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Synthesis and Crystal Structure of a New V^{IV}/V^{V} Mixed Valence Microporous Compound $V_3P_2O_{13}(H_2O)_2$, $H_3N(CH_2)_3NH_3$

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Hitherto unknown vanado(IV,V)phosphate, ideally $V^{IV}V^{V}_2P_2O_{13}(H_2O)_2$, $H_3N(CH_2)_3NH_3$ was obtained by hydrothermal synthesis (453 K, 24 hr, autogeneous pressure) from a mixture of V_2O_5, P_2O_5, 1,3-diaminopropane, and H_2O in the ratio 1 : 1 : 1.3 : 1 : 80. It is orthorhombic (space group *Pnma* (No. 62)) with $a = 10.567(1)$ Å, $b = 16.970(2)$ Å, $c = 8.413(1)$ Å, $V = 1508.1(7)$ Å^3, $Z = 4$. The three-dimensional network is built up from the corner linkage of pentameric secondary building units based on two PO_4 tetrahedra, one VO_5 square pyramid, and two $VO_5(H_2O)$ octahedra sharing vertices. The framework delimits large 10-membered ovoid zigzag tunnels along [100] and smaller eight-membered ones along [010]. The true composition of the solid is discussed. The diprotonated amines are inserted in the 10-membered ovoid channels, whose free aperture is 7.30 × 4.00 Å.

INTRODUCTION

Since the discovery of a new series of microporous aluminophosphates $AlPO_4$-*n* (1), synthesized by using organic amines or quaternary ammoniums cations as templates, numerous phosphate-based molecular sieves have been reported (2–4). However, if these compounds could be doped by small amounts of 3*d* transition metal cations, attempts to synthesize pure 3*d* transition metal containing microporous compounds failed up to the discovery of mixed-valence (III,IV) vanadium compounds recently reported (5, 6).

We report here the preparation and characterization of a new microporous phase synthesized in the system V_2O_5, P_2O_5, H_2O with 1,3-diaminopropane (hereafter noted DAP) as template: $V_3P_2O_{13}(H_2O)_2$ $H_3N(CH_2)_3NH_3$.

EXPERIMENTAL

Synthesis and Thermal Analysis

The title compound was prepared by hydrothermal synthesis under autogeneous pressure. The reactants were vanadium pentoxide (V_2O_5, Merck 99%+), phosphoric acid (85% H_3PO_4, Prolabo RP Normapur), and 1,3-diaminopropane ($H_2N(CH_2)_3NH_2$, Aldrich 99%+). The starting mixture corresponding to the molar composition 1 V_2O_5, 1 P_2O_5, 1.3 DAP and 80 H_2O was placed without stirring in a Teflon-lined stainless-steel autoclave, heated at 453 K for 24 hr, and then cooled to room temperature for 24 hr. The pH of the synthesis was 4.5 at the end of the reaction. The dark brown crystalline product obtained was filtered off, washed with distilled water, and dried at room temperature. The data concerning the X-ray powder pattern of the title compound, calculated

TABLE 1
Calculated Interplanar *d*-Spacings and Calculated Intensities for $V_3P_2O_{13}(H_2O)_2$, $H_3N(CH_2)_3NH_3$

h	*k*	*l*	d_{calc}	I_{calc}
0	2	0	8.49	50
0	1	1	7.54	100
1	0	1	6.58	41
1	1	1	6.14	45
2	0	0	5.28	12
1	2	1	5.20	11
0	3	1	4.694	12
2	0	1	4.477	7
2	1	1	4.327	33
0	0	2	4.207	10
2	2	1	3.958	41
1	1	2	3.809	5
1	4	1	3.566	5
1	2	2	3.550	6
3	0	1	3.249	15
2	1	2	3.231	38
0	5	1	3.148	30
0	4	2	2.9871	11
2	3	2	2.8445	47
0	6	0	2.8283	20
3	3	1	2.8174	11
4	0	0	2.6418	5
4	1	0	2.6103	6
1	6	1	2.5986	6
2	8	1	1.9167	12

