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## Mixed-Valence Complexes Containing the $V_2O_3^{3+}$ Core. Structure and Properties of $H[V_2O_3(\text{pmida})_2] \cdot 4H_2O$ and $K_7[V_9O_{16}(\text{bdta})_4] \cdot 27H_2O$

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Received February 28, 1984

$H[V_2O_3(\text{pmida})_2] \cdot 4H_2O$  (pmida = ((pyridylmethyl)imino)diacetate) crystallizes in the  $P2_1$  space group with  $a = 10.672$  (1) Å,  $b = 12.22$  (1) Å,  $c = 10.495$  (4) Å,  $\beta = 95.92$  (4) Å, and  $Z = 2$ . The structure has been solved to  $R = 0.056$  for 1916 observed reflections. The  $[V_2O_3(\text{pmida})_2]^-$  ion is almost centrosymmetric around the bridging oxygen atom. Small deviations to centrosymmetry are assigned to an asymmetric localization of the  $H^+$  ion rather than to valence trapping. The compound  $K_7[V_9O_{16}(\text{bdta})_4] \cdot 27H_2O$  (bdta = butanediaminetetraacetate) crystallizes in the  $P4n2$  space group with  $a = 25.34$  (1) Å,  $c = 17.09$  (2) Å, and  $Z = 4$ . The structure has been solved to  $R = 0.097$  for 2289 observed reflections. It shows an unusual arrangement of four V-O-V mixed-valence pairs around a central  $VO_4$  tetrahedron. Intervalence bands are observed near  $10000\text{ cm}^{-1}$  for the two complexes. However, in the case of  $[V_2O_3(\text{pmida})_2]^-$ , a single-crystal spectrum shows an additional band at  $8300\text{ cm}^{-1}$  with the expected polarization for an intervalence band. The magnetic behavior is consistent with the presence of a single unpaired electron in each mixed-valence unit, with very weak antiferromagnetic couplings. Finally, cyclic voltammetry of  $[V_2O_3(\text{pmida})_2]^-$  in acetonitrile shows the existence of  $V^V\text{-O-V}^V$  and  $V^{IV}\text{-O-V}^{IV}$  dimers that decompose upon preparative electrolysis.

### Introduction

As a part of a general study on mixed-valence compounds containing vanadium(IV) and vanadium(V),<sup>1,2</sup> we have prepared several complexes with amino acids as ligands. Indeed, the use of a tetradentate ligand such as nitrilotriacetate has allowed the preparation by Saito et al.<sup>3</sup> of the compound  $[V_2O_3(\text{nta})_2]^{3-}$ , in which the extra electron is extensively delocalized according to ESR. Since then, two structures of analogous compounds have been reported;<sup>2,4</sup> they all contain the  $V_2O_3^{3+}$  core with both terminal oxygen atoms cis to the bridge but trans to each other. This leads to a good overlap between  $d_{xy}$  orbitals so that the properties of the mixed-valence compounds are very near to those of fully delocalized (i.e., class III<sup>5</sup>) systems.

We report herein the complete crystal structure as well as optical and magnetic properties of the  $[V_2O_3(\text{pmida})_2]^-$  ion (pmida = ((pyridylmethyl)imino)diacetate). A preliminary report has been already published.<sup>2</sup> We have also prepared a mixed-valence compound with bdta (bdta = butanediaminetetraacetate) with the aim of changing of geometry of the  $V_2O_3^{3+}$  core. Actually, a much more complicated structure is obtained in which four mixed-valence units are linked together around a central  $VVO_4$  tetrahedron. The properties of this compound are compared with those of  $[V_2O_3(\text{pmida})_2]^-$ .

### Experimental Section

**Synthesis of  $H[V_2O_3(\text{pmida})_2] \cdot 4H_2O$ .** This compound was synthesized by a procedure already described.<sup>2</sup> Crystals were easily obtained after 1-2 days by spontaneous evolution of the solution.

**Synthesis of  $K_7[V_9O_{16}(\text{bdta})_4] \cdot 27H_2O$ .** Butanediaminetetraacetic acid ( $H_4\text{bdta}$ ) was prepared by the method of Schwarzenbach and Ackermann<sup>6</sup> and recrystallized in water. To 4 mL of 1 M KOH was added 0.32 g of the acid. After complete dissolution, 0.452 g of  $VOSO_4 \cdot 3.5H_2O$  was added and the mixture was stirred under a nitrogen atmosphere. From this pale blue solution appeared a pale blue precipitate after a few minutes, corresponding to the composition  $[V_2^{IV}O_2(\text{bdta})] \cdot 8H_2O$ . On the other hand, if an oxidation was carried out promptly by 85 mg of  $KNO_2$ , before this precipitation, the solution turned deep blue and remained limpid. The solution (pH ca. 4) was kept in the refrigerator, and a solid compound appeared after 1 night. It was collected and washed with a water-ethanol mixture.

Table I. Crystal Data

	$H[V_2O_3(\text{pmida})_2] \cdot 4H_2O$	$K_7[V_9O_{16}(\text{bdta})_4] \cdot 27H_2O$
color and habit	blue or yellow thin plates (depending upon orient)	blue truncated prisms
space gp	$P2_1$	$P4n2$
unit cell parameters	$a = 10.672$ (1) Å $b = 12.22$ (1) Å $c = 10.495$ (4) Å $\beta = 95.92$ (4)°	$a = b = 25.34$ (1) Å $c = 17.09$ (2) Å
fw	667	2738
$d_{\text{calcd}}$ , g cm <sup>-3</sup>	1.65	1.66
$d_{\text{measd}}$ , g cm <sup>-3</sup>	1.63	1.67
Z	2	4
$F(000)$	666	5400
radiation ( $\lambda$ , Å)	Mo $K\alpha$ (0.710 69)	Mo $K\alpha$ (0.710 69)
scan mode	$\theta-2\theta$	$\theta-2\theta$
Bragg range, deg	1.5-25	1-20
scan range in Bragg angle, deg	0.9	1.1
scan rate in Bragg angle, min <sup>-1</sup>	0.55	0.76
bkgd, before and after ea reflcn, in fixed posn, s	30	30
no. of measd reflcns (room temp)	2529	2797
no. of reflcns kept for refinement ( $F > 3\sigma$ )	1916	2289
std reflcns (every 100 reflcns)	511, 082	1400, 006
cor for dec in intens, %	-7	-25
cryst dimens, mm	0.25 × 0.25 × 0.04	0.33 × 0.33 × 0.32
abs coeff, cm <sup>-1</sup>	7.31	10.48
abs cor (transmission factor range)	no (0.98-0.99)	no (0.70-0.71)
wt scheme	1.97/ $\sigma^2$	4.3/( $\sigma^2 + 10^{-4}F^2$ )
R	0.065	0.092
$R_w$	0.056	0.097

Crystals suitable for X-ray were obtained from the filtrate. Anal. Calcd: C, 21.04; H, 4.31; N, 4.09; K, 9.97; V, 16.76. Found: C, 20.50; H, 4.29; N, 3.97; K, 9.00; V, 16.27. Number of  $V^{IV}$  by redox titration: 4.13.

**X-ray Data Collection and Computing Procedures.** Crystals of  $H[V_2O_3(\text{pmida})_2] \cdot 4H_2O$  and  $K_7[V_9O_{16}(\text{bdta})_4] \cdot 27H_2O$  were stuck into Pyrex tubes under argon. For the latter, it was necessary to introduce a small amount of the mother solution to limit desiccation. Space groups were determined from precession photographs. Intensity measurements were performed with a homemade diffractometer built from a STOE three-circles system and a Varian 620L computer. The parameters relevant to the unit cell and data collection are gathered on Table I. Computations were performed with the SHELX program.<sup>7</sup> Scattering

