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Dinuclear and Polynuclear Oxovanadium(IV) Compounds. 1. Synthesis and Structural Study of $V_2O_2Cl_4(\mu\text{-Hmhp})_3$, a Novel Complex Containing Three Neutral Bridging Ligands

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The reaction between $VCl_3\cdot 3THF$ and 3 equiv of 2-hydroxy-6-methylpyridine (Hmhp) after evaporation in air affords $V_2O_2Cl_4(\mu\text{-Hmhp})_3$, identified by X-ray crystallography and ESR and infrared spectra. This is the first reported neutral dinuclear oxovanadate(IV) complex containing exclusively neutral bridging ligands. It crystallizes in the monoclinic space group $P2_1$ with $a = 9.115$ (2) Å, $b = 10.684$ (3) Å, $c = 14.469$ (2) Å, $\beta = 92.37$ (1)°, and $Z = 2$. Least-squares refinement of the structure based on 3077 observations led to final discrepancy indices of $R_1 = 0.0367$ and $R_2 = 0.0482$. The structure consists of discrete dinuclear units that are not subject to any crystallographically imposed symmetry. The geometry around each vanadium atom is distorted square pyramidal with a weakly held sixth ligand trans to the V=O bond. There are two distinct bridging ligand types. O(1) and O(3), trans to V=O at V(1) and V(2), respectively, span the two metal atoms unsymmetrically: V(1)–O(1) = 2.345 (2) Å; V(2)–O(1) = 2.043 (2) Å; V(1)–O(3) = 2.016 (2) Å; V(2)–O(3) = 2.373 (2) Å. In contrast O(2) trans to two V–Cl bonds bridges symmetrically, with V(1)–O(2) = 2.104 (2) Å and V(2)–O(2) = 2.088 (2) Å. The ESR and infrared spectra of $V_2O_2Cl_4(\mu\text{-Hmhp})_3$ are consistent with the structure.

Introduction

Our recent research activity[1,2] in the inorganic chemistry of vanadium has had three motivations. First, we wish to devise simple synthetic routes to the elusive metal–metal-bonded dinuclear vanadium(II) and vanadium(III) compounds.[3–5] Second, through lack of crystallographic data, the last decade or so has witnessed a number of erroneous structure assignments, as discussed in an earlier paper;[1] we desire to establish some benchmark structures. Finally, in view of a current upsurge of interest in the bioinorganic chemistry of vanadium(III), -(IV), and -(V), particularly the work of Kustin et al.[6] and Hodgson et al.,[7] we have expanded our program to include the synthesis and more specifically the structural characterization of a variety of dinuclear and polynuclear vanadium complexes that might serve as useful model compounds.

In this paper we describe the synthesis, X-ray crystallographic characterization, and spectroscopic study of $V_2O_2Cl_4(\mu\text{-Hmhp})_3$, Hmhp = 2-hydroxy-6-methylpyridine, an unprecedented neutral dinuclear vanadium(IV) complex in which the bridging ligands are exclusively neutral moieties.

Experimental Section

All chemical operations were conducted under an atmosphere of dry argon with use of standard Schlenk techniques. Dichloromethane, which had been dried over P_2O_5 and purged with argon, was distilled immediately before use and transferred to reaction vessels by syringe.

Synthesis and Crystallization of $V_2O_2Cl_4(Hmhp)_3$. Dichloromethane (50 mL) was added to a Schlenk tube containing $VCl_3\cdot 3THF$,[8] 0.77 g (2 mmol), and 2-hydroxy-6-methylpyridine, 0.65 g (6 mmol). The resulting mixture was left undisturbed for a period of 1 week, during which time the solution changed from red to green. Slow evaporation of the green solution in dry air afforded large quantities (0.25 g) of bright blue crystals whose elemental composition was not that of the anticipated $V_2(mhp)_6$ but, as shown by X-ray crystallography, that of a novel dinuclear triply bridged vanadyl compound, $V_2O_2Cl_4(\mu\text{-Hmhp})_3\cdot CH_2Cl_2$.

