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Synthesis, Magnetism and Crystal Structure of $[V_2O_2(\mu\text{-}OH)_2(tpen)]I_2 \cdot 4H_2O$; a Binuclear Complex Containing the *syn*-$\{VO(\mu\text{-}OH)_2VO\}^{2+}$ Core (tpen = tetrakis(2-pyridylmethyl)ethylenediamine)

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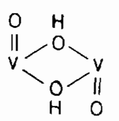
Abstract

The reaction of *N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine (tpen) with VCl_3 in CH_3CN yields $Cl_3V(tpen)VCl_3$ which was hydrolyzed in water in the presence of oxygen affording $[V_2O_2(\mu\text{-}OH)_2(tpen)]I_2 \cdot 2H_2O$, the crystal structure of which has been determined. A *syn*-$\{OV(\mu\text{-}OH)_2VO\}^{2+}$ core has been identified where the V(IV) centers are antiferromagnetically coupled ($J = -150$ cm^{-1}; $g = 1.80$).

Introduction

Binuclear μ-hydroxo bridged vanadyl complexes (d^1) are an interesting class of compounds for the study of intramolecular spin exchange coupling phenomena since they are complementary to investigations of Cu(II) dimers (d^9). Recently, we have reported the first such compound, $[([9]ane\text{-}N_3)_2V_2O_2(\mu\text{-}OH)_2]Br_2$, which contains an *anti*-$\{V_2O_2(\mu\text{-}OH)_2\}^{2+}$ core [1]. The *syn* configured analogue has not been described previously.



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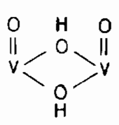
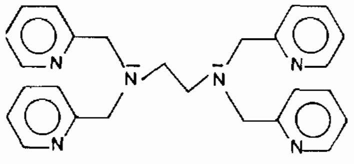


syn

In order to synthesize such a species we have used the potentially binuclear ligand *N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine (tpen) where two N_3-donor sets comprised each of one tertiary amine nitrogen atom and two pyridine N-atoms are strapped by an ethylene group [2].



tpen

The strapping $-(CH_2)_2-$ group should prevent the formation of an *anti*-configuration. The ligand has previously been shown to form monomeric complexes with first-row transition metals in the oxidation states +II and +III [2, 3].

In this work we show that tpen can indeed function as a binucleating ligand and the *syn*-$\{VO(\mu\text{-}OH)_2VO\}^{2+}$ entity can be stabilized.

Experimental

Synthesis

The ligand *N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine (tpen) was prepared as described in the literature [2, 3].

$[V_2Cl_6(tpen)] \cdot 2H_2O$

VCl_3 (0.48 g; 2.8 mmol) was dissolved in dry acetonitrile (15 ml) under an argon atmosphere and was refluxed for 15 min until a clear green solution was obtained. A solution of the ligand tpen (1.2 g; 2.8 mmol) in dry tetrahydrofuran (THF) (10 ml) was added to the above green solution which was refluxed for 15 min and then cooled to room temperature. A dark violet microcrystalline solid precipitated out immediately, which was filtered off, washed with THF and ether and stored under argon. Yield: 0.80 g (80%). The solid material is stable in the presence of air for at least two weeks. *Anal.* Calc. for $C_{26}H_{28}N_6Cl_6V_2 \cdot 2H_2O$: C, 40.30; H, 4.16; N, 10.84. Found: C, 40.5; H, 4.3; N, 10.9%.

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$[V_2O_2(\mu\text{-}OH)_2(tpen)]I_2 \cdot 2H_2O$

A suspension of $[V_2Cl_6(tpen)] \cdot 2H_2O$ (0.7 g, 0.9 mmol) in water (20 ml) which contained sodium acetate (1.5 g) was heated to 90 °C for 10 min under an argon atmosphere. The red–brown solution was then exposed to air until a clear green solution was obtained. After addition of sodium iodide (1.0 g) the solution was allowed to stand at room temperature for 24 h during which time green crystals of X-ray quality precipitated, which were filtered off and dried under vacuum over $CaSO_4$. Yield: 0.4 g (50%). *Anal.* Calc. for $C_{26}H_{30}N_6O_4I_2V_2 \cdot 2H_2O$: C, 35.40; H, 3.88; N, 9.52. Found: C, 35.6; H, 4.0; N, 9.5%. The crystal used for X-ray analysis was not dried as described above and four water molecules of crystallization per formula unit were found to be present.