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Table II. Atomic Parameters for H[V<sub>2</sub>O<sub>3</sub>(pmida)<sub>2</sub>]<sub>2</sub>·4H<sub>2</sub>O

atom	x	y	z
O(1)	-0.0024 (9)	0.0033 (8)	-0.2568 (8)
V	0.1088 (2)	0.1134 (1)	-0.2558 (1)
O(2)	0.1048 (7)	0.1446 (6)	-0.4034 (5)
O(3)	0.2418 (8)	0.2385 (6)	-0.2093 (5)
O(4)	0.3730 (6)	0.3161 (5)	-0.0579 (5)
O(5)	-0.0096 (6)	0.2140 (6)	-0.1757 (5)
O(6)	-0.1421 (6)	0.2182 (8)	-0.0307 (8)
N(2)	0.1617 (6)	0.0836 (4)	-0.0422 (6)
C(1)	0.1959 (8)	-0.0373 (6)	-0.0371 (6)
C(3)	0.3701 (7)	-0.1388 (7)	-0.1298 (7)
C(4)	0.4367 (7)	-0.1613 (7)	-0.2341 (5)
C(5)	0.4119 (7)	-0.1017 (7)	-0.3474 (5)
C(6)	0.3205 (7)	-0.0197 (7)	-0.3564 (5)
N(1)	0.2538 (7)	0.0028 (7)	-0.2522 (5)
C(2)	0.2786 (7)	-0.0568 (7)	-0.1389 (5)
C(7)	0.0393 (8)	0.1020 (0)	0.0151 (7)
C(9)	0.2658 (9)	0.1563 (9)	0.0018 (7)
C(8)	-0.0446 (7)	0.1828 (8)	-0.0675 (6)
C(10)	0.02968 (0)	0.2413 (8)	-0.0944 (6)
O(7)	0.2056 (1)	0.6297 (7)	-0.2025 (3)
O(8)	0.4084 (3)	0.4943 (4)	-0.1917 (5)
V'	-0.1079 (1)	-0.1134 (1)	-0.2465 (1)
O'(2)	-0.0954 (6)	-0.1406 (6)	-0.0947 (7)
O'(3)	-0.2399 (5)	-0.2263 (5)	-0.2951 (5)
O'(4)	-0.3693 (8)	-0.3151 (7)	-0.4352 (6)
O'(5)	0.0145 (6)	-0.2050 (5)	-0.3297 (5)
O'(6)	0.1320 (5)	-0.2161 (6)	-0.4879 (6)
N'(2)	-0.1659 (5)	-0.0825 (6)	-0.4575 (6)
C'(1)	-0.2152 (7)	0.0336 (7)	-0.4552 (7)
C'(3)	-0.3842 (7)	0.1389 (7)	-0.3742 (5)
C'(4)	-0.4442 (7)	0.1627 (7)	-0.2659 (5)
C'(5)	-0.4102 (7)	0.1069 (7)	-0.1515 (5)
C'(6)	-0.3161 (7)	0.0273 (7)	-0.1455 (5)
N'(1)	-0.2560 (7)	0.0035 (7)	-0.2538 (5)
C'(2)	-0.2901 (7)	0.0593 (7)	-0.3682 (5)
C'(7)	-0.0484 (6)	-0.0991 (7)	-0.5232 (7)
C'(9)	-0.2676 (9)	-0.1568 (7)	-0.5120 (6)
C'(8)	0.0333 (7)	-0.1864 (9)	-0.4479 (7)
C'(10)	-0.2884 (9)	-0.2419 (7)	-0.4123 (7)
O'(7)	-0.2065 (0)	-0.6343 (0)	-0.2855 (0)
O'(8)	-0.4040 (2)	-0.4936 (3)	-0.3213 (1)

factors were taken from ref 8, including  $\Delta f'$  and  $\Delta f''$  for vanadium and potassium. The full-matrix least-squares method was used to minimize  $\sum(w|F_o| - |F_c|)^2$ .

**Solution and Refinement of the Structure of H[V<sub>2</sub>O<sub>3</sub>(pmida)<sub>2</sub>]<sub>2</sub>·4H<sub>2</sub>O.** Systematic absences were consistent with either the  $P2_1$  or  $P2_1/m$  space groups. Statistical tests showed a centrosymmetry, thus favoring the last possibility ( $P2_1/m$ ). However, no solution could be found in this space group. We then noticed that the reflections  $h0l$  with  $l$  odd were very weak, showing that the space group was close to  $P2_1/c$ . In this system, the structure was easily solved by both Patterson and direct methods. The unique vanadium atom of the asymmetric unit was found, and a refinement of its coordinates gave  $R = 0.48$ . A vanadium-phased Fourier series then showed all remaining atoms, including the oxygen atoms of crystallization water molecules.

At this stage ( $R = 0.14$ ), the molecule was still constrained to be centrosymmetric around the bridging oxygen atom. However, the presence of nonzero reflections in the  $h0l$  plane with  $l$  odd (which was definitely established on precession exposures) proved that the actual space group was  $P2_1$  with a pseudocentrosymmetry of the asymmetric unit. The  $P2_1/m$  space group was ruled out considering the absence of a mirror plane in the molecule.

The structure determination was thus continued in  $P2_1$  (noncentrosymmetric). The  $R$  factor dropped from 0.142 to 0.119, which was significant according to Hamilton's test. In this group, we thus allowed the halves of the molecule to refine independently. Large correlation effects were observed that were partly overcome as follows: Firstly, the  $P2_1$  space group being polar, we chose, among other possibilities, to fix the  $y$  origin midway between the two vanadium atoms. Second, the weights of the reflections  $h0l$  with  $l$  odd were multiplied by 15 since they break the centrosymmetry. Third, it was found necessary to use con-

Table III. Interatomic Distances (Å) around Vanadium Atoms in H[V<sub>2</sub>O<sub>3</sub>(pmida)<sub>2</sub>]<sub>2</sub>·4H<sub>2</sub>O

		V			
ax	V-O(2)	1.592 (5)	eq	V-O(5)	2.010 (7)
eq	V-O(1)	1.79 (2)	ax	V-N(2)	2.282 (7)
eq	V-O(3)	2.107 (8)	eq	V-N(1)	2.052 (8)
		V'			
ax	V'-O'(2)	1.620 (8)	eq	V'-O'(5)	1.992 (7)
eq	V'-O'(1)	1.82 (2)	ax	V'-N'(2)	2.267 (6)
eq	V'-O'(3)	1.998 (6)	eq	V'-N'(1)	2.126 (8)

Table IV. Bond Angles (deg) in H[V<sub>2</sub>O<sub>3</sub>(pmida)<sub>2</sub>]<sub>2</sub>·4H<sub>2</sub>O

Angles around V			
O(2)-V-O(1)	102.9 (4)	O'(2)-V'-O'(1)	103.4 (4)
O(3)-V-O(2)	90.0 (3)	O'(3)-V'-O'(2)	95.3 (3)
O(3)-V-O(1)	167.0 (3)	O'(3)-V'-O'(1)	161.0 (3)
O(5)-V-O(1)	90.0 (3)	O'(5)-V'-O'(1)	88.4 (5)
O(5)-V-O(2)	107.9 (3)	O'(5)-V'-O'(2)	109.1 (3)
O(5)-V-O(3)	84.3 (3)	O'(5)-V'-O'(3)	88.8 (5)
N(2)-V-O(1)	89.0 (3)	N'(2)-V'-O'(1)	85.4 (3)
N(2)-V-O(2)	166.6 (3)	N'(2)-V'-O'(2)	168.8 (3)
N(2)-V-O(3)	78.3 (2)	N'(2)-V'-O'(3)	75.7 (2)
N(2)-V-O(5)	77.7 (2)	N'(2)-V'-O'(5)	77.8 (2)
N(1)-V-O(1)	90.4 (6)	N'(1)-V'-O'(1)	86.4 (6)
N(1)-V-O(2)	96.7 (3)	N'(1)-V'-O'(2)	99.0 (3)
N(1)-V-O(3)	89.0 (3)	N'(1)-V'-O'(3)	87.2 (3)
N(1)-V-O(5)	154.4 (2)	N'(1)-V'-O'(5)	151.9 (2)
N(1)-V-N(2)	76.7 (2)	N'(1)-V'-O'(2)	74.2 (2)
Angles around O			
V-O(1)-V' 175.3 (7)			
V-O(3)-C(10)	117.8 (6)	V'-O'(3)-C'(10)	122.9 (5)
V-O(5)-C(8)	116.2 (6)	V'-O'(5)-C'(8)	119.7 (6)
Angles around N			
C(1)-N(2)-V	102.9 (4)	C'(1)-N'(2)-V'	109.3 (5)
C(7)-N(2)-V	103.5 (4)	C'(7)-N'(2)-V'	105.7 (6)
C(9)-N(2)-V	108.4 (5)	C'(9)-N'(2)-V'	112.9 (6)
C(1)-N(2)-C(7)	110.2 (7)	C'(1)-N'(2)-C'(7)	111.3 (6)
C(1)-N(2)-C(9)	114.0 (6)	C'(1)-N'(2)-C'(9)	107.0 (6)
C(7)-N(2)-C(9)	116.5 (7)	C'(7)-N'(2)-C'(9)	110.7 (6)
Angles around C			
C(2)-C(1)-N(2)	106.9 (6)	C'(2)-C'(1)-N'(2)	108.3 (6)
C(1)-C(2)-N(1)	117.3 (7)	C'(1)-C'(2)-N'(1)	115.9 (7)
C(2)-C(3)-C(4)	120.0 (6)	C'(2)-C'(3)-C'(4)	120.0 (6)
C(5)-C(4)-C(3)	120.0 (7)	C'(5)-C'(4)-C'(3)	120.0 (7)
C(4)-C(5)-C(6)	120.0 (6)	C'(4)-C'(5)-C'(6)	120.0 (6)
N(1)-C(6)-C(5)	120.0 (6)	N'(1)-C'(6)-C'(5)	120.0 (6)
C(8)-C(7)-N(2)	110.3 (6)	C'(8)-C'(7)-N'(2)	108.1 (6)
C(7)-C(8)-O(5)	118.7 (7)	C'(7)-C'(8)-O'(5)	118.4 (8)
C(7)-C(8)-O(6)	120.8 (7)	C'(7)-C'(8)-O'(6)	119.2 (7)
O(5)-C(8)-O(6)	120.5 (8)	O'(5)-C'(8)-O'(6)	120.0 (8)
C(10)-C(9)-N(2)	114.8 (6)	C'(10)-C'(9)-N'(2)	108.0 (6)
C(9)-C(10)-O(3)	119.9 (9)	C'(9)-C'(10)-O'(3)	118.9 (7)
C(9)-C(10)-O(4)	118.5 (6)	C'(9)-C'(10)-O'(4)	120.6 (7)
O(3)-C(10)-O(4)	121.5 (8)	O'(3)-C'(10)-O'(4)	119.1 (8)

