Fund, administered by the American Chemical Society, and to the Research Corp. for support of this research. The purchase of the diffractometer was supported in part by NSF Grant CHE 8000670.

Registry No. $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$, 83945-00-0; $(Et_3NH)_2[Mn(Cat)_3]$, 89164-55-6; $[Mn(Cat)_3]^{2-}$, 89144-62-7; $(Et_3NH)[Mn^{III}(Cat)_2(OH_2)_2]$, 89144-61-6; $Mn(acac)_3$, 14284-89-0; Mn, 7439-96-5.

Supplementary Material Available: Listings of atomic positional and thermal parameters, bond distances and angles, observed and calculated structure factors, and magnetic susceptibility data (15 pages). Ordering information is given on any current masthead page.

Contribution from the Lehrstuhl für Anorganische Chemie I der Ruhr-Universität, D-4630 Bochum, West Germany, and Anorganisch-Chemisches Institut der Universität, D-6900 Heidelberg, West Germany

Synthesis and Crystal Structure of Bis(μ-hydroxo)bis[oxo(1,4,7-triazacyclononane)vanadium(IV)] Dibromide, a μ-Hydroxo-Bridged Cation with Antiferromagnetically Coupled V(IV) Centers

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The reaction of $VO(SO_4)\cdot 5H_2O$ with 1,4,7-triazacyclononane ([9]aneN_3, $C_6H_{15}N_3$) in H_2O yields dinuclear μ-hydroxo-bridged complexes of vanadium(IV). Blue $[V_2O_2(\mu\text{-}OH)(\mu\text{-}SO_4)([9]aneN_3)_2]ClO_4\cdot 2H_2O$ and gray salts (bromide, iodide, perchlorate) containing the cation $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2]^{2+}$ have been isolated. $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2]Br_2$ crystallizes in the monoclinic space group $P2_1/c$ (C_{2h}^5, No. 14) with $a = 7.236$ (1) Å, $b = 14.003$ (2) Å, $c = 10.405$ (2) Å, $\beta = 97.37$ (2)°, $V = 1045.8$ (3) Å^3, and $d_{calcd} = 1.861$ g/cm^3 for $Z = 2$ and molecular weight 586.1. Least-squares refinement of the structure based on 1199 observations led to final discrepancy indices of $R_1 = 0.043$ and $R_2 = 0.037$. The structure consists of discrete dinuclear cations with crystallographically imposed C_i symmetry. The geometry around each vanadium is distorted octahedral: a terminal oxo group, V–O2 = 1.603 (5) Å, two hydroxo bridges, V–O1 = 1.956 (5) Å and V–O1′ = 1.969 (5) Å, and the tridentate cyclic amine. There are two distinct V–N bond lengths of 2.303 (6) Å for the nitrogen trans to the terminal oxo group and 2.151 (5) and 2.159 (5) Å for the nitrogens trans to the hydroxo bridges. Magnetic susceptibility measurements indicate strong antiferromagnetic coupling of the two vanadium(IV) centers (d^1–d^1 configuration; $J = -177$ cm^{-1}).

Introduction

The structural chemistry of dinuclear complexes of vanadium(IV) has received surprisingly little attention in the past. Only a rather limited number of dinuclear complexes have been synthesized and characterized by X-ray diffraction methods.[2-4] In particular, although a dinuclear complex containing μ-fluoro bridges, $[N(CH_3)_4]_2[V_2O_2(OH)_2(\mu\text{-}F)_2F_4]$, with a V···V distance of 3.292 (1) Å has been reported,[4] no such complex appears to have been synthesized containing structurally very similar μ-hydroxo bridges. The neutral complex $V_2O_2Cl_4(\mu\text{-}Hmph)_3\cdot CH_2Cl_2$ (Hmph = 2-hydroxy-6-methylpyridine) has a V···V distance of 3.175 (1) Å[2]. No magnetic measurements on such dinuclear d^1–d^1 species of vanadium(IV) have been reported although interesting antiferromagnetic coupling should be expected.[5] An additional point of interest is the possibility of direct metal–metal bonding, which has been observed for dinuclear vanadium(II) and vanadium(III) compounds.[6,7]

In this paper we describe the synthesis and X-ray crystallographic and magnetic characterization of the first bis(μ-hydroxo)-bridged complex of vanadium(IV).

Experimental Section

The ligand 1,4,7-triazacyclononane was prepared according to procedures described in the literature.[8] The magnetic susceptibilities of powdered samples were measured by the Faraday method (Sartorius microbalance, Bruker B-E10C8 research magnet, and Bruker B-VT 1000 automatic temperature control) between 93 and 300 K.