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TABLE 2
Conditions of the X-Ray Data Collection of $V_3P_2O_{13}(H_2O)_2$, $H_3N(CH_2)_3NH_3$

Determination of cell parameters	30 reflections at $2\theta \approx 30°$
Space group	*Pnma* (No. 62)
Cell dimensions	a = 10.567(1) Å
	b = 16.970(2) Å
	c = 8.413(1) Å
Volume/Z	1508.1(7) Å^3/Z = 4
Wavelength/monochromator	0.71073 Å (Mo$K\alpha$)/graphite
Temperature	293 K
Scan mode	ω–2θ
Step scan	$37 \leq N \leq 43$, every 0.035° and 4 sec
Aperture	3 × 3 mm^2
Crystal dimensions	0.057 × 0.144 × 0.228 mm^3
Natural faces	{010}, {001}, {100}
Absorption corrections	Gaussian method
Transmission factors	T_{min} = 0.734, T_{max} = 0.883
Absorption coefficient	μ = 20.5 cm^{-1}
Angular range of data collection	$2\theta \leq 70°$
Range of measured h, k, l	$0 \leq h \leq 17$, $0 \leq k \leq 27$, $0 \leq l \leq 14$
Standard reflections (3)	3 0 4, −3 0 4, 2 8 1
Measured every	60 mn
Measured reflections	3751
Independent reflections ($\lvert F\rvert > 6\sigma(\lvert F\rvert)$)	2024
Weight	$w = 0.906/(\sigma^2(F) + 0.00227F^2)$
Secondary extinction	$X = 12.5 \times 10^{-7}$
Number of refined parameters	145
Final Fourier residuals	−0.45 to 0.53 $e \cdot$ Å^{-3}
R_w/R	0.029/0.026

TABLE 3a
Atomic Coordinates and Isotropic Displacement Factors in $V_3P_2O_{13}(H_2O)_2$, $H_3N(CH_2)_3NH_3$

	x	y	z	B_{eq} (Å^2)
V(1)	0.1406(1)	0.5643(1)	0.7798(1)	0.84(1)
V(2)	0.2209(1)	¼	0.1739(1)	0.92(1)
P	0.1293(1)	0.4132(1)	0.0291(1)	0.72(1)
O(1)	0.9841(1)	0.4147(1)	0.0508(2)	1.07(4)
O(2)	0.1641(1)	0.4546(1)	0.8717(2)	1.08(5)
O(3)	0.1940(1)	0.4543(1)	0.1704(2)	1.11(5)
O(4)	0.1740(2)	0.3270(1)	0.0108(2)	1.24(5)
O(5)	0.3408(2)	0.1739(1)	0.2414(2)	1.70(6)
O(6)	0.1099(3)	¼	0.3039(3)	2.3(1)
O(7)	0.4520(2)	0.0408(1)	0.1354(2)	1.56(5)
Ow	0.2171(2)	0.0949(1)	0.4862(2)	1.91(6)
N	0.4045(2)	0.1038(1)	0.7721(2)	1.44(6)
C(1)	0.9015(4)	¼	0.7405(4)	1.5(1)
C(2)	0.9628(2)	0.1775(1)	0.6684(3)	1.48(7)
H(1)	0.812(4)	¼	0.716(4)	0.6(7)
H(2)	0.411(5)	¼	0.663(6)	2.3(7)
H(3)	0.455(3)	0.177(2)	0.952(4)	1.3(6)
H(4)	0.548(4)	0.182(2)	0.813(4)	2.7(8)
H(5)	0.410(3)	0.101(2)	0.673(4)	1.5(6)
H(6)	0.447(4)	0.063(2)	0.818(4)	1.9(7)
H(7)	0.317(4)	0.093(3)	0.805(5)	3.5(9)

Note. B_{eq} is defined as $B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$.