straints on several bond lengths and angles of the pmida ligand, which were taken from ref 9. Distances: C-C inside the pyridine ring 1.395 Å; C<sub>1</sub>-N<sub>2</sub> 1.53 Å; C<sub>1</sub>-C<sub>2</sub> = 1.49 Å; C<sub>7</sub>-C<sub>8</sub>, C<sub>9</sub>-C<sub>10</sub> = 1.55 Å; N<sub>2</sub>-C<sub>1</sub>, N<sub>2</sub>-C<sub>7</sub>, N<sub>2</sub>-C<sub>9</sub> = 1.54 Å; C<sub>8</sub>-O<sub>5</sub>, C<sub>10</sub>-O<sub>3</sub> = 1.29 Å; C<sub>8</sub>-C<sub>6</sub>, C<sub>10</sub>-O<sub>4</sub> = 1.23 Å. The test for chirality showed a very small effect (0.0002 on  $R$ ), due to the pseudocentrosymmetry and the weakness of anomalous dispersion for vanadium.

After introduction of hydrogen atoms and anisotropic refinement of all non-hydrogen atoms, the final agreement factors were  $R = 0.065$  and  $R_w = 0.056$ . Atomic parameters with their standard deviations are given in Table II, and chemically significant interatomic distances and angles in Tables III and IV.

**Solution and Refinement of the Structure of K<sub>7</sub>[V<sub>5</sub>O<sub>16</sub>(bdta)<sub>4</sub>]<sub>2</sub>·27H<sub>2</sub>O.** The structure was solved by the MULTAN program. Systematic extinctions were consistent with  $P4_2/mnm$ ,  $P4n2$ , and  $P4_2nm$  space groups. Statistical tests were in favor of the last two noncentrosymmetric possibilities. The direct method was tried in both cases: the  $P4n2$  group gave the best figures of merit, and furthermore, only this group yielded a

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Table V. Atomic Parameters for  $K_7[V_9O_{16}(bdta)_4] \cdot 27H_2O$ 

atom	x	y	z
V(1)	0.30413	0.34684	0.28832
V(2)	0.14320	0.14942	0.01447
V(3)	0.37142	0.16446	0.08981
V(4)	0.22255	0.05168	0.46487
V(5)	0.29180	0.20820	0.25000
O(1)	0.24310	0.35376	0.29873
O(2)	0.13823	0.08950	0.01843
O(3)	0.41423	0.13212	0.14526
O(4)	0.19227	0.08181	0.53332
O(5)	0.30410	0.27152	0.25929
O(6)	0.32435	0.18582	0.16713
O(7)	0.32900	0.34405	0.38032
O(8)	0.40036	0.22337	0.06843
First bdta Ligand			
O(9)	0.12042	0.19646	-0.20789
O(10)	0.13145	0.15334	-0.10345
O(11)	0.00341	0.22297	0.05239
O(12)	0.06620	0.16577	0.02753
O(13)	0.31870	0.42411	0.28357
O(14)	0.33046	0.49686	0.20886
O(15)	0.38484	0.34257	0.23412
O(16)	0.43087	0.32153	0.12998
N(1)	0.29448	0.36213	0.15733
N(2)	0.13594	0.24231	-0.01129
C(1)	0.24262	0.34542	0.13287
C(2)	0.23295	0.35137	0.03695
C(3)	0.18091	0.33053	0.01077
C(4)	0.18299	0.26855	0.01359
C(5)	0.13153	0.24669	-0.10515
C(6)	0.12881	0.19816	-0.14004
C(7)	0.08839	0.25809	0.03015
C(8)	0.05155	0.21720	0.03563
C(9)	0.29843	0.42276	0.14748
C(10)	0.31937	0.44936	0.21461
C(11)	0.33828	0.32970	0.11893
C(12)	0.38464	0.33310	0.16080
Second bdta Ligand			
O(17)	0.14995	-0.09089	0.43900
O(18)	0.17548	-0.01105	0.47346
O(19)	0.34666	-0.03382	0.54370
O(20)	0.27352	0.01190	0.52946
O(21)	0.39359	0.13600	-0.01355
O(22)	0.38048	0.07509	-0.10185
O(23)	0.30006	0.18087	0.01483
O(24)	0.21783	0.16120	-0.01113
N(3)	0.31847	0.08665	0.08424
N(4)	0.26163	-0.01277	0.37964
C(13)	0.32601	0.06239	0.16389
C(14)	0.29859	0.00487	0.16520
C(15)	0.29768	-0.02048	0.24284
C(16)	0.26792	0.01231	0.29757
C(17)	0.22258	-0.05706	0.37388
C(18)	0.17907	-0.05249	0.43285
C(19)	0.31515	-0.02478	0.41794
C(20)	0.31097	-0.01538	0.50351
C(21)	0.34080	0.05627	0.01778
C(22)	0.37367	0.09266	-0.03510
C(23)	0.26489	0.10318	0.07459
C(24)	0.26168	0.14879	0.02531
Potassium Ions			
K(1)	0.42364	0.24035	0.16348
K(2)	0.45880	0.40058	0.09848
K(31)	0.13890	0.03630	0.14060
K(32)	0.16950	0.05480	0.15490
K(33)	0.11570	0.00770	0.13240
Crystallization Water Molecules			
O(25)	0.38850	0.34330	0.18880
O(26)	0.0607	0.41770	-0.04400
O(27)	0.06380	0.41460	0.04970
O(28)	0.06280	0.08730	0.24320
O(29)	0.44440	0.43490	-0.07390

Table VI. Interatomic Distances (Å) around Vanadium Atoms in  $K_7[V_9O_{16}(bdta)_4] \cdot 27H_2O$  (oxo, Terminal Oxygen; ax and eq, Axial and Equatorial Ligands with Respect to Oxo Oxygen)

		V(1)			
oxo	V(1)-O(1)	1.57 (2)	eq	V(1)-O(13)	1.99 (2)
ax	V(1)-O(15)	2.25 (2)	eq	V(1)-O(5)	1.97 (2)
eq	V(1)-N(1)	2.28 (2)	eq	V(1)-O(7)	1.69 (2)
		V(2)			
oxo	V(2)-O(2)	1.52 (2)	eq	V(2)-O(24)	1.96 (2)
ax	V(2)-N(2)	2.40 (2)	eq	V(2)-O(12)	2.01 (2)
eq	V(2)-O(10)	2.04 (2)	eq	V(2)-O(7)	1.91 (2)
		V(3)			
oxo	V(3)-O(3)	1.66 (2)	eq	V(3)-O(8)	1.70 (2)
ax	V(3)-O(23)	2.25 (2)	eq	V(3)-O(6)	1.86 (2)
eq	V(3)-N(3)	2.38 (2)	eq	V(3)-O(21)	1.99 (2)
		V(4)			
oxo	V(4)-O(4)	1.59 (2)	eq	V(4)-O(18)	1.99 (2)
ax	V(4)-N(4)	2.40 (2)	eq	V(4)-O(16)	2.02 (2)
eq	V(4)-O(8)	1.92 (2)	eq	V(4)-O(20)	1.97 (2)
		V(5)			
	V(5)-O(5)	1.64 (2)		V(5)-O(6)	1.73 (2)

chemically significant solution. The five vanadiums of the asymmetric unit were found, one of them lying on a twofold axis. Refinement of their coordinates yielded  $R = 0.45$ . Successive Fourier series revealed the oxygen atoms and bdta ligands but curiously not the potassium ions. The  $R$  factor was 0.30 and dropped to 0.20 after withdrawal of six very intense reflections with low Bragg angles ( $<2^\circ$ ) that were probably perturbed by the direct beam. At this stage, difference Fourier revealed three weak peaks outside the anion, which were considered to correspond to the potassium ions since the asymmetric unit contains  $3.5 K^+$ . However, a refinement with three potassium atoms lead to large values of the temperature coefficients ( $U \sim 0.3$ ). An alternative possibility was to introduce a site occupation factor near 0.5, but in this case, only half of the potassium atoms would have been located. The first possibility was considered more likely, and the large value of the temperature coefficients was assigned to the existence, for each of the three sites, of several close neighboring  $K^+$  positions with statistical occupancy. In one case ( $K(3)$ ), it was actually possible to resolve the site into three positions ( $K(31)$ ,  $K(32)$ ,  $K(33)$ ). This loose localization of the  $K^+$  ions can be explained by the crystal packing (see below). Finally, five water molecules were found. After anisotropic refinement of all atoms except potassium and water molecules, the agreement factors were  $R = 0.092$  and  $R_w = 0.097$ . These relatively poor agreement factors are assigned to the decomposition of the crystal during data recording ( $\sim 25\%$ ) and the impossibility to locate all the crystallization water molecules. Since the last Fourier maps revealed only very weak peaks, the missing crystallization water molecules are presumed to be disordered. Atomic parameters with their standard deviations are given in Table V, and chemically significant interatomic distances and angles in Table VI and VII.