X-ray Crystallography

A green, needle shaped crystal of $[V_2O_2(\mu\text{-}OH)_2(tpen)]I_2 \cdot 4H_2O$ was attached to a glass fiber and mounted on an AED II (Siemens) diffractometer. The unit cell dimensions were obtained by a least-squares fit of 26 reflections (5.8° < 2θ < 25°). The data are summarized in Table I. Intensity data were corrected for Lorentz and polarization effects; an empirical absorption correction (ψ-scans) was also carried out*. The function minimized during least-squares refinements was $\Sigma w(|F_o| - |F_c|)^2$ with final convergence to $R = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$, where $w =$

TABLE I. Summary of Crystallographic Data

Formula	$C_{26}H_{30}N_6O_4I_2V_2 \cdot 2H_2O$
Formula weight	882.29
Crystal system	triclinic
Space group	$P\bar{1}$
Z	2
a (Å)	11.086(4)
b (Å)	11.426(4)
c (Å)	15.406(6)
α (°)	104.02(3)
β (°)	104.22(3)
γ (°)	97.42(3)
V (Å^3)	1816.4
D_{calc} (g cm^{-3})	1.68
Crystal dimensions (mm)	0.11 × 0.19 × 0.55
Temperature (°C)	20
Radiation	Mo Kα (graphite)
Scan type	ω
2θ range (°)	$3 \leqslant 2\theta \leqslant 57$
Data collected	$\pm h, \pm k, +l$
No. data collected	2351
No. unique data	2145 ($I \geqslant 2.5\sigma(I)$)
Absorption coefficient (cm^{-1})	17.8
Transmission coefficient	0.78–1.00
Least-squares parameters	255
R	0.077
R_w	0.066

TABLE II. Atom Parameters (×10^4) of $[V_2O_2(\mu\text{-}OH)_2(tpen)]I_2 \cdot 4H_2O$ and Temperature Factors (Å × 10^3)

Atom	x	y	z	U[a]
I1	1378(2)	2798(2)	1621(2)	86(1)
I2	7797(2)	574(2)	5475(1)	79(1)
V1	2242(3)	5080(4)	8597(3)	30(2)
V2	3086(4)	7581(4)	8459(3)	32(2)
O1	2796(12)	5277(13)	9682(9)	34(7)
O2	3693(12)	8301(13)	9504(9)	38(7)
O3	1518(11)	6516(11)	8424(9)	29(6)
O4	3598(11)	5977(12)	8261(9)	33(7)
C1	1560(20)	4757(19)	6317(14)	37(6)
C2	1322(18)	6004(18)	6290(14)	35(6)
N1	1165(15)	4170(15)	7010(11)	35(8)
C3	1377(22)	2887(22)	6772(16)	56(7)
C4	−223(19)	4194(20)	6924(14)	40(7)
N2	2970(16)	3492(15)	8262(11)	40(9)
C11	3953(20)	3228(20)	8831(16)	40(7)
C12	4542(21)	2261(19)	8585(15)	49(7)
C13	4139(20)	1546(21)	7671(15)	58(8)
C14	3123(19)	1773(19)	7099(15)	36(6)
C15	2562(19)	2713(20)	7405(14)	29(6)
N3	424(14)	4038(13)	8515(11)	28(8)
C16	238(20)	3761(19)	9281(16)	42(7)
C17	−972(21)	3220(20)	9239(16)	47(7)
C18	−1895(21)	3025(20)	8479(15)	53(7)
C19	−1778(21)	3282(20)	7676(16)	53(7)
C20	−537(21)	3790(21)	7726(15)	44(7)
N4	2366(14)	7159(14)	6846(11)	35(8)
C5	3498(18)	7031(20)	6488(14)	44(7)
C6	1906(21)	8284(20)	6627(16)	57(8)
N5	4640(16)	8391(16)	8025(11)	36(9)
C21	5621(19)	9260(19)	8629(15)	46(7)
C22	6601(22)	9778(22)	8358(16)	58(8)
C23	6586(22)	9361(20)	7426(16)	50(7)
C24	5606(21)	8536(20)	6831(15)	46(7)
C25	4586(20)	8037(20)	7140(14)	46(7)
N6	1983(16)	8926(15)	8224(12)	42(9)
C26	1736(20)	9709(20)	8912(15)	45(7)
C27	928(23)	10516(23)	8823(18)	72(9)
C28	284(21)	10492(21)	7881(16)	54(7)
C29	606(21)	9703(21)	7192(17)	59(8)
C30	1467(21)	8999(21)	7357(15)	40(7)
O_w1	4085(23)	4548(23)	1529(17)	167(10)
O_w2	4843(26)	−1777(27)	4333(19)	213(13)
O_w3	3025(43)	4579(43)	4266(32)	139(19)
O_w4	4952(40)	5930(40)	3771(29)	133(17)
O_w5	1750(43)	2625(42)	4015(30)	153(19)
O_w6	2964(52)	2641(51)	5012(38)	199(24)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor for I, V, O, N atoms; carbon atoms and oxygen atoms of water of crystallization (O_w) were refined isotropically.