Preparation of $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2]Br_2$. To 1,4,7-triazacyclononane ($C_6H_{15}N_3$ = [9]aneN_3) (1.3 g) dissolved in 40 mL of water was added $VOSO_4\cdot 5H_2O$ (2.5 g). The temperature was raised to 60 °C for 15 min. To the filtered solution was added NaBr (15 g), and the pH of the solution was adjusted to 4 with 0.1 M NaOH. A blue-violet precipitate formed, which was filtered off and was recrystallized from an aqueous solution with NaBr. Gray crystals were obtained (1.2 g). X-ray-quality single crystals were grown from such solutions at 0 °C. Anal. Calcd for $V_2C_{12}H_{32}N_6O_4Br_2$: C, 24.59; H, 5.5; N, 14.34; Br, 27.27; V, 17.38. Found: C, 24.4; H, 5.2; N, 13.7; Br, 27.3; V, 17.4. Iodide and perchlorate salts were obtained analogously.

Preparation of $[VO(NCS)_2([9]aneN_3)]$. To 1,4,7-triazacyclononane (1.3 g) dissolved in 40 mL of water was added $VOSO_4\cdot 5H_2O$ (2.5 g). A precipitate formed immediately, which dissolved slowly upon heating the solution to 60 °C, during which time the pH of the solution dropped from ~9 to 3. To the filtered solution was added NaSCN (15 g). When the solution was cooled (10 °C), blue-violet crystals precipitated, which were filtered off, washed with ethanol and ether, and air-dried. The material was recrystallized from acetone; yield 2.1 g. Anal. Calcd for $VO(SCN)_2$ $(C_6H_{15}N_3)$: C, 30.77; H, 4.84; N, 22.43; S, 20.53. Found: C, 30.7; H, 4.9; N, 22.4; S, 20.3.

Preparation of $[V_2O_2(\mu\text{-}OH)(\mu\text{-}SO_4)([9]aneN_3)_2](ClO_4)\cdot 2H_2O$. To a solution of 1,4,7-triazacyclononane (0.65 g) in 10 mL of water was added a solution of $VOSO_4\cdot 5H_2O$ (1.2 g) in 10 mL of H_2O. The solution was heated to 60 °C until the formed precipitate was redissolved and the pH of the solution had dropped to 4–3. To the filtered solution was added solid $NaClO_4$ (10 g). When the mixture was cooled, a blue microcrystalline product was obtained. Attempts to recrystallize this material from aqueous solutions afforded the sulfate-free $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2](ClO_4)_2\cdot H_2O$. Anal. Calcd for $[V_2O_2(\mu\text{-}OH)(\mu\text{-}SO_4)(C_6H_{15}N_3)_2]ClO_4\cdot 2H_2O$: C, 22.49; H, 5.51; N, 13.11; V, 15.90; ClO_4, 15.52; SO_4, 14.99. Found: C, 22.1; H, 5.1; N, 12.8; V, 15.9; ClO_4, 16.1; SO_4, 14.5. An iodide salt, $[V_2O_2(\mu\text{-}OH)(\mu\text{-}SO_4)([9]aneN_3)_2]I$, has been prepared with use of NaI instead of $NaClO_4$.

X-ray Structural Determination of $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2]Br_2$. A gray prismatic crystal of $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2]Br_2$ was attached to the end of a glass fiber and mounted on a Syntex R3 four-circle diffractometer. Preliminary examinations showed that the crystal belonged to the monoclinic system, space group $P2_1/c$. The

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Table I. Crystallographic Data and Data Collection Parameters at 22 °C

formula	$C_{12}H_{32}Br_2N_6O_4V_2$
fw	586.1
space group	$P2_1/c$
a, Å	7.236 (1)
b, Å	14.003 (2)
c, Å	10.405 (2)
β, deg	97.37 (2)
V, Å^3	1045.8 (3)
Z	2
d_{calcd}, g/cm^3	1.861
cryst size, mm	0.3 × 0.3 × 0.4
μ(Mo Kα), cm^{-1}	46.8
diffractometer	Syntex R3
radiation	Mo Kα (λ = 0.71069 Å)
scan method	θ-2θ, $2 < 2\theta < 55°$
no. of unique data ($I > 2.5\sigma(I)$)	1199
no. of variables refined	151
std reflcns	2 every 150 reflcns, no decay obsd
largest shift/esd, final cycle	0.01
total reflcns	1325
octants	$\pm h, +k, l$
monochromator	graphite
range of transmission factors	1.0-0.8