Table I. Crystallographic Data and Data Collection Parameters

formula	$V_2Cl_6O_5C_{19}H_{23}$
fw	645.99
space group	$P2_1$
a, Å	9.115 (2)
b, Å	10.684 (3)
c, Å	14.469 (2)
β, deg	92.37 (1)
V, Å^3	1408.0 (8)
Z	2
d_{calcd}, g/cm^3	1.524
cryst size, mm	0.5 × 0.5 × 0.3
μ(Mo Kα), cm^{-1}	12.431
data collection instrument	Enraf-Nonius CAD 4
radiation	graphite-monochromated Mo Kα
scan method	ω–2θ
data collection range, deg	$+h, +k, \pm l$, $0 < 2\theta \leqslant 56$
no. of unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	3484
no. of parameters refined	315
R^a	0.0367
$R_w{}^b$	0.0482
esd	1.678
largest shift/esd, final cycle	0.06
largest peak, e/Å^3	0.427

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)^2$.

Spectra. An EPR spectrum was recorded at −196 °C on a Varian E-6S spectrometer and referenced to 2,2-diphenyl-1-picrylhydrazyl (DPPH). Infrared spectra were recorded as 1% KBr pellets on a DigiLab FTS-20C spectrometer.

Crystallographic Data Collection. Crystals of $V_2O_2Cl_4(\mu\text{-Hmhp})_3\cdot CH_2Cl_2$ form as rectangular blocks. A single well-developed specimen, approximately 0.5 × 0.5 × 0.3 mm, was mounted in a thin glass capillary and sealed in place with epoxy cement. Preliminary X-ray examination established a monoclinic unit cell and revealed only a single systematic absence, namely, in $0k0$ for $k = 2n + 1$, consistent with either of the space groups $P2_1/m$ or $P2_1$. Solution and refinement of the structure confirmed the choice of $P2_1$. Least-squares refinement of the setting angles of 25 reflections for which $17° < 2\theta < 28°$ provided accurate unit cell dimensions. These, along with other specific diffractometer operating parameters, are presented in Table I. Intensity data were collected at room temperature on an Enraf-Nonius CAD-4 instrument with graphite-monochromated Mo Kα radiation. An ω–2θ scan mode with a scan range determined by $\Delta\omega = 0.95 + 0.35 \tan\theta$ was used. Background measurements were made at the beginning and end of each scan, each measurement for one-fourth of the scan time. Three standard reflections, $41\bar{5}$, $\bar{3}\bar{0}\bar{8}$, and $\bar{3}1\bar{8}$, were measured after every 150 reflections

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Table IIA. Table of Positional Parameters and Their Estimated Standard Deviations for $V_2O_2Cl_4(Hmhp)_3$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
V(1)	−0.09891 (6)	−0.47215 (0)	−0.20352 (4)	C(3)	−0.6072 (5)	−0.6903 (6)	−0.0420 (3)
V(2)	−0.40777 (6)	−0.49604 (7)	−0.31175 (4)	C(4)	−0.5144 (5)	−0.7430 (5)	0.0268 (3)
Cl(1)	0.0087 (1)	−0.6497 (1)	−0.13668 (7)	C(5)	−0.3677 (4)	−0.7300 (4)	0.0213 (3)
Cl(2)	−0.4908 (1)	−0.6968 (1)	−0.34919 (8)	C(6)	−0.2578 (5)	−0.7804 (5)	0.0910 (3)
Cl(3)	−0.1283 (1)	−0.3806 (1)	−0.05853 (6)	C(7)	−0.2729 (4)	−0.2358 (4)	−0.2712 (3)
Cl(4)	−0.3880 (1)	−0.4467 (1)	−0.46751 (6)	C(8)	−0.3501 (5)	−0.1696 (5)	−0.3400 (3)
Cl(5)	−0.3497 (4)	−0.4727 (3)	−0.82689 (23)	C(9)	−0.3508 (6)	−0.0410 (5)	−0.3341 (4)
Cl(6)	−0.1194 (4)	−0.5209 (5)	−0.68304 (24)	C(10)	−0.2806 (6)	0.0241 (5)	−0.2639 (4)
O(1)	−0.3333 (3)	−0.5563 (3)	−0.1843 (2)	C(11)	−0.2064 (5)	−0.0416 (4)	−0.1964 (3)
O(2)	−0.2602 (3)	−0.3568 (3)	−0.2676 (2)	C(12)	−0.1245 (8)	0.0123 (5)	−0.1137 (4)
O(3)	−0.1618 (3)	−0.5671 (3)	−0.3189 (2)	C(13)	−0.0904 (4)	−0.6322 (4)	−0.3773 (2)
O(4)	0.0391 (3)	−0.3966 (3)	−0.2372 (2)	C(14)	0.0618 (4)	−0.6422 (5)	−0.3809 (3)
O(5)	−0.5527 (3)	−0.4258 (3)	−0.2844 (2)	C(15)	0.1200 (4)	−0.7133 (6)	−0.4492 (3)
N(1)	−0.3153 (3)	−0.6658 (3)	−0.0515 (2)	C(16)	0.0317 (5)	−0.7768 (5)	−0.5136 (3)
N(2)	−0.2055 (4)	−0.1694 (3)	−0.2034 (2)	C(17)	−0.1164 (5)	−0.7669 (5)	−0.5087 (3)
N(3)	−0.1707 (3)	−0.6963 (4)	−0.4411 (2)	C(18)	−0.2288 (6)	−0.8251 (7)	−0.5752 (4)
C(1)	−0.3996 (4)	−0.6129 (4)	−0.1203 (2)	C(19)	−0.2549 (11)	−0.4209 (15)	−0.7307 (8)
C(2)	−0.5520 (4)	−0.6258 (5)	−0.1142 (3)				