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*All computations were carried out on an ECLIPSE computer using the SHELXTL program package.

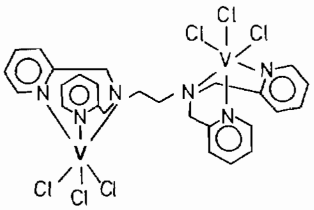
$1/\sigma^2(I)$. The structure was solved via conventional Patterson and Fourier syntheses. The positions of methylene and ring protons were calculated and were included in the final refinement cycle with isotropic thermal parameters. The I, V, O and N atoms were refined with use of anisotropic thermal parameters whereas due to the low reflections to parameter ratio the carbon atoms of the ligand tpen were refined with isotropic displacement parameters only. In the final refinement cycle maximum $(\Delta/\sigma) = 0.07$ and the maximum height in the final ΔF map was 1.0 e/A^3 near an iodine atom. During all calculations the analytical scattering factors for neutral atoms were corrected for both $\Delta f'$ and $i(\Delta f'')$ terms [4]. The final atom parameters are given in Table II; bond lengths and angles are summarized in Table III. See also 'Supplementary Material'.

TABLE III. Selected Bond Distances (Å) and Angles (°) in the Cation of $[V_2O_2(\mu\text{-}OH)_2(tpen)]I_2 \cdot 2H_2O$

V1...V2	2.965(6)	V2–O2	1.55(1)
V1–O1	1.58(1)	V2–O3	1.97(1)
V1–O3	1.96(1)	V2–O4	1.96(2)
V1–O4	1.95(2)	V2–N4	2.32(2)
V1–N1	2.35(2)	V2–N5	2.17(2)
V1–N2	2.08(2)	V2–N6	2.13(2)
V1–N3	2.16(2)	C1–C2	1.49(3)
N4–C2	1.545(21)		
C1–N1	1.51(3)		
O1–V1–O3	107.9(7)	O3–V1–O4	79.9(6)
O1–V1–O4	104.3(6)	O3–V1–N1	85.1(6)
O1–V1–N1	161.9(7)	O3–V1–N2	158.5(7)
O1–V1–N2	92.6(7)	O3–V1–N3	92.4(6)
O1–V1–N3	93.8(7)	O4–V1–N1	90.1(6)
O4–V1–N2	89.1(7)	N1–V1–N2	76.5(6)
O4–V1–N3	161.7(6)	N1–V1–N3	72.6(6)
N2–V1–N3	92.4(6)		
O2–V2–O3	104.9(7)	O3–V2–O4	79.6(6)
O2–V2–O4	107.5(7)	O3–V2–N4	89.2(5)
O2–V2–N4	160.7(8)	O3–V2–N5	161.2(6)
O2–V2–N5	93.7(7)	O3–V2–N6	87.6(6)
O2–V2–N6	92.2(7)	O4–V2–N4	87.7(6)
O4–V2–N5	92.4(7)	N4–V2–N5	73.4(6)
O4–V2–N6	158.6(5)	N4–V2–N6	75.0(6)
N5–V2–N6	94.4(7)		
V1–O3–V2	97.8(6)	V1–O4–V2	98.3(7)
V1–N1–C1	117.4(10)	C1–N1–C3	106.7(17)
V1–N1–C3	106.9(12)	C1–N1–C4	109.0(16)
V1–N1–C4	105.4(11)	C3–N1–C4	111.4(16)
V2–N4–C2	118.5(13)	C2–N4–C5	107.4(14)
V2–N4–C5	106.8(10)	C2–N4–C6	108.8(14)
V2–N4–C6	107.8(11)	C5–N4–C6	107.0(18)
N4–C2–C1	120.2(16)	C2–C1–N1	120.3(19)