**Spectroscopic and Magnetic Measurements.** UV-visible-near-IR spectra were recorded on a Beckman 5240 spectrometer between 1400 and 300 nm. In the case of  $H[V_2O_3(pmida)_2] \cdot 4H_2O$  a single crystal having a shape of a plate with approximate dimensions  $1 \times 1 \times 0.05$  mm was mounted in front of the sample beam. Polaroid films (HR type for near-IR studies) were used as polarizers.

ESR spectra were recorded on a JEOL X-band spectrometer.

The magnetic susceptibility was measured by the Faraday method on a powder pellet of 8-mm diameter and 2-mm thickness. The temperature was controlled from 4 K to room temperature. Magnetic susceptibilities were corrected from the diamagnetic contribution.

**Electrochemical Studies.** Cyclic voltammetry was performed with Tacussel equipment comprised of a Tacussel PRT 30-0.1 potentiostat, a GSATP generator, and an X-Y recorder. The electrode was a glassy-carbon rod polished with alumina and cleaned by ultrasound. Controlled-potential electrolyses were performed with a Tacussel PRT 20-2 potentiostat and a IG4 integrator on either platinum or mercury electrodes. The background electrolyte was 0.1 M  $NBu_4BF_4$ .

## Results and Discussion

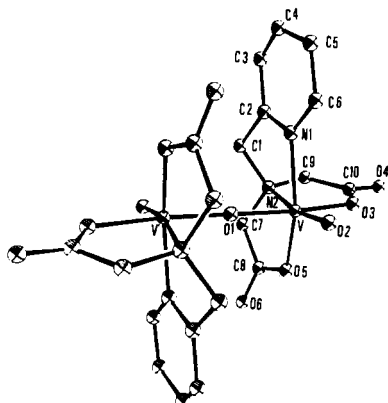
**Crystal Structure of  $H[V_2O_3(pmida)_2] \cdot 4H_2O$ .** The  $[V_2O_3-(pmida)_2]^-$  ion is pseudocentrosymmetric (see Figure 1) with a nearly linear oxygen bridge. As in Saito's complex  $[V_2O_3(nta)_2]^{3-}$ , the terminal oxygen atoms O(2) and O'(2) are trans to each other but cis to the bridging oxygen. Each vanadium atom is surrounded by a distorted octahedron formed by the terminal oxygen O(2), the bridging oxygen O(1), and four atoms of the pmida ligand:

Table VII. Bond Angles (deg) in  $K_7[V_9O_{16}(bdta)_4] \cdot 27H_2O^a$ 

Angles around Vanadium Atoms			
O(7)-V(1)-O(5)	101.1 (7)	O(24)-V(2)-O(10)	85.0 (8)
O(13)-V(1)-O(5)	160.1 (8)	O(2)-V(2)-O(10)	94.6 (9)
O(13)-V(1)-O(7)	90.6 (8)	O(2)-V(2)-O(24)	104 (1)
O(1)-V(1)-O(5)	97.8 (9)	O(12)-V(2)-O(10)	87.6 (8)
O(1)-V(1)-O(7)	105.4 (9)	O(12)-V(2)-O(24)	158.4 (9)
O(1)-V(1)-O(13)	94.4 (0)	O(12)-V(2)-O(2)	97 (1)
O(15)-V(1)-O(5)	81.4 (7)	N(2)-V(2)-O(10)	76.1 (8)
O(15)-V(1)-O(7)	92.4 (8)	N(2)-V(2)-O(24)	83.3 (9)
O(15)-V(1)-O(13)	82.0 (9)	N(2)-V(2)-O(2)	168 (1)
O(15)-V(1)-O(1)	162 (1)	O(21)-V(3)-O(8)	90.3 (8)
N(1)-V(1)-O(5)	85.3 (7)	O(3)-V(3)-O(8)	106 (1)
N(1)-V(1)-O(7)	163 (1)	O(3)-V(3)-O(21)	98.3 (9)
N(1)-V(1)-O(13)	79.3 (8)	O(6)-V(3)-O(21)	156.5 (9)
N(1)-V(1)-O(1)	89.2 (8)	O(6)-V(3)-O(3)	99.0 (9)
N(1)-V(1)-O(15)	72.6 (7)	O(23)-V(3)-O(8)	93.5 (7)
O(2)-V(4)-O(4)	97 (1)	O(23)-V(3)-O(21)	78 (1)
O(18)-V(4)-O(4)	92 (1)	O(23)-V(3)-O(3)	160.2 (9)
O(18)-V(4)-O(20)	87 (1)	O(23)-V(3)-O(6)	80.6 (7)
N(4)-V(4)-O(4)	166 (1)	N(3)-V(3)-O(8)	163.3 (8)
N(4)-V(4)-O(20)	74 (1)	N(3)-V(3)-O(21)	80 (1)
N(4)-V(4)-O(18)	75 (1)	N(3)-V(3)-O(3)	89.0 (9)
N(6)-V(5)-O(5)	108 (1)	N(3)-V(3)-O(6)	85 (1)
		N(3)-V(3)-O(23)	71.3 (7)

Oxygen Bridge Angles			
V(1)-O(7)-V(2)'	167 (1)	V(5)-O(5)-V(1)	166 (1)
V(3)-O(8)-V(4)'	164 (1)	V(5)-O(6)-V(3)	169 (1)

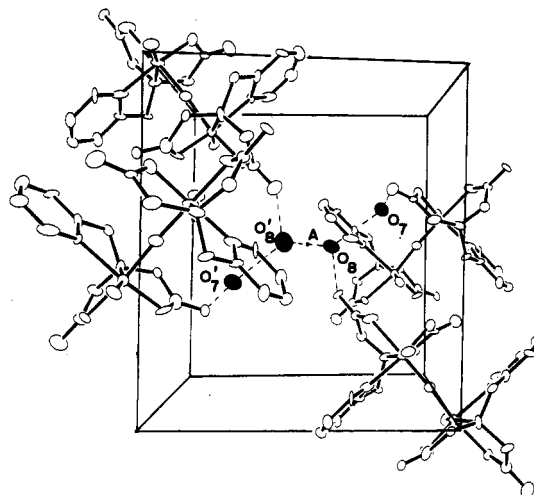
<sup>a</sup> Symmetry code: unprimed,  $x, y, z$ ; primed,  $1/2 - y, 1/2 - x, 1/2 - z$ .

Figure 1. Structure of the  $[V_2O_3(pmida)_2]^{7-}$  anion.

the tertiary nitrogen N(2), the pyridinic nitrogen N(1), and the carboxylate oxygens O(3) and O(5).

The V-O(2) and V-O'(2) distances are close together (average 1.60 Å) and characteristic of oxo-type oxygen atoms with strong  $\pi$  bonding. The V-O(1) and V'-O(1) distances (1.80 Å) also reveal some  $\pi$  bonding but to a lesser extent. The coordination of the pmida ligand is entirely analogous to that found in  $[VO(pmida)(H_2O)]$ ,<sup>9</sup> the bridging oxygen replacing the coordinated water molecule of the last complex. The tertiary nitrogen N(2) is trans to the terminal doubly bonded oxygen atom; the two carboxylate oxygens and the pyridine nitrogen are in equatorial positions.

The departure from centrosymmetry has been carefully investigated since we first thought that it might have been the result of a partial electronic localization on one side of the molecule, i.e. one of the vanadium atoms having more than 50%  $V^V$  character and the other more  $V^{IV}$  character. However, in such a case one would expect differences in bond lengths around the vanadium atoms, especially in the equatorial plane, since the extra electron in  $V^{IV}$  lies in a  $d_{xy}$  orbital, which is perpendicular to the metal-terminal oxygen axis. Actually, this effect is not observed: taking into account the standard deviation, no systematic variation in the bond lengths around the two vanadium atoms can be detected. However, it is instructive to compare the coordinates of the corresponding atoms in both halves of the anion, considering the

Figure 2. Arrangement of the four water molecules (shaded circles are their oxygen atoms) in the unit cell of  $H[V_2O_3(pmida)_2] \cdot 4H_2O$ .

symmetry operation  $x, y, z \rightarrow \bar{x}, \bar{y}, z - 1/2$ . It is then found that the greatest deviations from centrosymmetry occur for the uncoordinated oxygens of the carboxylate groups. This suggests that the noncentrosymmetry is due to an external cause in relation with the arrangement in the crystal (see below).