Table II. Positional Parameters and Their Estimated Standard Deviations for $[V_2O_2(\mu\text{-OH})_2([9]aneN_3)_2]Br_2$

atom	x	y	z
Br	0.2974 (1)	0.72186 (5)	0.02610 (9)
V	1.0412 (2)	1.01118 (7)	0.1458 (1)
O1	0.9029 (6)	0.0736 (3)	−0.0049 (5)
O2	0.8847 (6)	−0.0431 (3)	0.2140 (5)
N1	1.2926 (8)	0.0985 (4)	0.0967 (6)
N2	1.2697 (7)	−0.0335 (4)	0.2856 (6)
N3	1.0541 (8)	0.1324 (4)	0.2750 (6)
C1	1.4720 (9)	0.0649 (5)	0.1678 (7)
C2	1.4449 (9)	−0.0320 (5)	0.2273 (7)
C3	1.2762 (9)	0.0268 (5)	0.4038 (7)
C4	1.1039 (11)	0.0865 (5)	0.4026 (8)
C5	1.1838 (10)	0.2107 (5)	0.2488 (8)
C6	1.2491 (10)	0.1992 (5)	0.1195 (8)
H1	1.294 (6)	0.095 (3)	0.009 (5)
H2	1.243 (6)	−0.093 (3)	0.312 (5)
H3	0.932 (6)	0.153 (3)	0.277 (5)
HO1	0.862 (8)	0.115 (4)	−0.009 (6)

Table III. Important Bond Distances (Å) and Bond Angles (deg) in $[V_2O_2(\mu\text{-OH})_2([9]aneN_3)_2]^{2+}$

	Distances		
V···V	3.0333 (3)	N1-H1	0.91 (5)
V-O1	1.956 (5)	N2-H2	0.90 (5)
V-O1	1.969 (5)	N3-H3	0.93 (5)
V-O2	1.603 (5)	O1-HO1	0.65 (5)
V-N1	2.303 (6)	N1-C1	1.486 (8)
V-N2	2.151 (5)	C1-C2	1.515 (10)
V-N3	2.159 (5)	C2-N2	1.474 (9)
C4-N3	1.477 (9)	N2-C3	1.487 (9)
N3-C5	1.492 (9)	C3-C4	1.500 (10)
C5-C6	1.491 (12)	C6-N1	1.471 (9)
	Angles		
O2-V-O1	104.4 (2)	O2-V-O1	105.5 (2)
N1-V-O1	85.5 (2)	N1-V-O1	84.9 (2)
N2-V-O1	160.5 (2)	N2-V-O1	96.6 (2)
N3-V-O1	97.2 (2)	N3-V-O1	160.2 (2)
O1-V-O1	78.8 (2)	N1-V-O2	166.7 (2)
N3-V-N1	75.5 (2)	N2-V-O2	95.1 (2)
N2-V-N1	75.2 (2)	N3-V-O2	94.2 (2)
N2-V-N3	80.8 (2)	V-O1-V′	101.2 (2)

unit cell dimensions were obtained by a least-squares fit of 25 strong reflections. The data are summarized in Table I. Intensity data were measured by θ–2θ scans at 22 °C and were corrected for Lorentz and polarization effects. An empirical absorption correction was carried out.[9] The function minimized during least-squares refinements was $\sum w(|F_o| - |F_c|)^2$ with final convergence to

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.043$$

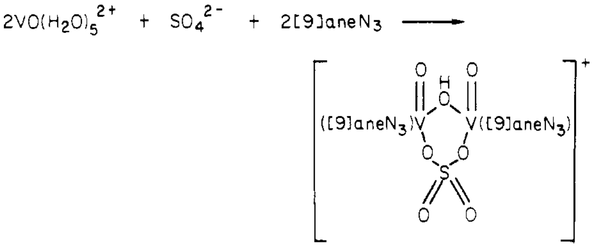
$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.037$$

The structure was solved via a three-dimensional Patterson synthesis, which yielded the positions of the vanadium and bromine atoms. Subsequent Fourier syntheses revealed the locations of all remaining non-hydrogen atoms. Idealized positions of the H atoms bound to carbon atoms of the cyclic amine were calculated (on the basis of d(C–H) of 0.97 Å and sp^3-hybridized C atoms) and included in the refinement cycles with a fixed isotropic thermal parameter (U = 0.0405 Å^2). All other atoms were refined with use of anisotropic thermal parameters (supplementary material). At this stage a difference Fourier synthesis clearly showed the positions of the remaining H atoms bound to the nitrogens of the ligand and the oxygen of the μ-hydroxo bridges. These were included in the final cycles of refinement with variable isotropic thermal parameters. A final difference Fourier synthesis was essentially featureless, and the structure was judged to be complete. The final atomic parameters are given in Table II and bond distances and angles in Table III. A list of observed and calculated structure factors and a list of anisotropic thermal parameters are available as supplementary material.

