	6.2 (3)
C(16)	0.2666 (2)	0.089 (1)	0.6693 (4)	5.6 (3)
C(17)	0.2905 (2)	0.201 (1)	0.6399 (4)	5.1 (2)
C(18)	0.3298 (2)	0.1527 (9)	0.6601 (3)	4.0 (2)
C(19)	0.3772 (2)	−0.261 (1)	0.6242 (3)	4.2 (2)
C(20)	0.3457 (2)	−0.192 (1)	0.5566 (4)	4.2 (2)
C(21)	0.3132 (2)	−0.308 (1)	0.5258 (4)	5.1 (2)
C(22)	0.2858 (2)	−0.241 (1)	0.4608 (4)	5.7 (3)
C(23)	0.2922 (2)	−0.069 (1)	0.4270 (4)	5.6 (3)
C(24)	0.3247 (2)	0.035 (1)	0.4613 (4)	4.9 (2)
O(W)	1/2	0.442 (1)	3/4	12.0 (4)

Table 2. *Selected geometric parameters* (Å, °)

V—O(1)	1.602 (5)	V—N(1)	2.259 (5)
V—O(2)	1.905 (5)	V—N(2)	2.204 (5)
V—O(3)	1.928 (5)	V—N(3)	2.214 (6)
O(1)—V—O(2)	107.9 (2)	O(2)—V—N(3)	87.1 (2)
O(1)—V—O(3)	100.5 (2)	O(3)—V—N(1)	81.9 (2)
O(1)—V—N(1)	165.5 (2)	O(3)—V—N(2)	91.4 (2)
O(1)—V—N(2)	91.1 (2)	O(3)—V—N(3)	169.7 (2)
O(1)—V—N(3)	88.6 (2)	N(1)—V—N(2)	74.5 (2)
O(2)—V—O(3)	85.6 (2)	N(1)—V—N(3)	90.4 (2)
O(2)—V—N(1)	86.4 (2)	N(2)—V—N(3)	93.2 (2)
O(2)—V—N(2)	160.9 (2)		

The x and z coordinates of the O(W) atom were held fixed, and the corresponding anisotropic components U_{23} and U_{12} were fixed at zero due to symmetry restrictions. H atoms were included at geometrically idealized positions but their coordinates were recalculated after each cycle. The H(W) atom of the water molecule was located as the highest peak from the last difference map. The other water H atom, H(W^i), is generated by symmetry. Data collection, cell refinement and data reduction were performed using *SDP-Plus* (Frenz, 1985). *SHELX*86 (Sheldrick, 1986) was used for structure solution, *SHELX*76 (Sheldrick, 1976) for refinement. Graphics were prepared using *ORTEP* (Johnson, 1965). Most of the calculations were performed on a IBM 3090 computer at the Universidade Federal de Santa Catarina.

This work was supported by grants from PADCT, CNPq, FINEP, FAPESP and FUNCITEC. We thank Drs A. S. Ceccato and V. Kolm for their help with the preparation of the complex.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1102). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bruening, R. C., Olttz, E. M., Furukawa, J., Nakanishi, K. & Kustin, K. (1985). *J. Am. Chem. Soc.* **107**, 5298–5300.

Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Harris, W. R. & Carrano, C. J. (1984). *J. Inorg. Biochem.* **22**, 201–218.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Neves, A., Ceccato, A. S., Erasmus-Buhr, C., Gehring, S., Haase, W., Paulus, H., Nascimento, O. R. & Batista, A. A. (1993). *J. Chem. Soc. Chem. Commun.* **23**, 1782–1784.

Neves, A., Ceccato, A. S., Vencato, I. & Mascarenhas, Y. P. (1994). In preparation.

Neves, A., Walz, W., Wieghardt, K., Nuber, B. & Weiss, J. (1988). *Inorg. Chem.* **27**, 2484–2489.

Riley, P. E., Pecoraro, V. L., Carrano, C. J., Bonadies, J. A. & Raymond, K. N. (1986). *Inorg. Chem.* **25**, 154–160.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELX86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1994). **C50**, 1419–1422

A Cobalt 1-Aminocyclohexanecarboxylate Complex

Helmut M. Haendler

Department of Chemistry,
University of New Hampshire, Durham,
New Hampshire 03824-3598, USA

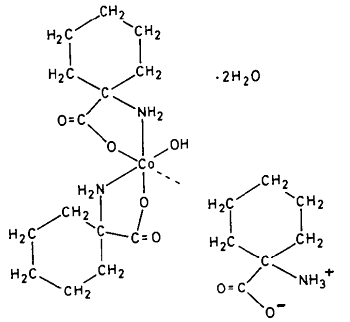
(*Received* 21 *April* 1993; *accepted* 10 *December* 1993)

Abstract

The crystal structure of di-μ-hydroxo-bis[bis(1-aminocyclohexanecarboxylato-*N*,*O*)cobalt(III)]–1-aminocyclohexanecarboxylic acid–water (1/2/4), $[Co_2(C_7H_{12}NO_2)_4(OH)_2].2C_7H_{13}NO_2.4H_2O$, contains two asymmetric units related through a center of symmetry. Each molecule contains two hexacoordinate Co atoms, each of which is chelated to two bidentate 1-aminocyclohexanecarboxylato ligands. The Co atoms are linked by two hydroxo bridges. This results in two slightly distorted octahedral coordination polyhedra, which have an edge in common. In each polyhedron the N atoms are in *cis* positions. Each asymmetric unit is completed by an uncoordinated molecule of the ligand, in the zwitterionic form, and by two water molecules, which are involved in hydrogen bonding. The hydrogen-bonding scheme may also involve the amino groups of the free ligand molecule.

Comment

The structure analysis of the title compound (I) is a continuation of the investigation of metal complexes of aromatic and heterocyclic amino acids (Haendler, 1989, 1993; Boudreau & Haendler, 1992). 1-Aminocyclohexanecarboxylic acid can act as a bidentate ligand with several metals, forming a five-membered ring system. The amino and carboxyl groups are attached to the same C atom; their proximity results in some unexpected configurations. The Cu complex, for example, exhibits both planar and bipyramidal (or its rectangular pyramidal distortion) structures in the two molecules within each asymmetric unit. In the Ni complex, the Ni atom is hexacoordinate, coordinated by the two chelating bidentate ligands and by the O atoms of two water molecules, while a third water molecule forms part of a hydrogen-bond network.



(I)

In the Co complex studied here, the ligand is again bidentate, but two asymmetric units combine around the center of symmetry to form a dihydroxo-bridged molecule, the Co^{III} atoms being thus hexacoordinate. The resultant complex contains two slightly distorted octahedral coordination polyhedra sharing an O···O edge of 2.514 (4) Å, and having a Co···Co distance of 2.864 (1) Å. In addition, the unit cell contains two uncoordinated molecules of the ligand (in the zwitterionic form) and four water molecules. The result is an extensive hydrogen-bonding network, in which it is possible that the N atoms of the free ligand may also be involved.