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

to check stability and crystal decay. No significant change in the standards was noted over the course of data collection. Of the 3484 symmetry-independent reflections measured ($0 \le 2\theta \le 56°$) those 3077 with intensities $I \ge 3\sigma(I)$ were used in subsequent calculations. Standard deviations were estimated from counting statistics. Data were reduced to unscaled, observed structure factor amplitudes after correction for Lorentz and polarization factors. With $\mu = 12.431$ cm^{-1} no absorption correction was deemed necessary.

Solution and Refinement of the Structure. The structure was solved by Patterson and Fourier methods and refined[9] by full-matrix least squares. In view of the indications of acentricity provided by the programs NZTEST and NORMAL[9] (and later confirmed by inferior refinement in the centric space group $P2_1/m$) the Patterson map was solved for two vanadium atoms with use of the vectors derived from the general positions in space group $P2_1$. Three cycles of isotropic least-squares refinement of the positions of the two metal atoms gave values of $R_1 = 0.45$ and $R_2 = 0.56$ where the R_i values are defined as

$$R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$$
$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$$

Subsequent least-squares cycles and difference Fourier maps permitted the location of all 33 non-hydrogen atoms, including those of a molecule of dichloromethane of crystallization. After anisotropic refinement of these atoms the discrepancy indices were $R_1 = 0.0395$ and $R_2 = 0.0537$. The choice of enantiomorph was now considered. Refinement of the mirror image of the original structure produced $R_1 = 0.0384$ and $R_2 = 0.0524$. The result suggests at the 99+% confidence level[10] that the original (arbitrary) choice of enantiomorph was wrong. The positional parameters of the two enantiomorphs are (except for the coordinate transformation) virtually identical. We report positional parameters (Table IIA) and thermal parameters (Table IIB, supplementary material) for the second enantiomorph. At this time the twelve non-methyl hydrogen atoms of the Hmhp ligands were located in a difference electron density map and their contributions included in F_c values, but they were not refined. Inclusion of these atoms in the refinement gave convergence at $R_1 = 0.0367$ and $R_2 = 0.0482$. The error in an observation of unit weight was 1.678, and the largest shift/error ratio in the final cycle was 0.06. A final difference synthesis showed random fluctuations not exceeding ±0.427 e/Å^3.

Final positional parameters of non-hydrogen atoms are given in Table IIA. The thermal parameters for all atoms are listed in Table IIB, which is available as supplementry material. Table IIC (also supplementary material) gives positional parameters for hydrogen atoms. Values of F_o vs. F_c for the 3077 observed data are also available as supplementary material.