During all calculations the analytical scattering factors for neutral atoms were corrected for both $\Delta f'$ and $i(\Delta f'')$ terms.[16]

Results and Discussion

The reaction of $VO(SO_4)\cdot5H_2O$ with the cyclic ligand 1,4,7-triazacyclononane ([9]aneN_3) (1:1) in H_2O at 50 °C yields blue acidic solutions, from which a blue perchlorate salt was precipitated upon addition of $NaClO_4$. Analyses are in accordance with the dihydrate of the perchlorate salt of a μ-sulfato–μ-hydroxo-bridge dimer as in I. With use of NaI

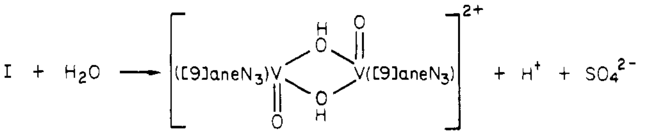


(1)

I

a blue iodide salt was obtained. The infrared spectrum of this material exhibits in addition to bands due to the coordinated triamine a strong ν(V=O) stretching frequency at 950 cm^{-1} and three strong absorptions at 1210, 1140, and 1030 cm^{-1} typical for a μ-sulfato ligand of C_{2v} symmetry[10] (a fourth ν(S–O) band is believed to coincide with the ν(V=O) frequency at 950 cm^{-1}).

Attempts to recrystallize I from aqueous solutions always resulted in the release of sulfate from I and formation of the bis(μ-hydroxo)-bridge species II with concomitant release of protons (eq 2). Upon addition of $NaClO_4$, NaBr, or NaI gray



II

(2)

salts of II were obtained. The infrared spectra exhibit strong bands at 950 cm^{-1} (ν(V=O)) and a new band at 540 (vs) cm^{-1},

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[9] Computations were carried out on a NOVA3 (General Data) computer using SHELXTL (revision 3.0, July 1981) by G. M. Sheldrick, University of Göttingen.

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which is assigned to ν(V—O) vibrations of the μ-hydroxo bridges. To our knowledge I and II represent the first fully characterized μ-hydroxo-bridged dimers of vanadium(IV).

Interestingly, addition of NaSCN to aqueous solutions of $VO(SO_4)\cdot 5H_2O$ and 1,4,7-triazacyclononane (1:1) leads to the precipitation of a mononuclear neutral complex of vanadium(IV), $VO(NCS)_2([9]aneN_3)$ (III). The infrared spectrum shows accordingly a ν(V═O) stretching frequency at 950 cm^{-1} and ν(NCS) at 2040 (vs) cm^{-1}. This complex may be recrystallized from hot acetone.

Titration of a 4×10^{-3} M solution (25 mL) of II (as either the perchlorate or bromide salt) in 0.1 M $NaClO_4$ with 10^{-2} M NaOH at 25 °C using a calibrated glass electrode to monitor pH changes revealed two inflection points with acid dissociation constants $pK_1 = 7.1 \pm 0.1$ and $pK_2 = 9.7 \pm 0.1$. These two dissociation constants are attributed to the loss of one proton from each of the two μ-hydroxo groups present in II.

Measurements of the magnetic susceptibility, which were corrected for diamagnetic contributions, of powdered samples of complexes I, II, and III between 93 and 293 K using the Faraday method are in excellent agreement with the proposed structures. The data for the temperature dependence of the magnetic susceptibility of III fit the Curie–Weiss law between 93 and 293 K with $\mu = 1.63$ (1) μ_B and $\Theta = 12.0$ K, which is expected for a mononuclear complex of vanadium(IV) (d^1 configuration) with no or very small intermolecular magnetic coupling. In marked contrast is the magnetic behavior of II, which appears to be more complex. The effective magnetic moment per vanadium(IV) is reduced as compared to a spin-only value of ~ 1.7 μ_B and is strongly dependent on the temperature. At 103 K $\mu_{eff} = 0.27$ μ_B per vanadium(IV), and at 293 K $\mu_{eff} = 1.20$ μ_B is observed, which indicates intramolecular antiferromagnetic coupling of the two d^1–d^1 centers.[5] Magnetic susceptibility data for solid II in the range 103 K $\leq T \leq$ 293 K were fit to the expression for χ_M vs. T derived from the spin exchange Hamiltonian $H' = -2JS_1S_2$, with $S_1 = S_2 = {}^1/_2$. A J value of -177 cm^{-1} was calculated. Magnetic measurements of *I* are hampered by small impurities of II but indicate very weak—if any—intramolecular antiferromagnetic coupling. Magnetic superexchange mechanisms have been proposed in detail for bis(μ-hydroxo)-bridged complexes of chromium(III) (d^3–d^3) and copper(II) (d^9–d^9).[5] A more detailed investigation of the magnetic behavior of II will be the subject of a future publication.