TABLE 3b
Anisotropic Thermal Parameters in $V_3P_2O_{13}(H_2O)_2$, $H_3N(CH_2)_3NH_3$ ($U_{ij} \times 10^4$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V(1)	94(1)	135(1)	90(1)	6(1)	6(1)	−6(1)
V(2)	118(2)	116(2)	114(2)	0	−4(2)	0
P	92(2)	85(2)	96(2)	0(2)	−3(4)	5(2)
O(1)	99(5)	186(6)	121(5)	−16(5)	−17(5)	11(5)
O(2)	145(6)	131(6)	133(6)	30(5)	−39(5)	−17(5)
O(3)	144(6)	118(6)	160(6)	−49(5)	54(5)	−23(5)
O(4)	223(7)	95(6)	152(6)	−9(5)	29(5)	−19(5)
O(5)	239(8)	141(6)	268(8)	19(6)	−66(6)	44(6)
O(6)	256(13)	395(15)	222(12)	0	113(10)	0
O(7)	193(7)	249(8)	149(6)	0(6)	47(6)	42(6)
Ow	201(8)	322(9)	201(7)	9(7)	11(6)	43(7)
N	191(8)	159(7)	197(8)	−17(7)	43(7)	−7(7)
C(1)	256(14)	145(12)	184(13)	0	24(12)	0
C(2)	209(9)	140(8)	213(9)	14(8)	21(8)	−8(7)

from the results of the structure determination, are given in Table 1.

TGA measurements were performed on a Dupont thermoanalyzer under air flow with a heating rate of 20°C/min between 300 and 900 K.

Structure Determination

A prism-shaped single crystal was selected for structural analysis by X-ray diffraction. Its quality was tested by optical observation and Laue photographs. Intensity data collection was performed with a Siemens AED-2 four-circle diffractometer with conditions of data collection summarized in Table 2 and led to a description of the structure with space group *Pnma* (No. 62). The scattering factors and anomalous dispersion corrections were taken from the "International Tables for X-Ray Crystallography" (7). The structure was solved by using the direct method analysis of the SHELXS-86 program (8). Vanadium and phosphorus atoms were first located. The anions of the matrix were then found by difference Fourier maps.

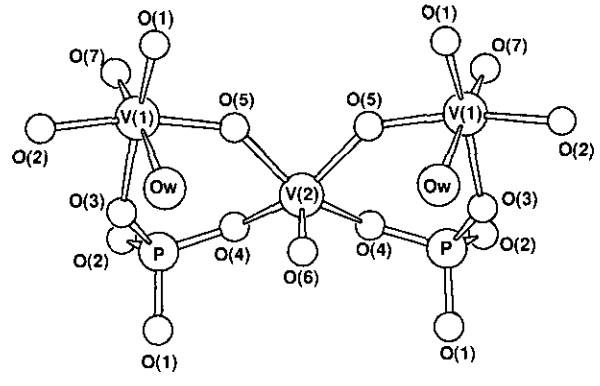

FIG. 1. View of the pentameric building unit with two $VO_5(H_2O)$ octahedra, one VO_5 square pyramid, and two PO_4 tetrahedra.

TABLE 4
Selected Interatomic Distances (Å) and Angles (°) in $V_3P_2O_{13}(H_2O)_2$, $H_3N(CH_2)_3NH_3$

PO_4 tetrahedron

P	O(3)	O(2)	O(4)	O(1)
O(3)	**1.539(2)**	2.533(2)	2.552(2)	2.527(2)
O(2)	110.5(1)	**1.544(2)**	2.464(2)	2.519(2)
O(4)	111.7(1)	105.8(1)	**1.545(2)**	2.521(2)
O(1)	110.0(1)	109.3(1)	109.3(1)	**1.545(1)**