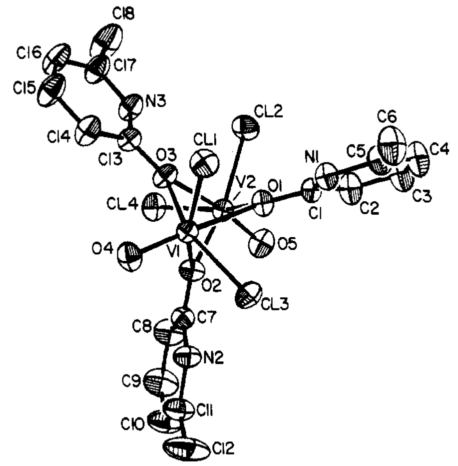
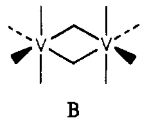


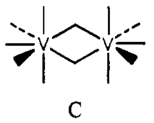
Figure 1. The $V_2O_2Cl_4(\mu\text{-Hmhp})_3$ molecule showing the atom-labeling scheme. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 40% of its electron density.

Results and Discussion

The dinuclear complexes of vanadium(III), -(IV), and -(V) that have previously been characterized structurally are of three structural types, A–C. In structure type A, two octahedra share a face. Examples are provided by the anions in $Cs_3[V_2Cl_9]$[11] and $Cs_3[V_2O_2F_4(\mu\text{-F})_3]$.[12] The latter has two V=O groups, and the V···V distance is 2.995 (7) Å. Another dinuclear oxovanadium(IV) complex, this time having a structure of type B, is the anion in $[N(CH_3)_4]_2[V_2O_2(OH)_2F_4(\mu\text{-F})_2]$, with a V···V distance of 3.292 (1) Å.[13] The oxovanadium(V) compound $[V_2O_2(OCH_3)_4(\mu\text{-OCH}_3)_2]_n$ is also of structure type B. A coordination number of 6 about each vanadium atom is achieved by the bridging role of some terminal methoxide ligands, whereby the dinuclear units are linked into infinite chains. The V···V distance is 3.18 (2) Å.[14] The only example of structure type C is provided by the anion


A


B


C

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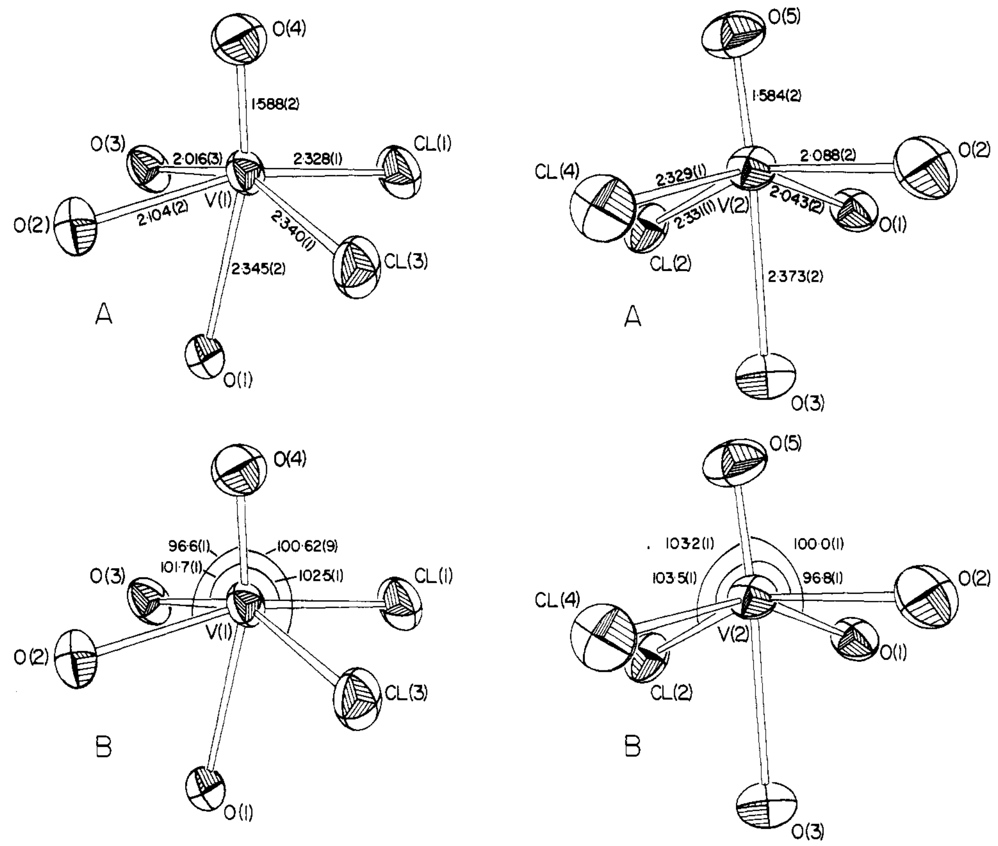