Since II represents the first bis(μ-hydroxo) species of vanadium(IV), it was decided to determine the crystal structure of II by single-crystal X-ray diffraction methods. The structure of $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2]Br_2$ consists of the dinuclear cation $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2]^{2+}$ and bromide anions. Figure 1 shows the atomic labeling scheme and a perspective view of the structure. The two vanadium(IV) centers are in a distorted-octahedral environments of a facially coordinated 1,4,7-triazacyclonane ligand, a terminal oxo group, and two bridging hydroxo groups (two edge-sharing octahedra). The complex cation has a crystallographically imposed center of symmetry; the $V(\mu\text{-}OH)_2V$ four-membered ring is planar within experimental error. The V···V intramolecular distance is 3.033 (3) Å, and the O1–V–O1′ angle is acute (78.8 (2)°) whereas the V–O1–V′ angle is obtuse (101.2 (2)°). This together with the observed paramagnetism of II clearly indicates that there is no direct metal–metal bonding in II. It is noted that in the analogous d^1–d^1 dimer of molybdenum(V) containing two oxo bridges, $[Mo_2O_2(\mu\text{-}O)_2([9]aneN_3)_2]^{2+}$, a metal–metal single bond has been proposed on the basis of its diamagnetism and Mo–Mo distance of 2.556 Å. The O_b–Mo–O_b angle is obtuse whereas the Mo–O–Mo′ angle is now acute.[11]

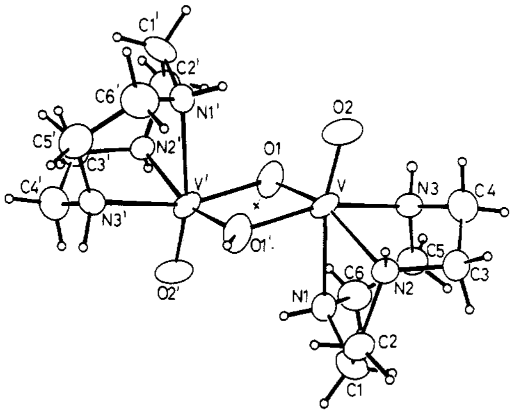

Figure 1. View of the $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2]^{2+}$ cation showing the atomic labeling scheme. Each non-hydrogen atom is represented by its ellipsoid of thermal vibration scaled to enclose 40% of its electron density. × denotes a crystallography imposed center of symmetry.

The terminal oxo groups in II are trans with respect to each other, and the V═O bond distance of 1.603 Å indicates double-bond character; it is much shorter than the V–OH bond lengths of $\sim$1.96 Å. These terminal oxo groups exert considerable trans influence on the V–N bond length trans to the terminal oxo group (Table III).

The V–O distances of the μ-hydroxo bridges (1.956 (5) and 1.969 (5) Å) are shorter than V–OH_2 distances observed in $VO(SO_4)\cdot 5H_2O$[12] (2.006 (1)–2.019 (2) Å) and $(NH_4)_2[VO(oxalato)_2(H_2O)]\cdot H_2O$[13] (2.033 (3) Å). Bond distances within the cyclic amine ligand exhibit no extraordinary features; they agree well with those reported for a series of binuclear transition-metal complexes.[14-16]

Acknowledgment. Financial support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. $[V_2O_2(\mu\text{-}OH)(\mu\text{-}SO_4)([9]aneN_3)_2](ClO_4)$, 89178-83-6; $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2]Br_2$, 89178-84-7; $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2](ClO_4)_2$, 89178-86-9; $[V_2O_2(\mu\text{-}OH)(\mu\text{-}SO_4)([9]aneN_3)_2]I$, 89178-87-0; $VO(NCS)_2([9]aneN_3)$, 89178-88-1.

Supplementary Material Available: Table IV (thermal parameters and their estimated standard deviations), Table V (calculated positional parameters of H atoms), and a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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