⟨P–O⟩ = 1.543(2) Å

$V(2)O_5$ square pyramid

V(2)	O(6)	O(5)	O(5)	O(4)	O(4)
O(6)	**1.604(3)**	2.810(4)	2.810(4)	2.872(3)	2.872(3)
O(5)	106.5(1)	**1.896(2)**	2.583(3)	2.621(3)	3.691(3)
O(5)	106.5(1)	85.9(1)	**1.896(2)**	3.691(3)	2.621(3)
O(4)	107.0(1)	146.4(1)	85.7(1)	**1.959(2)**	2.613(3)
O(4)	107.0(1)	85.7(1)	146.4(1)	83.7(1)	1.959(2)

⟨V(2)–O⟩ = 1.863(2) Å

$V(1)O_5(H_2O)$ octahedron

V(1)	O(7)	O(5)	O(1)	O(3)	O(2)	Ow
O(7)	**1.610(2)**	2.698(3)	2.767(2)	2.743(2)	2.756(2)	3.120(3)
O(5)	100.2(1)	**1.898(2)**	2.759(2)	2.738(2)	3.880(2)	2.783(3)
O(1)	100.6(1)	90.9(1)	**1.973(2)**	3.457(2)	2.792(2)	2.843(2)
O(3)	98.3(1)	89.2(1)	160.8(1)	**2.000(2)**	2.740(2)	2.796(2)
O(2)	97.7(1)	161.9(1)	88.4(1)	85.6(1)	**2.031(2)**	2.859(2)
Ow	177.4(1)	81.0(1)	81.6(1)	79.4(1)	81.0(1)	**2.355(2)**

⟨V(1)–O⟩ 1.978(2) Å

1,3-diaminopropane (DAP)

N–C(2)	1.481(3)	C(2)–C(1)–C(2)	108.4(3)
C(1)–C(2)	1.517(3)	N–C(2)–C(1)	111.8(2)
C(1)–H(1)	0.97(4)		
C(1)–H(2)	0.82(5)	N–H(5)	0.83(3)
C(2)–H(3)	1.02(3)	N–H(6)	0.92(3)
C(2)–H(4)	0.92(4)	N–H(7)	0.98(5)

Distances template–framework

H(1)–O(4)	2.73(3)	H(1)–O(8)	3.77(3)
H(2)–O(4)	3.40(5)	H(2)–O(1)	3.41(3)
H(3)–O(5)	2.72(3)	H(3)–O(7)	2.78(3)
H(4)–O(8)	2.87(4)	H(4)–O(4)	3.03(4)
H(5)–O(1)	**2.06(3)**	H(5)–O(8)	2.58(3)
H(5)–O(3)	2.72(3)	H(5)–O(2)	2.87(3)
H(6)–O(7)	**2.09(3)**	H(6)–O(3)	2.67(4)
H(6)–O(7)	2.70(3)	H(6)–O(2)	2.81(4)
H(7)–O(2)	**1.89(5)**	H(7)–O(3)	2.62(4)
H(7)–O(4)	2.66(4)	H(7)–O(8)	2.89(4)

TABLE 5
Valence Bond Calculations in $V_3P_2O_{13}(H_2O)_2$, $H_3N(CH_2)_3NH_3$

	V(1)	V(1)′	V(2)	V(2)′	P	Σ
O(1)	0.632	—	—	—	1.215	**1.847**
	—	0.600	—	—	1.215	**1.815**
O(2)	0.540	—	—	—	1.218	**1.758**
	—	0.513	—	—	1.218	**1.731**
O(3)	0.587	—	—	—	1.235	**1.822**
	—	0.558	—	—	1.235	**1.793**
O(4)	—	—	0.656	—	1.215	**1.871**
			0.656			
	—	—	—	0.623	1.215	**1.838**
				0.623		
O(5)	0.774	—	0.778	—	—	1.552
	—		0.778	—	—	
	—	0.735	—	0.739	—	1.474
	—	—	—	0.739		
O(6)	—	—	1.712	—	—	1.712
	—	—	—	1.627	—	1.627
O(7)	1.685	—	—	—	—	1.685
	—	1.600	—	—	—	1.600
Ow	0.225	—	—	—	—	0.225
	—	0.214	—	—	—	0.214
Σ	**4.443**	**4.220**	**4.580**	**4.351**	**4.883**	

Note. The results refer to the equation $s = \exp[(R_0 - d)/0.37]$ (10) with R_0 = 1.803, 1.784, 1.617, and 0.882 for V^{5+}, V^{4+} P, and H, respectively. For each vanadium the first column refers to the calculation as V^{5+} and the second as V^{4+}.