Figure 2. Bond distances (Å) and angles (deg) in the coordination spheres of the two vanadium atoms in $V_2O_2Cl_4(\mu\text{-Hmhp})_3$.

in $[enH_2][V_2(hedta\text{-}H)_2]\cdot 2H_2O$, where the V···V distance is 3.296 (1) Å.[15]

The crystal structure of the oxovanadium(IV) compound $V_2O_2Cl_4(\mu\text{-Hmhp})_3\cdot CH_2Cl_2$ contains discrete dinuclear molecules that are not subject to any crystallographically imposed symmetry. This molecule is depicted in Figure 1, where the atom labeling scheme is defined. There is an approach to C_2 symmetry, with the approximate C_2 axis passing through O(2) and the midpoint of a line joining the vanadium atoms. Important interatomic distances and angles are listed in Table III. This molecule provides a new example of structure type A. It is unusual, and we believe unique, in having the two distorted VO_4Cl_2 octahedra joined by atoms of three neutral ligands, namely, by O(1), O(2), and O(3) belonging to 2-oxo-6-methylpyridinium molecules. These are tautomers of 2-hydroxy-6-methylpyridine, a ligand most commonly seen in its deprotonated (anionic) form.

Actually, the VO_4Cl_2 "octahedra" are very distorted indeed and can probably be better described as square-pyramidal $O_2Cl_2V{=}O$ units with the position trans to the V=O oxygen atom occupied by a relatively weakly bonded oxygen atom. The details of these $O\cdots V(O)O_2Cl_2$ moieties are shown in Figure 2. The V···V separation is quite large, 3.175 (1) Å, as in previously reported examples of binuclear oxovanadium(IV) compounds. At this distance we do not expect V—V bonding and hence there should be two unpaired electrons, each essentially localized on one V=O unit.

The V=O oxygen atoms, O(4) and O(5), are each trans to a bridging oxygen atom, and these are also trans to halogen atoms, Cl(4) and Cl(3), respectively, an arrangement similar to that previously observed in $[NMe_4]_2[V^{IV}{}_2O_2(OH)_2F_4(\mu\text{-}F)_2]$,[13] and again it results in the asymmetry of two of the bridging ligands as a consequence of the considerable trans influence of the vanadyl oxygen atoms. Thus, we find the following V–(μ-O) distances: V(1)–O(1) = 2.345 (2) Å; V(2)–O(1) = 2.043 (2) Å; V(1)–O(3) = 2.016 (2) Å; V(2)–O(3) = 2.373 (2) Å. For comparison the V–(μ-F) distances are 1.960 (3) and 2.173 (3) Å in $[NMe_4]_2[V^{IV}{}_2O_2(OH)_2F_4(\mu\text{-}F)_2]$.[13] The three fluorine bridges appear to be symmetric in $Cs_3V_2O_2F_4(\mu\text{-}F)_3$, but because of a statistical distribution of V=O and V—F bonds over the six terminal coordination sites in this complex, it is impossible to draw any conclusion about individual bond lengths. In the oxovanadium(V) compound $[V_2O_2(OCH_3)_4(\mu\text{-}OCH_3)_2]_n$ the V=O bonds lie cis to the symmetrical methoxide bridges;[14] in the compound reported here a similar situation is observed for O(2), which is cis to both the O(4) and the O(5) vanadyl oxygen atoms.

Since it is impossible to tell from the method of preparation what the oxidation state, IV or V, of the vanadium atoms should be in the product, we have sought other evidence to establish this. Either a vanadium(IV) complex, $V_2O_2Cl_4(Hmhp)_3$, or a vanadium(V) complex, $V_2O_2Cl_4(hmp)_2(Hmhp)$, might be considered consistent with the observation that there are two distinct types of bridging ligands, one symmetrical and two unsymmetrical. The V=O distances, 1.588 (2) and 1.584 (2) Å, are consistent with either oxidation state as far as the limited amount of accurate information on V=O distances goes. They are comparable with the V=O distance of 1.576 (6) Å recently found[1] in $V_3O_3(C_6H_5CO_2)(THF)$, a V^{IV} compound, and in the $[V_2O_2(OH)_2F_4(\mu\text{-}F)_2]^{2-}$ ion[13] the distance, 1.607 (5) Å, is only slightly greater.

