

Hydrothermal Synthesis and Structural Characterization of Two Layered Diamine Pentamolybdates: $(C_2H_{10}N_2)[Mo_5O_{16}]$ and $(C_4H_{12}N_2)[Mo_5O_{16}]$

Nathalie Guillou and Gérard Férey¹

Institut Lavoisier, UMR CNRS C0173, Université de Versailles Saint-Quentin-en-Yvelines, 45 Avenue des États-Unis, 78035 Versailles cedex, France

Received October 12, 1998; in revised form February 16, 1999; accepted February 26, 1999

DEDICATED TO PROFESSOR JEAN ROUXEL

The two diamine pentamolybdates, $(C_2H_{10}N_2)[Mo_5O_{16}]$ and $(C_4H_{12}N_2)[Mo_5O_{16}]$, have been hydrothermally synthesized (180°C, 24 h, autogenous pressure). The ethylenediamine pentamolybdate was powdered and its structure was solved *ab initio* from conventional X-ray powder diffraction. Single crystals of piperazine pentamolybdate could be isolated. Despite a similar topology, the structures crystallize in different unit cells: ethylenediamine pentamolybdate crystallizes in the monoclinic system with $a = 15.801(1)$ Å, $b = 5.5878(4)$ Å, $c = 9.3743(7)$ Å, and $\beta = 116.321(6)^\circ$, space group is $P2/n$ with $Z = 2$; piperazine compound is also monoclinic, space group $C2/c$ with $a = 23.3997(3)$ Å, $b = 5.6222(1)$ Å, $c = 14.4131(2)$ Å, $\beta = 115.960(1)^\circ$ and $Z = 4$. Both structures are built from $[Mo_5O_{16}]^{2-}$ layers composed of stripes of ReO_3 -type, as already found in $Cs_2Mo_5O_{16}$. Diamine cations are located between the layers and ensure the connectivity of the structure via hydrogen bonds. The relationship between the two structures is discussed. © 1999

Academic Press

INTRODUCTION

Hydrothermal synthesis has been widely used for obtaining templated metal phosphates. In this way, numerous reduced molybdenum phosphates have been reported by Haushalter and Mundi (1). Molybdates and molybdenum oxides are of interest especially in the fields of intercalation chemistry and catalysis. A large number of di-, tri-, and tetramolybdates using secondary and tertiary amines was also extensively studied (2–4) due to their photochromic properties. More recently, some organic–inorganic compounds constructed from molybdenum (VI) oxide and containing diamine have been reported in the literature (5–13). The influence of the templating agent as well as the acidity have been demonstrated by the wide range of the struc-

tures. With ethylenediamine, three structures are known: $(C_2H_{10}N_2)[MoO_4]$ (5), which consists of isolated MoO_4 tetrahedra and ethylenediamine cations connected together via hydrogen bonds, the trimolybdate (VI), $(C_2H_{10}N_2)[Mo_3O_{10}]$ (6, 13), consisting of infinite $[Mo_3O_{10}]^{2-}$ chains made up from distorted MoO_6 octahedra and the mixed Mo(V)–Mo(VI) molybdate, $(C_2H_{10}N_2)[Mo_4O_{12}]$ (14), which exhibits $[Mo_4O_{12}]^{2-}$ layers made up of an organization of isolated tetrameric Mo(V) clusters of octahedra linked by edges to tetrameric Mo(VI) ones. With piperazine, only the octamolybdate $(C_4H_{12}N_2)_3[Mo_8O_{27}]$ (8) has been synthesized. It consists of $[Mo_8O_{27}]^{6-}$ chains made up of $[Mo_8O_{28}]^{8-}$ clusters of Mo(VI) octahedra. During the investigation of the MoO_3 – $ZnCl_2$ –ethylenediamine– H_2O system, a pulverulent phase was also obtained mixed to the fibrous crystals of the trimolybdate (6, 13) and could be isolated. It was identified as the pentamolybdate $(C_2H_{10}N_2)[Mo_5O_{16}]$. The study of the analogous system with piperazine led also to the pentamolybdate $(C_4H_{12}N_2)[Mo_5O_{16}]$. Although it crystallizes in another unit cell, it exhibits the skeleton of ethylenediamine pentamolybdate. Here we report the crystal structures of ethylenediamine and piperazine compounds determined from *ab initio* X-ray powder diffraction and from single crystal analysis, respectively.

EXPERIMENTAL

Synthesis

$(C_2H_{10}N_2)[Mo_5O_{16}]$ was synthesized hydrothermally (180°C, 24 h, autogenous pressure) from MoO_3 (Aldrich 99.5%+), $ZnCl_2$ (Aldrich 98%+), ethylenediamine (Aldrich, 99%+), and H_2O . In the molar ratio 1:1:0.4:40, a white powder of $(C_2H_{10}N_2)[Mo_5O_{16}]$ was obtained on a 70% yield mixed with fibrous colorless crystals of $(C_2H_{10}N_2)[Mo_3O_{10}]$, whose structure has been solved previously from X-ray single crystal data (6, 13). The pH

¹To whom correspondence should be addressed.

decreased from 5 to 3 during the reaction. The mixture was then washed with demineralized water and dried in air at room temperature. The density of the powder was measured with a pycnometer Micromeritics AccuPyc 1330. The experimental value of 3.605(8) is in agreement with the chemical formula (C₂H₁₀N₂)[Mo₅O₁₆] (theoretical value: 3.571). The TGA measurements under oxygen flow show a total weight loss of 9.59% (% th = 9.79) and the final product is the orthorhombic molybdenum oxide MoO₃, which confirms the chemical formula previously mentioned.