Refinement was performed by full-matrix least-squares analysis of SHELX-76 (9). Valence bond calculations (10) were performed to appreciate the oxidation number of V and discriminate between O^{2-}, OH^-, or H_2O in the structure. At this stage of the refinement, all the atoms of the amino group became visible. The refinement with anisotropic thermal parameters for V, P, O and isotropic ones for C, N and H give R_w = 0.029 and R = 0.026. The hydrogens of the water molecule were not located.

The atomic coordinates with isotropic thermal parameters and selected bond distances and angles are listed in Tables 3 and 4, respectively. Table 5 provides the valence bond analysis of the compound. The list of U_{ij} and of structure factors can be obtained upon request to the authors.

DESCRIPTION OF THE STRUCTURE

In the title compound, the vanadium atoms, located on two different crystallographic sites in a 2/1 ratio, exhibit two different coordinations. V(1) atoms are surrounded by five oxygens and one water molecule, as deduced from valence bond calculations in Table 5. The water molecule (Ow), weakly bonded with V(1) (2.355 Å), is opposite to the classical short-bond V=O(7) (1.610 Å). V(2) adopts a fivefold square pyramidal coordination, also with a short

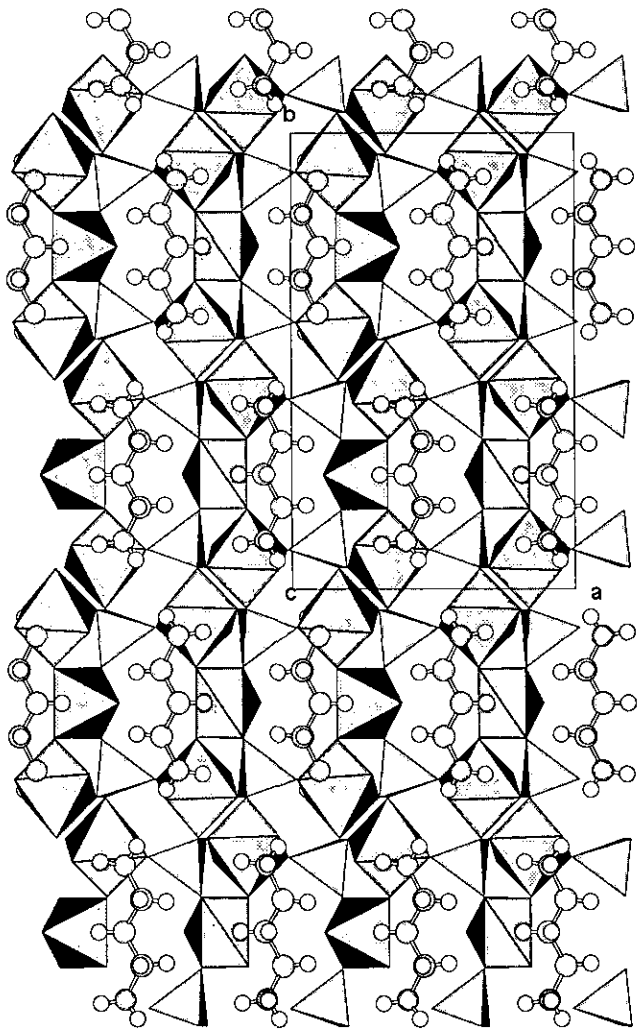

FIG. 2. [001] projection of the structure.