The presence of oxovanadium(IV) rather than oxovanadium(V) is shown positively by the observation of an ESR spectrum that is similar to those previously recorded for a number of oxovanadate(IV) complexes.[16] It consists of a

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Table III. Important Bond Distances (Å) and Bond Angles (deg) in $V_2O_2Cl_4(Hmhp)_3$[a]

Distances

V(1)-V(2)	3.175 (1)	N(2)-H(N2)	0.854 (3)
-Cl(1)	2.328 (1)	N(3)-C(13)	1.342 (4)
-Cl(3)	2.340 (1)	-C(17)	1.346 (4)
-O(1)	2.345 (2)	-H(N3)	1.089 (3)
-O(2)	2.104 (2)	C(1)-C(2)	1.403 (4)
-O(3)	2.016 (2)	C(2)-C(3)	1.365 (5)
-O(4)	1.588 (2)	C(3)-C(4)	1.398 (6)
V(2)-Cl(2)	2.331 (1)	C(4)-C(5)	1.350 (5)
-Cl(4)	2.329 (1)	C(5)-C(6)	1.492 (5)
-O(1)	2.043 (2)	C(7)-C(8)	1.389 (5)
-O(2)	2.088 (2)	C(8)-C(9)	1.377 (6)
-O(3)	2.373 (2)	C(9)-C(10)	1.368 (7)
-O(5)	1.584 (2)	C(10)-C(11)	1.361 (6)
Cl(5)-C(19)	1.70 (1)	C(11)-C(12)	1.499 (6)
Cl(6)-C(19)	1.75 (1)	C(13)-C(14)	1.395 (4)
O(1)-C(1)	1.278 (4)	C(14)-C(15)	1.370 (5)
O(2)-C(7)	1.299 (4)	C(15)-C(16)	1.384 (6)
O(3)-C(13)	1.291 (4)	C(16)-C(17)	1.359 (5)
N(1)-C(1)	1.355 (4)	C(17)-C(18)	1.511 (5)
-C(5)	1.359 (4)	Cl(1)-H(N1)	2.397 (1)
N(1)-H(N1)	0.884 (3)	Cl(2)-H(N3)	2.225 (1)
N(2)-C(7)	1.340 (5)	Cl(3)-H(N2)	2.311 (1)
-C(11)	1.369 (5)		