Results and Discussion

The reaction of vanadium trichloride dissolved in acetonitrile with the ligand *N,N,N′,N′*-tetrakis(2-pyridylmethyl)ethylenediamine (tpen) in the ratio 1:1 affords a dark violet precipitate of $[Cl_3V(tpen)VCl_3] \cdot 2H_2O$. The ligand functions here as a binucleating ligand, in contrast to other known monomeric complexes of first-row transition metals, where it is a hexadentate ligand [2, 3]. We propose the following structure for this species:



Temperature dependent measurements of the magnetic susceptibility of a powdered sample using a Faraday-type magnetic balance are in agreement with the above structure. A temperature independent magnetic moment between 98 and 293 K of 2.93 μ_B per vanadium(III) is typical for an uncoupled octahedral vanadium(III) complex (d^2) [5].

The complex is insoluble in polar and unpolar solvents; it is stable in the solid state and can be stored for weeks without detectable decomposition in the presence of oxygen.

Hydrolysis of $[Cl_3V(tpen)VCl_3] \cdot 2H_2O$ in water in the presence of sodium acetate under an argon atmosphere at 90 °C yielded a red–brown solution which changed to green upon exposure to air. Addition of solid sodium iodide to such a solution initiated the precipitation of green crystals of $[V_2O_2(\mu\text{-}OH)_2(tpen)]I_2 \cdot 4H_2O$ which were suitable for X-ray crystallography.

Crystals of $[V_2O_2(\mu\text{-}OH)_2(tpen)]I_2 \cdot 4H_2O$ consist of the binuclear dication $[V_2O_2(\mu\text{-}OH)_2(tpen)]^{2+}$, uncoordinated iodide anions and water molecules of crystallization. Figure 1 shows the structure of the dication and the atom labeling scheme. Table III summarizes selected distances and angles of the cation. The hexadentate ligand coordinates two vanadium(IV) centers which are connected by two μ-hydroxo bridges (edge-sharing octahedra); each vanadium(IV) center has an additional terminal oxo-group. Thus air-oxidation of $Cl_3V(tpen)VCl_3$ yields a dimeric vanadyl complex. The vanadium atoms are in a distorted octahedral environment of three facially coordinated nitrogen atoms and three oxygen atoms (one V=O and two μ-OH groups). The V–N bond distances *trans* to the V=O group are significantly longer than the other V–N bonds. This is due to the pronounced *trans*-influence of the V=O group and has been observed in many vanadyl complexes—mononuclear [6] and binuclear [1].

The terminal oxo-groups are in *syn*-positions with respect to each other; the V=O bond length is short and indicates considerable double bond character