The unit cell contains two formula units of  $H[V_2O_3(pmida)_2] \cdot 4H_2O$  while the asymmetric unit coincides with the formula unit. Both  $[V_2O_3(pmida)_2]^-$  anions of the unit cell are related by an helicoidal axis. The four water molecules are arranged in such a way that they form hydrogen bonds with the free carboxylate oxygens of the four different molecules, thus ensuring the stability of the overall structure (see Figure 2). They exhibit also a pseudocentrosymmetric arrangement around the point  $1/2, 1/2, -1/4$  (point A, Figure 2). The  $H^+$  ion cannot be directly localized but is assumed to be associated with the "cluster" of water molecules O(7), O(8), O'(7), and O'(8). Then, two hypotheses can be made concerning the location of the  $H^+$  ion with respect to the pseudocenter (point A): (i) The  $H^+$  ion is located symmetrically, i.e. equidistant from O(8) and O'(8), thus constituting a  $H_3O_2^+$  ion. (ii) The  $H^+$  ion is located asymmetrically with respect to point A; the most probable location is then either O(8) or O'(8), since there are examples for which  $H_3O^+$  is triply hydrogen bonded. One of the hydrogen bonds would link O(8) with O'(8).

In hypothesis i, the O(8)---O'(8) distance should be very short, about 2.44 Å,<sup>10</sup> whereas a distance of 2.55 Å is observed. We thus consider that hypothesis ii is more probable and formulate the cluster of water molecules as  $H_3O^+ + 3H_2O$ . Thus, it seems that the presence of the  $H^+$  ion on either O(8) or O'(8) is responsible for the loss of the centrosymmetry for the overall structure.

**Crystal and Molecular Structure of  $K_7[V_9O_{16}(bdta)_4] \cdot 27H_2O$ .** The  $[V_9O_{16}(bdta)_4]^{7-}$  anion exhibits a very unusual structure (see Figure 3). The anion lies on a twofold axis, but its effective symmetry is close to  $S_4$ . It is organized around a central tetrahedral  $V^VO_4$  group from which four mixed-valence binuclear groups span (Figure 4). The mixed-valence "arms" are linked together by the four bdta ligands: each one connects the first vanadium of a pair to the second vanadium of the opposite pair (see Figure 5 where two such pairs have been represented). As a first approximation, each end of the bdta ligand behaves as a tridentate group through the tertiary nitrogen atom and two oxygens of the carboxylate groups. However, both ends do not coordinate in the same way: around the second atom of a pair (for instance V(4), see Figure 5) the tertiary nitrogen atom is trans to the terminal oxo group, and the carboxylate oxygens are therefore in cis positions. This is the usual type of coordination

(10) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 219.

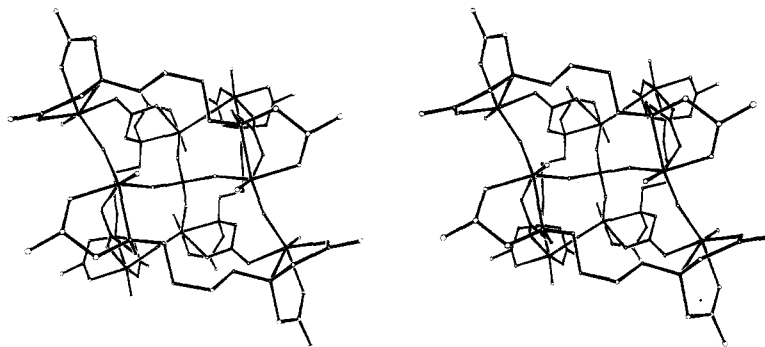


Figure 3. Stereoscopic view of the  $[V_9O_{16}(bdta)_4]^{7-}$  anion.

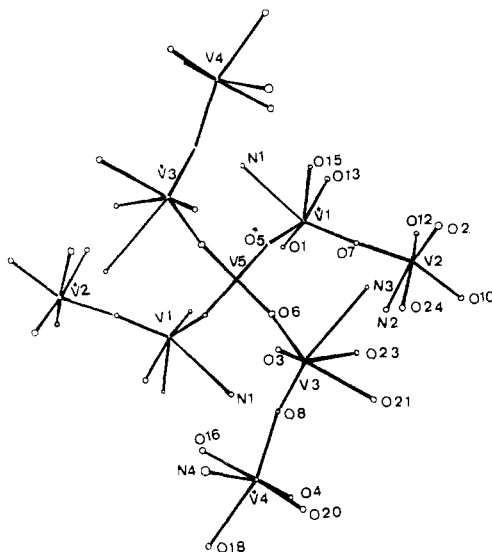


Figure 4. Arrangement of the four mixed-valence pairs around the central tetrahedron in  $[V_9O_{16}(bdta)_4]^{7-}$ .

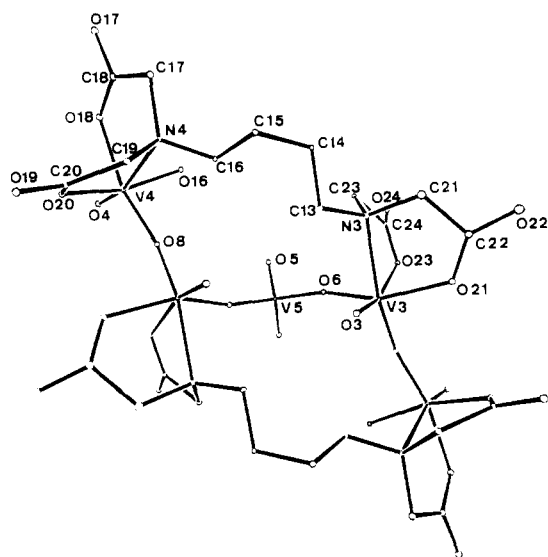


Figure 5. Coordination mode of the bdta ligand in  $[V_9O_{16}(bdta)_4]^{7-}$ .

for this class of ligands, as already found in  $[VO(pmida)(H_2O)]$ ,<sup>9</sup>  $[V_2O_3(nta)_2]^{3-}$ ,<sup>3</sup>  $[VO(S-peida)H_2O]$ ,<sup>4</sup>  $[V_2O_3(S-peida)_2]^{-}$ ,<sup>4</sup> and  $[V_2O_3(pmida)_2]^{-}$ .<sup>2</sup> On the contrary, around the first vanadium atom of a pair, the nitrogen atom is *cis* to the terminal oxo group (and *trans* to the bridge) so that one carboxylate oxygen is *cis* and the other *trans* to  $V=O$ . This type of coordination does not seem to have been reported so far.

There is however an additional linkage involving the free oxygen of one  $COO^-$  group that links to the second vanadium atom of another arm. Thus, one finds four  $COO^-$  bridges linking the pairs

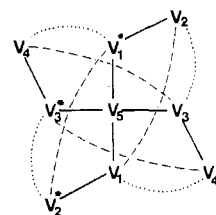


Figure 6. Connections between the nine vanadium atoms: —, V—O—V link; ---, connection by bdta ligand; ···, bridging carboxylate.

$V(1)-V(2)^*$  and  $V(1)^*-V(2)$  on one hand with  $V(3)-V(4)^*$  and  $V(3)^*-V(4)$  on the other hand. In all, the bdta ligand is hepta-coordinated. The complete scheme of all connections between vanadium atoms is given in Figure 6.

According to stoichiometry, vanadium(IV) titration, and spectroscopic properties, each pair of octahedral vanadium atoms constitutes a mixed-valence  $V^{IV}---V^V$  system. The terminal oxygen atoms are *trans* to each other, as in the *pmida*, *nta*, or *S-peida* mixed-valence systems. Thus, until now, the mixed-valence  $V_2O_3^{3+}$  moiety has been always observed with the same geometry even with the bdta ligand, which in principle does not favor it.