Angles

Cl(1)-V(1)-Cl(3)	91.73 (3)	V(2)-O(3)-C(13)	134.7 (2)
-O(1)	90.50 (6)	C(1)-N(1)-C(5)	125.0 (3)
-O(2)	159.26 (7)	-H(N1)	113.9 (3)
-O(3)	91.97 (7)	C(5)-N(1)-H(N1)	120.2 (3)
-O(4)	102.5 (1)	C(7)-N(2)-C(11)	125.3 (3)
Cl(3)-V(1)-O(1)	85.14 (6)	-H(N2)	106.3 (3)
-O(2)	92.68 (7)	C(11)-N(2)-H(N2)	128.4 (4)
-O(3)	155.98 (7)	C(13)-N(3)-C(17)	125.4 (3)
-O(4)	100.62 (9)	-H(N3)	111.8 (3)
O(1)-V(1)-O(2)	69.72 (8)	C(17)-N(3)-H(N3)	117.2 (3)
-O(3)	71.10 (9)	O(1)-C(1)-N(1)	117.3 (3)
-O(4)	165.5 (1)	-C(2)	126.2 (3)
O(2)-V(1)-O(3)	76.11 (9)	N(1)-C(1)-C(2)	116.5 (3)
-O(4)	96.6 (1)	C(1)-C(2)-C(3)	119.6 (3)
O(3)-V(1)-O(4)	101.7 (1)	C(2)-C(3)-C(4)	121.2 (3)
Cl(2)-V(2)-Cl(4)	91.18 (4)	C(3)-C(4)-C(5)	119.2 (3)
-O(1)	90.72 (7)	N(1)-C(5)-C(4)	118.6 (3)
-O(2)	157.76 (7)	-C(6)	117.3 (3)
-O(3)	89.64 (6)	C(4)-C(5)-C(6)	124.2 (4)
-O(5)	103.2 (1)	O(2)-C(7)-N(2)	117.4 (3)
Cl(4)-V(2)-O(1)	155.35 (7)	-C(8)	125.3 (3)
-O(2)	93.44 (7)	N(2)-C(7)-C(8)	117.3 (3)
-O(3)	85.36 (6)	C(7)-C(8)-C(9)	117.9 (4)
-O(5)	103.5 (1)	C(8)-C(9)-C(10)	123.4 (4)
O(1)-V(2)-O(2)	76.26 (9)	C(9)-C(10)-C(11)	118.3 (4)
-O(3)	70.08 (8)	N(2)-C(11)-C(10)	117.8 (4)
-O(5)	100.0 (1)	-C(12)	116.0 (4)
O(2)-V(2)-O(3)	69.10 (8)	C(10)-C(11)-C(12)	126.3 (4)
-O(5)	96.8 (1)	O(3)-C(13)-N(3)	116.7 (3)
O(3)-V(2)-O(5)	164.1 (1)	-C(14)	126.5 (3)
V(1)-O(1)-V(2)	92.44 (8)	N(3)-C(13)-C(14)	116.7 (3)
-C(1)	136.7 (2)	C(13)-C(14)-C(15)	119.0 (3)
V(2)-O(1)-C(1)	130.8 (2)	C(14)-C(15)-C(16)	121.8 (3)
V(1)-O(2)-V(2)	98.5 (1)	C(15)-C(16)-C(17)	118.5 (3)
-C(7)	131.3 (2)	N(3)-C(17)-C(16)	118.5 (3)
V(2)-O(2)-C(7)	129.9 (2)	-C(18)	115.7 (3)
V(1)-O(3)-V(2)	92.29 (8)	C(16)-C(17)-C(18)	125.8 (4)
-C(13)	132.8 (2)		

single broad, symmetric line showing no hyperfine structure. The *g* value is 1.9757, which is in the normal range,[17] 1.95–2.00, for VO^{2+} complexes. These observations require that the compound contain V^{IV} rather than V^{V} and are consistent with a weak interaction between the two VO^{2+} groups that is sufficient to broaden the hyperfine structure usually found for an isolated VO^{2+} unit.

Figure 3. Infrared spectrum in the V═O region of $V_2O_2Cl_4(Hmhp)_3$ as a 1% KBr pellet.

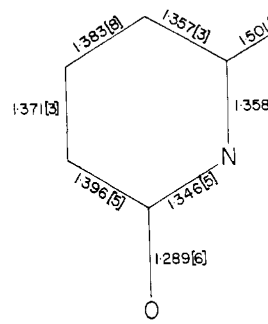

Figure 4. Average bond distances (Å) of the three Hmhp ligands in $V_2O_2Cl_4(\mu\text{-}Hmhp)_3$. Numbers in brackets are mean deviations from the arithmetic mean values.

The infrared spectrum, obtained with use of KBr pellets containing 1% of the compound, was examined carefully in the region where V═O stretching frequencies are expected.[19] The absorption, shown in Figure 3, is complex and indicates that there is probably both intramolecular coupling (to give symmetric and antisymmetric modes) and intermolecular (Davydov) splitting, since there are two formula units in the crystallographic unit cell. Our attempts to be more precise about relating the observed frequencies to the V═O distances,[20] in this as well as other compounds, have been impeded by the generally poor accuracy of available structural data. We hope to obtain data leading to such correlations in the future. We have noted, however, that the spectrum we have observed is similar to that of the anhydrous compound $[N(CH_3)_4]_2[V_2O_2(OH)_2F_4(\mu\text{-}F)_2]$, from which Bukovec et al.[13] inferred that after removal of water from the originally hydrated compound there remain $[VOF_3]^-$ moieties that are weakly coupled with no center of symmetry between them.