V=O(6) bond (1.604 Å). Ow, O(6), and O(7) are terminal, and the bonds formed with the two former points in the same direction. The two O(5) atoms of the basal plane of the square pyramid are shared between V(2) and the two V(1), thus forming isolated trimers of vanadium. The two other oxygen atoms of the basal plane of V(2) are shared with the almost regular tetrahedra around P (1.539–1.545 Å), creating the pentameric secondary building unit of the structure (Fig. 1).

From the crystal formula of the title compound, it may be thought that it contains both V^{5+} and V^{4+} in a 2/1 ratio. A question arises from this fact: is there a cationic ordering between these two species, i.e., V^{5+} occupying V(1) site and V^{4+} the V(2) site? The criterion of distances is not useful in this case since the abundant literature on vanadium(IV) and (V) oxides shows that the corresponding distances are very close to each other. On the contrary, valence bond calculations show very clearly that V^{5+} and V^{4+} coexist on each of the two sites (Table 5). Moreover, preliminary EPR measurements show that the electron is delocalized on the two sites and therefore rule out any cationic ordering. From this, it may be anticipated that the valence bond sums on both sites are equal. Finally, the potentiometric analysis of vanadium species shows that the ratio between V^{5+} and V^{4+} is closer to 1/1 than 2/1. This analysis could also explain the anomaly observed on the weak-bond valence of O(5) ($\approx$1.5 instead of 2) which could be a consequence of the existence of more V^{4+} than expected, inducing correlatively a distribution between O^{2-} and OH^- species on this O(5) site. The corresponding formula would be $V^{5+}_{1+x}V^{4+}_{2-x}P_2O_{12}[(OH)_{1-x}O_x](H_2O)_2$, DAP ($x \approx 0.5$).

Whatever the nature of the vanadium species in the pentameric secondary building units (SBU), their linkage via corners ensures a three-dimensional network. Along [100], these units share O(1) atoms between the two PO_4 of one unit and the $VO_5(H_2O)$ octahedra of the other one in order to form corrugated chains alternatively at $z \approx \frac{1}{4}$ and $\frac{3}{4}$. The terminal bonds point alternatively above and below the chain. With such a connection, six-membered windows appear along [001] (Fig. 2). Two consecutive chains at $z \approx \frac{1}{4}$ and $\frac{3}{4}$ are connected via O(2) atoms and then create the framework. Such an arrangement creates large 10-membered ovoid zigzag tunnels along [100] and smaller 8-membered ones along [010] (Figs. 3a, 3b, and 4). The terminal V=O bonds point toward the center of the latter tunnels. The diprotonated amines are located at the intersection of the 10- and 6-membered channels, via strong hydrogen bonds (Fig. 5).

Finally, the TGA curve of the title compound (Fig. 6) shows that the water molecules first evolve of the structure between 190 and 320°C (weight loss, calc, 6.72%, exp, 6.87%). At this stage of the dehydration, all the vanadium atoms adopt a fivefold coordination and point directly at the surface of the tunnels. The amine leaves the structure after 320°C, probably in two steps. The evolution is complete at 530°C. At this temperature, and owing the air flow used in the experiment, some weight increase is observed and corresponds to the oxidation of V^{4+}. The resulting compound is a mixture of β-$VOPO_4$ and V_2O_5.