Contrary to the case of  $[V_2O_3(pmida)_2]^{-}$ , the two vanadiums of a pair are in chemically different environments. Therefore, one could expect some slight tendency to localization of the valence states. As in the case of  $[V_2O_3(pmida)_2]^{-}$  we have compared the average bond lengths in the equatorial plane around the four independent vanadium atoms  $V(1)-V(4)$ . They are found identical (1.98 Å). However, there is a striking and apparently significant asymmetry of the  $V(1)-O-V(2)$  and  $V(3)-O-V(4)$  bridges; the V—O distances are close to 1.70 Å on one side of the bridge ( $V(1)$  or  $V(3)$ ) vs. 1.91 Å on the other side ( $V(2)$  or  $V(4)$ ). This could mean that the first atom of a pair ( $V(1)$  or  $V(3)$ ) has more  $V^V$  character while the second ( $V(2)$  or  $V(4)$ ) has more  $V^{IV}$  character. According to Saito<sup>4</sup>, there is a second difference between the coordinations of  $V^{IV}$  and  $V^V$ :  $V^{IV}$  is more displaced than  $V^V$  with respect to the equatorial plane. In our case the deviations are as follows (Å):  $V(1)$ , 0.249;  $V(2)$  0.350;  $V(3)$ , 0.289;  $V(4)$  0.336. This provides a second indication that  $V(1)$  and  $V(3)$  have more  $V^V$  character than  $V(2)$  and  $V(4)$ . For sake of comparison, Saito's values are 0.40 for  $V^{IV}$  and 0.36 for  $V^V$ .

The vanadium—oxygen distances involving the carboxylate groups range from 1.86 to 2.04 Å for equatorial carboxylates and are markedly longer (2.25 Å) for axial carboxylates. A similar trend is observed with the vanadium—nitrogen distances, but the vanadium—nitrogen distances are longer than the vanadium oxygen ones: from 2.28 to 2.38 Å for equatorial nitrogen and 2.40 Å for an axial nitrogen. The distances inside the bdta ligand exhibit normal values.

Finally, the structure of  $[V_9O_{16}(bdta)_4]^{7-}$  shows cavities between the carboxylate groups linked to the two vanadium atoms of a mixed-valence pair. These cavities are possible sites for the  $K^+$  ions, but their size is such that the alkaline ion can "rattle" inside it. This would explain the three possible locations for the disordered  $K(3)$  ion.

**Stability and Geometry of the  $V_2O_3^{3+}$  Moiety.** In view of Saito's earlier results<sup>3</sup>, the geometry of the  $[V_2O_3(pmida)_2]^{-}$  ion was not

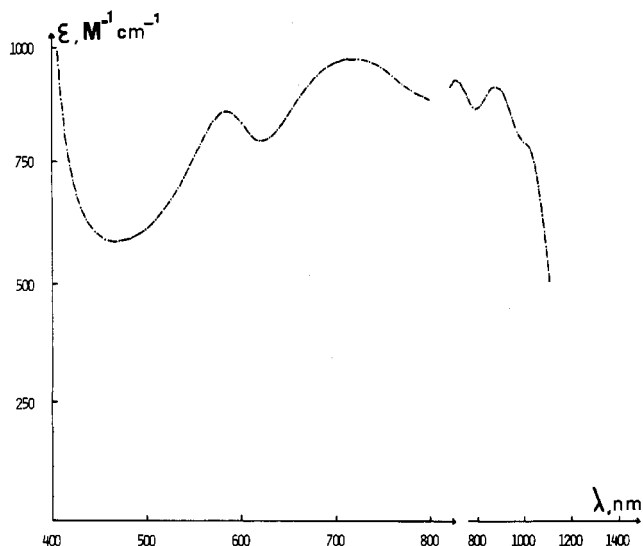


Figure 7. Spectrum of  $[V_9O_{16}(bdta)_4]^{7-}$  in acetonitrile. The extinction coefficient is given for one V–O–V pair.

a surprise. On the contrary, the structure of  $[V_9O_{16}(bdta)_4]^{7-}$  was unexpected. Originally, it was hoped that the two ends of the bdta ligand would have coordinated to each one of the vanadium atoms of the same V–O–V pair, giving a compound with the formula  $[V_2O_3(bdta)(H_2O)_2]^-$ . In this hypothesis molecular models showed that the two terminal oxygen atoms would have been in a cis configuration, which perhaps some twist angle. As a matter of fact, this geometry has been recently observed in the case of vanadium(V) dimers.<sup>11</sup>

The actual structure shows that the  $V_2O_3^{3+}$  moiety “prefers” the trans configuration. The overall structure of  $[V_9O_{16}(bdta)_4]^{7-}$  can be broadly rationalized as follows: since each end of the bdta ligand is only tridentate, the complexation of vanadium is not so effective than with the quadridentate pmida. Thus, a small amount of vanadium(V) may remain in the solution in the form of a tetrahedral species around which the complex anion can organize. Finally, the bdta ligand, which has a relatively long chain, spans between different V–O–V pairs instead of connecting the two vanadiums of a same pair; however, since the  $VO_4$  tetrahedron has already connected two  $V_2O_3$  groups, an additional constraint is introduced in the structure. This might explain the unusual coordination around V(1) and V(3).

**Electronic Spectra in Solution.** The electronic spectra of  $[V_2O_3(pmida)_2]^-$  and  $[V_2O_3(nta)_2]^{3-}$  in nitromethane and propylene carbonate respectively have been already described.<sup>2</sup> They show two bands in the d–d band range of the corresponding vanadium(IV) monomeric complexes, i.e. 560–600 and 710–770 nm. In addition, a new band is present near 1000 nm in the spectra of the mixed-valence compounds. It is assigned to the intervalence transition. We have described elsewhere the results of a computer simulation of this band according to the PKS model;<sup>12</sup> this yields parameters consistent with strongly delocalized systems, very near to Robin and Day’s class III.<sup>5</sup>

The spectrum of  $[V_9O_{16}(bdta)_4]^{7-}$  is the same in solution (acetonitrile and 18-crown-6 to assist dissolution) and in the solid state (KBr pellet), showing that the peculiar structure is retained in solution. There are two bands at 585 and 720 nm, corresponding to the d–d bands observed at 615 and 800 nm in  $[V^{IV}_2O_2(bdta)]$ .<sup>13</sup> However, the intervalence band is clearly split in two components: a maximum at 900 nm and a shoulder at 1020 nm (see Figure 7). This splitting could be explained by an interaction between

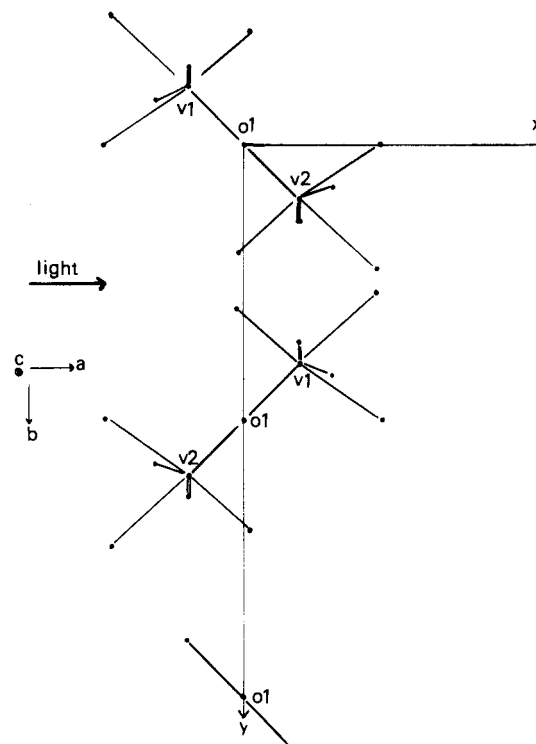


Figure 8. Orientation of the two  $[V_2O_3(pmida)_2]^-$  anions in the unit cell.

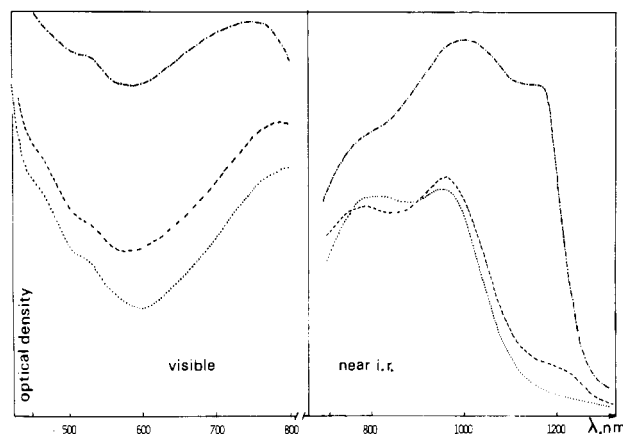


Figure 9. Polarized and unpolarized spectra of  $H[V_2O_3(pmida)_2] \cdot 4H_2O$ : ---, without polarization; - · -, with electric field vector parallel to  $\bar{b}$ ; ···, with electric field vector parallel to  $\bar{z}$ .