The bridging molecules are defined rather clearly and precisely and provide further evidence for the proposed formula of the compound, since hydrogen atoms are distinctly observed

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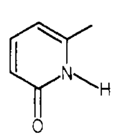
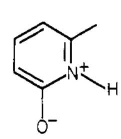
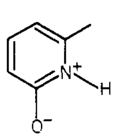
on each of the three ring nitrogen atoms. There is a close, hydrogen-bonded contact made by each of these N–H groups with an adjacent chlorine atom, at distances of 2.2–2.4 Å. We have previously observed such bonds in $[Mo_2(O_2CC_5H_4NH)_4Cl_2]Cl_2 \cdot nH_2O$, where the (N–H)···Cl distance is 2.22 (4) Å.[21] The average bond distances for the three Hmhp ligands are summarized in Figure 4. These results do not distinguish between the reasonable resonance contributors to the electronic structure, D, E, E′, and probably all three are contributors.


D


E


E′

Acknowledgment. We are grateful to the National Science Foundation for support, Mr. M. Ward for the ESR spectra, and Mr. P. Killough for the infrared spectra.

Registry No. $V_2O_2Cl_4(\mu\text{-Hmhp})_3 \cdot CH_2Cl_2$, 83801-80-3; $VCl_3 \cdot 3THF$, 19559-06-9.

Supplementary Material Available: Tables of observed and calculated structure factors, thermal parameters (Table IIB), hydrogen atom parameters (Tables IIC and IV), and torsion angles (Table V) (19 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, Texas A&M University, College Station, Texas 77843,
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Preparation and Structure of Crystalline Tetrakis(D-mandelato)dimolybdenum(II) Bis(tetrahydrofuranate)

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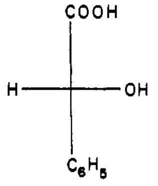
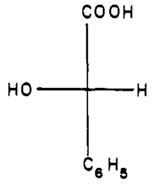
The preparation and structural characterization of the quadruply bonded, chiral dimolybdenum complex $Mo_2(C_8H_7O_3)_4$ are reported. Reaction of an aqueous solution of the Mo_2^{4+} unit with an aqueous solution of D-mandelic acid yielded the yellow product, which was recrystallized from a mixture of tetrahydrofuran and hexane. The crystals were found to be orthorhombic, in space group $P2_12_12_1$, with unit cell dimensions a = 13.199 (3) Å, b = 22.302 (9) Å, c = 27.289 (6) Å, V = 8033 (7) Å^3, and Z = 8. The asymmetric unit consists of two molecules of the molybdenum dimer and four uncoordinated molecules of tetrahydrofuran (THF, C_4H_8O). The two independent molecules are almost identical, with $Mo\overset{4}{-}Mo$ distances of 2.104 (1) and 2.101 (1) Å. A network of hydrogen bonds connects the extended structure. The absolute configuration has been determined and is in agreement with previous conformational analyses of mandelic acid by chemical means.

Introduction

The preparation and study of compounds in which chiral ligands are coordinated to the Mo_2^{4+} unit traces back to work done several years ago in this laboratory on substances in which the ligands were amino acids.[2-4] The two compounds that have previously been subjected to X-ray crystallographic study are $[Mo_2(\text{L-leu})_4]Cl_2(CH_3C_6H_4SO_3)_2 \cdot 2H_2O$[3] and $[Mo_2(\text{L-isoleu})_2(NCS)_4] \cdot 4^1/_2H_2O$.[4] More recently, as the result of work by G. Snatzke and co-workers,[5-7] there has been a new impetus for the study of such substances, involving chiral ligands in general and not just amino acids. They have shown that chiral carboxylic acids as well as other chiral organic molecules with functionalities capable of coordinating to the Mo_2^{4+} unit can give rise to conveniently measurable CD and ORD spectra in the visible region when small amounts of $Mo_2(O_2CCH_3)_4$ are added to their solutions. Presumably, partial replacement of CH_3CO_2 takes place and the chirality of the replacing ligand imposes the observed Cotton effects on the Mo_2^{4+} chromophore. It has even been possible to develop empirical quadrant rules for correlating the signs of the observed CD and ORD effects with absolute configurations. However, an explicit and fundamental examination of these effects using well-defined Mo_2^{4+}-containing molecules is lacking.

We have been engaged in such a fundamental investigation, and we provide here our first report, which deals with the preparation and structural characterization of a compound containing the D-mandelate anion (I). This was one of the chiral substances covered by Snatzke's survey, and the mandelate ion has also been mentioned in a recent Russian publication.[8] However, the latter paper is largely if not entirely concerned with racemic mandelic acid and it does not,


I (R)


II (S)

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