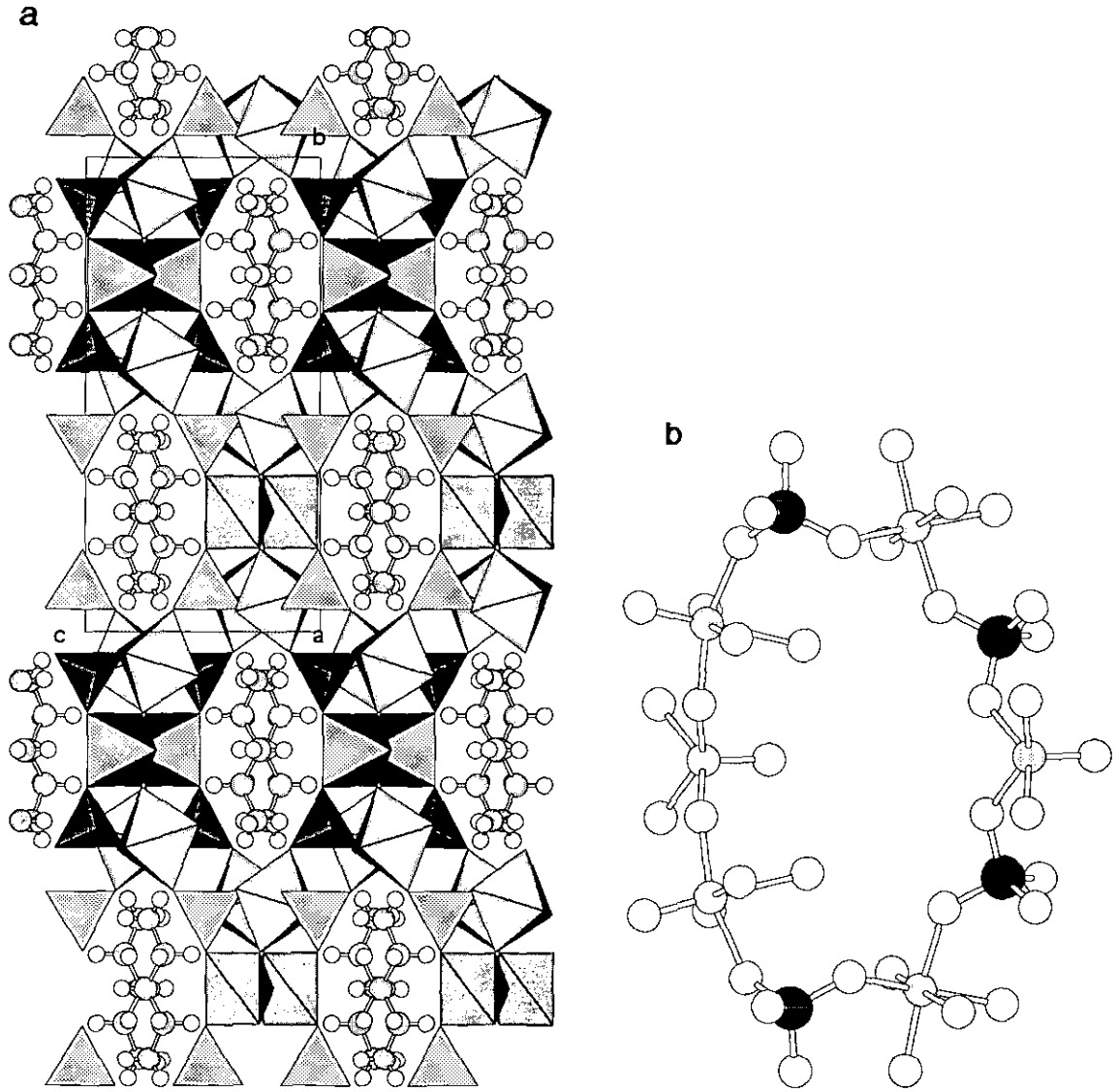

FIG. 3. (a) [100] projection showing the 10-membered ring channels and (b) detailed view of this ring: V and P are slightly and heavily shaded respectively.

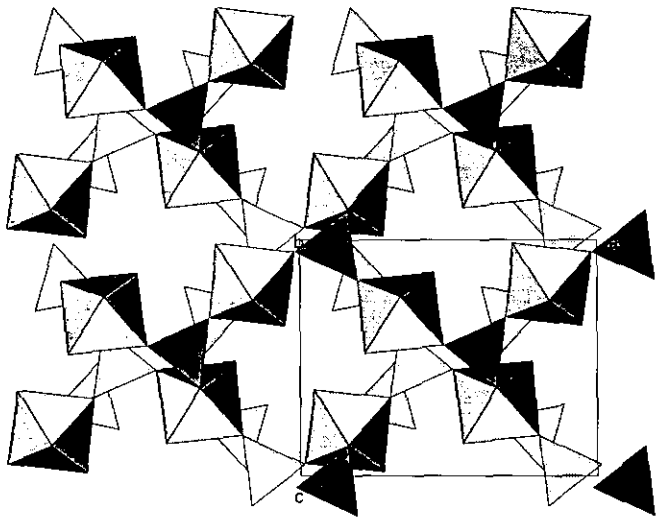

FIG. 4. [010] projection of the structure.