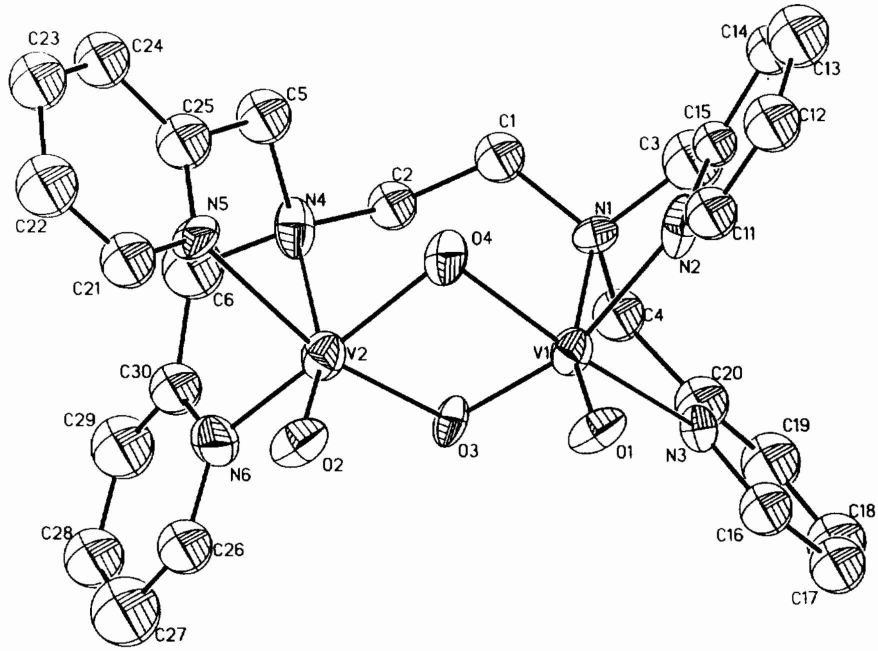


Fig. 1. Perspective view of the dication in $[V_2O_2(\mu\text{-}OH)_2(tpen)]I_2\cdot 4H_2O$ and atom labeling scheme.

as is usual for vanadyl complexes. In $[([9]aneN_3)_2\text{-}V_2O_2(\mu\text{-}OH)_2]Br_2\cdot H_2O$ the terminal oxo-groups are *anti*-configured ($[9]aneN_3$ = 1,4,7-triazacyclononane) [1]. These two compounds are the first example for the *syn*- and *anti*-$\{V_2O_2(\mu\text{-}OH)_2\}^{2+}$ core. The *syn*-configuration in the present case is enforced by the steric requirements of the binucleating ligand tpen. Interestingly, the substitution of the ethylene group in tpen by a longer saturated carbon chain ($-(CH_2)_4-$) as in tetrakis(2-pyridylmethyl)-1,4-butanediamine (tpbn) [3] leads to a situation where the binucleating ligand does not encompass two μ-oxo (or otherwise) bridged metal ions, but rather a tetranuclear species forms where two binuclear moieties are connected via the 1,4-butanediamine straps (pair of dimers). This has been observed in $[Fe_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2(tpbn)]_2\text{-}(NO_3)_4\cdot 4H_2O$ [7]. The strapping ethylene group is strained. This is born out by the two bond angles N4–C2–C1 and C2–C1–N1 of 120.2° which are larger than the usual tetrahedral angle of 109°; the N4–C2, C1–C2, and C1–N1 bond lengths are normal (Table III).

The $V_2(\mu\text{-}OH)_2$ four-membered ring is not quite planar (the sum of the four bonding angles is 355.6°) but slightly puckered contrasting in this respect to the planar ring in *anti*-$[([9]aneN_3)_2V_2O_2(\mu\text{-}OH)_2]\text{-}Br_2$ [1]. The non-bonding V...V distance is 2.965(6) Å which compares well with the distance of 3.033(3) Å found in the *anti*-$[([9]aneN_3)_2V_2O_2(\mu\text{-}OH)_2]Br_2$ complex. The O–V–O bond angles within the four-membered ring are acute (average 79.9°) whereas the corresponding V–OH–V bond angles are obtuse (average 98.0°). This is typical for edge-sharing bioctahedral complexes without bonding metal–metal interactions.

Measurements of the magnetic susceptibility, which were corrected for diamagnetic contributions in the usual manner, of a powdered sample of $[V_2\text{-}O_2(\mu\text{-}OH)(tpen)]I_2\cdot 4H_2O$ in the temperature range 98 to 298 K using the Faraday method indicated a strongly reduced, temperature dependent magnetic moment per vanadium(IV) center as compared to a spin-only value of 1.7 μ_B. Intramolecular antiferromagnetic coupling of the two d^1–d^1 centers has been observed. The magnetic susceptibility data were readily fitted to the expression for χ_M *versus* T derived from the spin exchange Hamiltonian $\mathcal{H}' = -2JS_1S_2$, with $S_1 = S_2 = 1/2$. A J value of $-150\ cm^{-1}$ ($g = 1.80$) was calculated. For $[([9]\text{-}aneN_3)_2V_2O_2(\mu\text{-}OH)_2]Br_2$ a similar J value of $-177\ cm^{-1}$ has been reported [1]. The electronic spectrum measured in aqueous solution exhibits an absorption maximum at 731 nm ($\epsilon = 48\ l\ mol^{-1}\ cm^{-1}$ per dimer).

Supplementary Material

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, F.R.G., on quoting the depository number CSD 52891, the names of the authors, and the journal citation.

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