Table VIII. Absorption Spectra of  $[V_2O_3(pmida)_2]^-$  in Solution and in the Solid State (Band Positions in  $cm^{-1}$ , Extinction Coefficient in Parentheses)

soln <sup>a</sup> or powder	single cryst	soln <sup>a</sup> or powder	single cryst
10 000 (1070)	8 300	17 700 (515)	19 000 (sh)
13 900 (915)	10 500	27 000 (1850)	21 500 (sh)

<sup>a</sup> As the  $NEt_4^+$  salt in nitromethane.

the four different possible excited states corresponding to the excitation of each of the four mixed-valence units (cf. exciton theory<sup>14</sup>).

**Single-Crystal Spectra of  $H[V_2O_3(pmida)_2] \cdot 4H_2O$ .** This study was undertaken in view of the particular shape of the crystals as thin tablets and of their marked pleochroism. Due to the crystal axes orientation (see Figure 8) it was only possible to have the light propagating along  $\bar{z}$ . Thus, two polarized spectra could be recorded: one with the electric field parallel to the  $\bar{z}$  axis and therefore perpendicular to the V(1)–V(2) vectors and one with

(11) Yamada, S.; Katayama, C.; Tanaka, J.; Tanaka, M. *Inorg. Chem.* **1984**, *23*, 253. Saussine, L.; Mimoun, H.; Mitschler, A.; Fisher, J. *Nouv. J. Chim.* **1980**, *4*, 235.

(12) Piepho, S. B.; Krausz, E. R.; Schatz, P. N. *J. Am. Chem. Soc.* **1978**, *100*, 2996.

(13) This species is the pale blue precipitate mentioned in the Experimental Section. We use it as a reference for a vanadium(IV) complex of bdta.

the electric field parallel to  $\vec{b}$ , thus making an angle of  $45^\circ$  with the  $V(1)-V(2)$  vectors (see Figure 8). These spectra are represented Figure 9 together with the unpolarized spectrum, and the band positions are gathered on Table VIII. Generally speaking, the single-crystal spectrum has a shape different from that of the solution spectrum. The two most striking differences are (i) the appearance of a shoulder near  $465 \text{ nm}$  ( $21\,500 \text{ cm}^{-1}$ ) whereas the solution absorption is minimal in this range (as a result, the crystal appears *yellow* whereas the solution was deep blue) and (ii) the crystal exhibits a weak band near  $1200 \text{ nm}$  ( $8300 \text{ cm}^{-1}$ ) that is not visible on the solution spectrum. The spectrum of the powder of  $H[V_2O_3(\text{pmida})_2] \cdot 4H_2O$  in a KBr pellet was found to be identical with the solution spectrum, showing that the solid and the solution contain the same species.

For all bands in the single-crystal spectrum the absorption was greater for  $\vec{E}$  parallel to  $b$  than for  $\vec{E}$  parallel to  $\vec{c}$ . However, the  $8300\text{-cm}^{-1}$  band was the only one to be completely polarized (see Figure 9), i.e. a complete extinction was observed for  $\vec{E}$  parallel to  $\vec{c}$ .

Since the unit cell contains two molecules, the possibility of a Davydov splitting<sup>14</sup> was considered. Thus, for instance, the two bands at  $8300$  and  $10\,500 \text{ cm}^{-1}$  in the single-crystal spectrum could result from the splitting of the unique band at  $10\,000 \text{ cm}^{-1}$  in the solution spectrum, due to interactions in the solid state. This hypothesis is however unlikely for the following reasons: (i) The theory of the Davydov splitting predicts that one of the bands would be polarized along  $b$  and the second one along  $\vec{a}$ . Consequently, this second band should not be observed on the crystal spectrum. (ii) In a recent paper, Saito et al.<sup>15</sup> have observed a weak band at  $8600 \text{ cm}^{-1}$  in a circular dichroism study of  $[V_2O_3(S\text{-peida})_2]^-$  in solution. Thus, the extra band at this energy seems to be characteristic of the mixed-valence ion and not to be caused by a crystal effect. The appearance of this band only on the single-crystal spectra is assigned to the fact that one selects one direction of propagation among the three possible directions. On the contrary, the solution or powder spectra can be considered as averages over all possible directions and polarizations. The  $8300\text{-cm}^{-1}$  band could thus exist in the solution spectrum but with a weak extinction coefficient, so that it would be buried in the edge of the intense  $10\,000\text{-cm}^{-1}$  band.

We have thus two candidates for the intervalence band: one at  $10\,500 \text{ cm}^{-1}$  and the other one at  $8300 \text{ cm}^{-1}$ , the latter having the predicted polarization for an intervalence band. The presence of two bands in the intervalence region could be explained by a vibronic structure. The energy differences between the two bands is too high to correspond to a metal-ligand stretching mode but curiously fall near the carboxylate stretching mode.<sup>16</sup>

An alternative assignment would be to consider the  $8300\text{-cm}^{-1}$  band as the unique intervalence band, while the two bands at  $10\,500$  and  $12\,800 \text{ cm}^{-1}$  would be the two components of the  $d-d$   $B_2 \rightarrow E$  transition split by the low site symmetry of vanadium. At the present stage a definitive answer is not possible; indeed, the use of more sophisticated techniques such as Raman resonance or magnetic circular dichroism is very difficult in this spectral range.

**Magnetic Behavior.** The magnetic susceptibilities of  $H[V_2O_3(\text{pmida})_2] \cdot 4H_2O$  and  $K_7[V_9O_{16}(\text{bdta})_4] \cdot 27H_2O$  were found independent of the magnetic field. The Curie law was followed from about  $45 \text{ K}$  to room temperature, with an effective magnetic moment of  $1.79 \mu_B$  for  $H[V_2O_3(\text{pmida})_2] \cdot 4H_2O$  and  $1.76 \text{ BM}$  for  $K_7[V_9O_{16}(\text{bdta})_4] \cdot 27H_2O$  (for the last compound, this value has been calculated for one  $V^{IV}-V^V$  pair). These values are in the normal range for systems containing a single unpaired electron with negligible influence of spin-orbit coupling. Below  $45 \text{ K}$ , the magnetic moment decreases markedly in both compounds, showing some antiferromagnetic coupling<sup>17</sup> (see Figure 10). The analogy

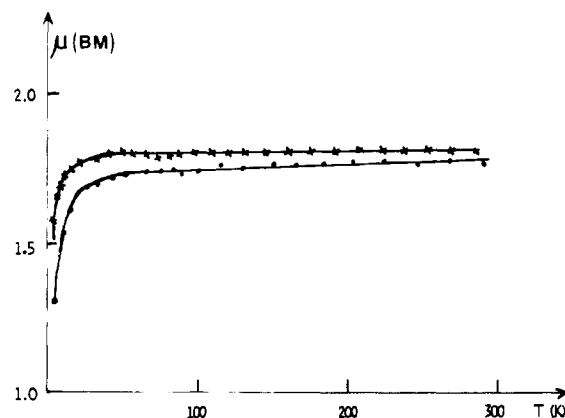
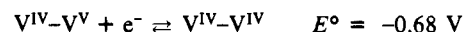
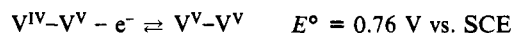


Figure 10. Effective magnetic moments, in  $\mu_B$ , as functions of  $T$ :  $\times$ ,  $H[V_2O_3(\text{pmida})_2] \cdot 4H_2O$ ;  $\cdot$ ,  $K_7[V_9O_{16}(\text{bdta})_4] \cdot 27H_2O$  ( $\mu_{\text{eff}}$  given for one  $V-O-V$  pair).

in the magnetic behavior of both compounds is at first sight surprising since in  $H[V_2O_3(\text{pmida})_2]$  the magnetic interactions are intermolecular whereas in  $K_7[V_9O_{16}(\text{bdta})_4]$  they are intramolecular. The present result suggests that the magnetic coupling between the four mixed-valence units of  $[V_9O_{16}(\text{bdta})_4]^{7-}$  is rather weak, of the same order of magnitude (perhaps  $\sim -1 \text{ cm}^{-1}$ ) as the intermolecular interactions in  $H[V_2O_3(\text{pmida})_2]$ .

The ESR of  $[V_2O_3(\text{pmida})_2]^-$  has been already described.<sup>2</sup> At room temperature a well-resolved 15-line spectrum is observed in weak donor solvents (nitromethane), showing a complete delocalization on the two vanadium atoms in the ESR time scale. In the case of  $[V_9O_{16}(\text{bdta})_4]^{7-}$ , a broad unresolved signal is observed at any temperature. This is ascribed to the existence of intramolecular interactions between the four mixed-valence units. Since the energy quantum of ESR is  $0.3 \text{ cm}^{-1}$ , even a weak magnetic coupling, which is barely visible in magnetic susceptibility, can lead to dramatic effects on the ESR spectra. In view of this broadening, no detailed analysis of the ESR spectra has been attempted.