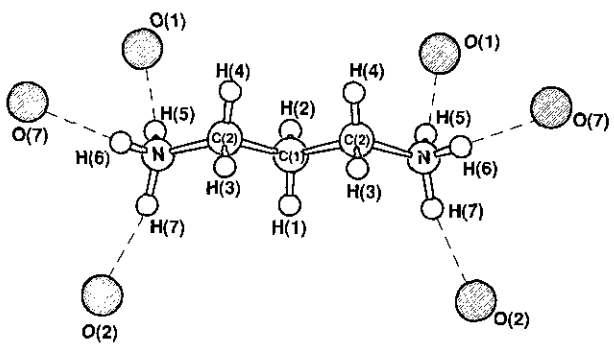

FIG. 5. Conformation of the amine.

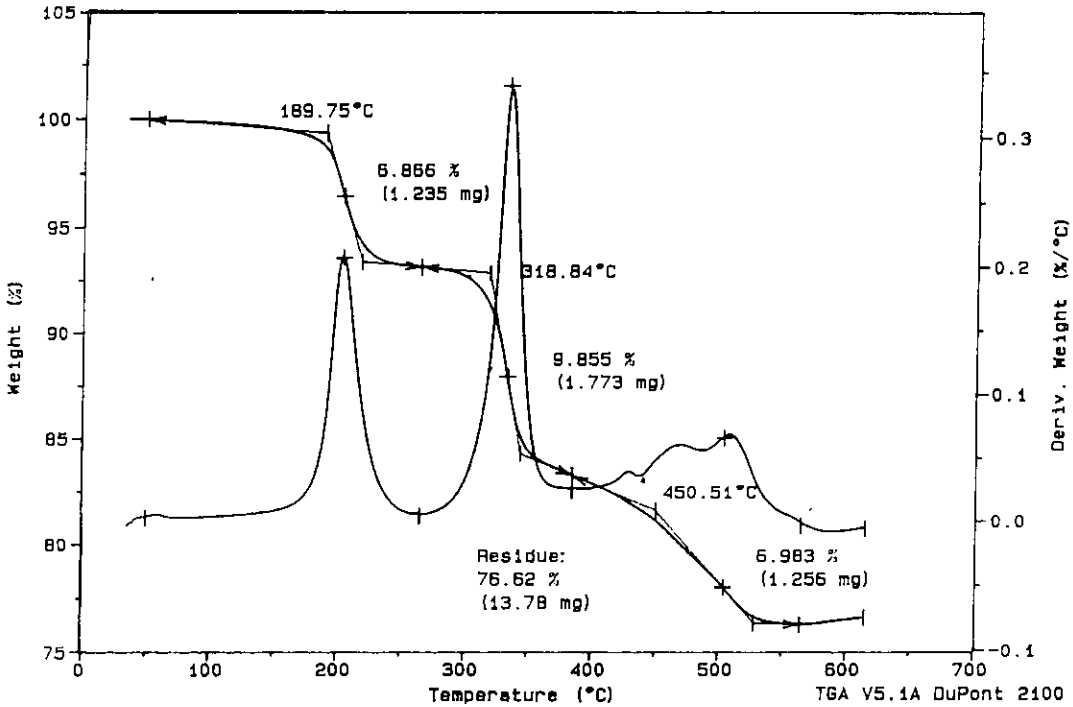

FIG. 6. TGA curve of the compound and its derivative.

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