**Electrochemical Behavior.** The  $[V_2O_3(\text{pmida})_2]^-$  ion exhibits two reversible waves in acetonitrile on a glassy-carbon electrode. They correspond to the anodic and cathodic processes:



From the above values, one can compute the comproportionation constant  $K_c = |V^{IV}-V^V|^2 / |V^{IV}-V^{IV}||V^V-V^V|$  which is found to be very large (about  $10^{24}$ ). This is usually taken as an indication of a strong delocalization in the mixed-valence complex.<sup>18</sup>

Attempts to prepare the homovalent complexes were unsuccessful due to fast decomposition. During the electrochemical oxidation at  $+0.9 \text{ V}$ , a transient UV band at  $370 \text{ nm}$  was observed, which could correspond to the vanadium(V) dimer  $[V_2O_3(\text{pmida})_2]^{19}$ . However, at the end of electrolysis, the spectrum of the solution revealed only the presence of the monomeric species  $[VO_2(\text{pmida})]^-$ . Upon reduction of  $[V_2O_3(\text{pmida})_2]^-$  on a mercury pool at  $-1.0 \text{ V}$ , a transient brown color was observed, that faded rapidly. After exhaustive electrolysis, the spectrum of the solution was characteristic of  $[V^{IV}O(\text{pmida})(OH)]^-$ . The breakdown of the dimeric structure upon oxidation or reduction is assigned to side reactions involving the residual water of the solvent.

In the case of  $[V_9O_{16}(\text{bdta})_4]^{7-}$  dissolved in  $\text{Me}_2\text{SO}$ , three anodic waves are observed with peak potentials  $+0.30$ ,  $+0.50$ , and  $+0.65 \text{ V}$ . They are roughly of the same height and thus should correspond to the consecutive oxidation of three of the four mixed-valence units. Controlled-potential electrolysis at the potential

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of the first wave, which is reversible, resulted in discoloration of the solution with disappearance of the intervalence bands, showing that the structure is not retained. In this case also, the electron transfer is followed by chemical reactions leading to a breakdown of the structure.

### Conclusion

The present study has shown the stability of the  $V_2O_3^{3+}$  mixed-valence core with the trans geometry. Electronic and ESR spectra are consistent with a large amount of ground-state delocalization, especially in the  $[V_2O_3(\text{pmida})_2]^-$  ion for which the two vanadium sites are chemically equivalent. With the bda ligand, a complicated structure with four mixed-valence units is observed. The interactions between these units are believed to

be responsible of the differences in behavior with respect to "normal" binuclear mixed-valence systems: the splitting of the intervalence band, the broadening of the ESR spectrum, and finally the presence of several waves in electrochemical oxidation.

**Acknowledgment.** We thank A. De Kozak for magnetic susceptibility measurements.

**Registry No.**  $H[V_2O_3(\text{pmida})_2] \cdot 4H_2O$ , 84049-50-3;  $K[V_9O_{16}(\text{bdta})_4] \cdot 27H_2O$ , 94904-37-7;  $VOSO_4$ , 27774-13-6;  $[V_2O_3(\text{pmida})_2]$ , 94904-38-8;  $[V_2O_3(\text{pmida})_2]^{2-}$ , 94904-39-9;  $[V_2O_3(\text{pmida})_2]^-$ , 84032-45-1.

**Supplementary Material Available:** Listings of anisotropic thermal parameters and observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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## Synthetic and NMR Studies on Fluorinated Alkoxides of Platinum(II): An Investigation of the Trans Influence of Alkoxides and the Nature of the Pt-O Bond, Using Phosphine and Thioether Complexes

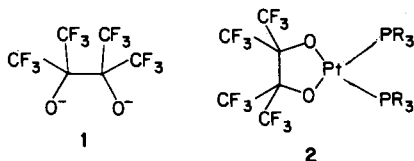
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Received July 24, 1984

A number of new cis platinum(II) complexes have been synthesized incorporating the chelating dianion of perfluoropinacol,  $[-OC(\text{CF}_3)_2C(\text{CF}_3)_2O]^{2-}$ , PFP, in conjunction with phosphine and thioether coligands. The general formula is  $(\text{PFP})\text{PtL}_2$ , where  $L = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2, \text{PPh}_3, \text{SMe}_2, \text{MeSEt}, \text{SEt}_2$ , or S-bonded  $\text{Me}_2\text{SO}$  or  $L_2 = \text{MeS}(\text{CH}_2)_2\text{SMe}$ . The last complex exists as two stereoisomers, with the S-methyl groups in syn or anti conformations. Through the use of NMR measurements, in particular the value of  $^1J(\text{Pt},\text{P})$  in the phosphine complexes, the static trans influence of the fluorinated alkoxy group has been estimated for the first time. It is similar to that of the halides and pseudohalides, the ordering being  $\text{Cl}^- < -C(\text{CF}_3)_2\text{O}^- \approx \text{Br}^- < \text{I}^-$ . By contrast, measurements of the barrier to inversion in the thioether complexes show  $-C(\text{CF}_3)_2\text{O}^-$  to have a dynamic trans effect less than that of  $\text{Cl}^-$ . These observations are interpreted on the basis that platinum(II) forms bonds to alkoxides with a higher degree of electrostatic character than those to chloride, but a lower degree of covalent character.

### Introduction

In our previous studies on fluorinated alkoxides of transition metals, we have demonstrated the use of the dianion of perfluoropinacol,  $\text{PFP}^{2-}$  (**1**), as a bidentate ligand forming a wide



range of complexes.<sup>1</sup> In particular, we were able to prepare a stable fluorinated alkoxide of platinum(II) with phosphines as coligands, **2**; the geometry of  $\text{PFP}^{2-}$  requires that these be cis.<sup>2</sup>

At the time when we reported the synthesis of **2**, few alkoxides of platinum were known, an effect attributed to the incompatibility between the hard alkoxy ligand and the soft  $\text{Pt}^{2+}$  ion.<sup>3</sup> Subsequent work has somewhat extended the range of this type of compound, but stable alkoxy platinum complexes are still described as "rare".<sup>4</sup> The stability and ready accessibility of the  $\text{PFP}^{2-}$  derivatives therefore make this ligand particularly suitable for the investigation of compounds containing the platinum-oxygen linkage. In this paper, we report an extension of the range of type **2** complexes using different phosphines as coligands, together with the synthesis of new  $\text{Pt}^{2+}$  complexes where a thioether or sulfoxide is used as a coligand with  $\text{PFP}^{2-}$ . By the use of NMR methods, including

the measurement of coupling constants and, in the case of the thioether complexes, the observation of inversion at sulfur, the trans influence and the trans effect of the fluorinated alkoxy ligand may then be estimated relative to other common ligands, enabling the Pt-OR bond to be contrasted with the Pt-halide bond.

### Experimental Section

**General Information.** Organophosphines and dimethyl thioether were commercial samples (Alfa, Aldrich). Diethyl thioether, ethyl methyl thioether, and 2,5-dithiahexane were prepared by standard methods.<sup>5</sup> Perfluoropinacol ( $\text{H}_2\text{PFP}$ ) was prepared as described previously.<sup>2</sup> Microanalysis was performed by Guelph Analytical Laboratories, Guelph, Ontario; all analytical data are in Table I. Infrared spectra were recorded on a Beckman 4250 spectrometer, mass spectra on a Varian Mat 311A instrument, and NMR spectra on a Varian XL-100 spectrometer at 100.1 MHz for  $^1\text{H}$ , 94.1 MHz for  $^{19}\text{F}$ , and 40.5 MHz for  $^{31}\text{P}$ . Variable-temperature NMR spectra were recorded over the range  $-120$  to  $+160$  °C; temperature settings of the spectrometer were checked with a Doric Trendicator 400 type T digital thermometer calibrated to  $\pm 0.5$  °C at the ice point.

**Preparation of Complexes.**  $\text{Pt}(\text{PFP})(\text{PMe}_3)_2$  (**3**). *cis*- $\text{PtCl}_2(\text{PMe}_3)_2$  was prepared by a modification of the literature method.<sup>6</sup> A mixture of  $\text{K}_2\text{PtCl}_4$  (1.9 g) and  $(\text{AgI} \cdot \text{PMe}_3)_4$  (2.5 g) was refluxed in water (50 mL) for 1 h; some decomposition was observed. After removal of water by rotary evaporation, extraction with boiling methanol followed by cooling to 0 °C gave *cis*- $\text{PtCl}_2(\text{PMe}_3)_2$  (1.4 g, 83%) as flaky white crystals, mp 345 °C dec.

*cis*- $\text{PtCl}_2(\text{PMe}_3)_2$  (0.670 g, 1.45 mmol) was suspended in  $\text{CH}_2\text{Cl}_2$  (80 mL) and  $\text{H}_2\text{PFP}$  (0.48 g, 1.45 mmol) added with stirring, followed by KOH (2.69 mmol) in ethanol. (In this and the following reactions, it was found convenient to measure out KOH volumetrically with a standardized solution, about 0.6 M, in ethanol.) After stirring for 2 h, the reaction

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