(C₄H₁₂N₂)[Mo₅O₁₆] was quantitatively prepared in the same way with piperazine as template and was obtained as a pure phase with an initial molar ratio 1:1:0.2:80. The pH decreased from 6 to 2 during the reaction. The experimental density of 3.242(5) is in agreement with the chemical formula (C₄H₁₂N₂)[Mo₅O₁₆] (theoretical value: 3.210).

Structural Investigations

(C₂H₁₀N₂)[Mo₅O₁₆]. Precise powder diffraction data were collected with a Siemens D5000 powder diffractometer using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). To minimize preferred orientation effects, the powder was first ground in ethanol with a McCrone micronizing mill and was then side loaded. The powder diffraction pattern was scanned over the angular range 4–120° (2θ), with a step size of 0.02° (2θ). The counting times were 26 s.step⁻¹ to 59.60° (2θ) and 52 s.step⁻¹ from 59.62° (2θ) to the end of the scan, in order to improve the counting statistic of the high angle region. The full pattern was then scaled to the lower counting time. The contribution of CuK α_2 radiation was removed from the pattern by means of the software package DIFFRACT-AT and an accurate determination of the peak positions and relative intensities for CuK α_1 radiation was carried out. The pattern was indexed with the program DICVOL91 (15). A monoclinic solution was found with satisfactory figures of merit [$M_{20} = 68$, $F_{20} = 111$ (0.0035, 51)]. From the complete data set, reviewed by means of the program NBS*AIDS83 (16), the refined cell parameters given in Table 2 were obtained [$M_{20} = 93$ and $F_{30} = 119$ (0.0041, 62)]. The powder diffraction data are reported in Table 1 for CuK α_1 radiation ($\lambda = 1.5406 \text{ \AA}$). Systematic absences ($h0l$, $h + l = 2n + 1$) were consistent with the two space groups $P2/n$ and Pn .

Integrated intensities in the angular range 4–80° (2θ) were extracted by means of the iterative fitting procedure (17) available in the Rietveld refinement program FULLPROF (18). First calculations were performed with the SIRPOW92 program (19). The centrosymmetric space group $P2/n$ was chosen to solve the structure. Direct methods and Fourier calculations provided the location of all nonhydrogen atoms, which were refined by the Rietveld method. A pseudo-Voigt function was selected to describe individual line profiles. In order to describe the angular dependence of

TABLE 1
X-Ray Powder Diffraction Pattern of (C₂H₁₀N₂)[Mo₅O₁₆]

h	k	l	$2\theta_{\text{obs}}$ (°)	$2\theta_{\text{calc}}$ (°)	d_{obs} (Å)	I_{obs}
$\bar{1}$	0	1	9.571	9.558	9.23	100
2	0	0	12.489	12.489	7.08	1L ^a
1	0	1	14.435	14.435	6.13	1L
$\bar{3}$	0	1	16.970	16.966	5.22	1L
$\bar{1}$	1	0	17.045	17.045	5.20	1
0	1	1	19.056	19.059	4.653	1L
$\bar{2}$	0	2	19.187	19.183	4.622	1
2	1	0	20.221	20.227	4.388	1
0	0	2	21.135	21.130	4.200	1L
1	1	1	21.500	21.499	4.130	3
$\bar{4}$	0	2	24.660	24.653	3.607	9
3	1	0		24.667		
$\bar{1}$	1	2	24.970	24.970		
$\bar{2}$	1	2	24.970	24.978	3.563	8
4	0	0	25.134	25.130	3.540	1L
2	1	1	25.331	25.333	3.513	1
0	1	2	26.533	26.523	3.357	4
$\bar{3}$	1	2	26.533	26.546		
$\bar{4}$	1	1	27.638	27.637	3.225	4
$\bar{3}$	0	3	28.949	28.947	3.082	9
2	0	2	29.112	29.105	3.065	1
1	1	2	29.407	29.407	3.035	1
4	1	0	29.853	29.849	2.990	1L
0	2	0	32.001	32.008	2.794	2
1	2	0	32.640	32.642	2.741	1L
$\bar{5}$	1	1	32.705	32.701	2.736	1L
$\bar{2}$	1	3	32.845	32.848	2.725	5
$\bar{5}$	0	3	33.537	33.543	2.670	10
$\bar{2}$	2	1	34.397	34.393	2.605	2
1	2	1	35.289	35.274	2.541	1
1	0	3		35.286		
0	1	3	35.832	35.834	2.504	1L
$\bar{3}$	2	1	36.451	36.443	2.4629	1L
$\bar{6}$	1	2	38.002	38.010	2.3659	1L
6	0	0	38.088	38.092	2.3608	1L
0	2	2	38.683	38.672	2.3258	1L
$\bar{3}$	2	2		38.689		
4	0	2	39.877	39.882	2.2589	1L
$\bar{6}$	1	3	40.803	40.807	2.2097	1
$\bar{4}$	2	2	40.803	40.815		
$\bar{7}$	0	1	40.954	40.956	2.2019	1L
4	2	0	41.121	41.122	2.1934	1L
5	1	1		41.143		
3	2	1	41.291	41.289	2.1847	1L
$\bar{3}$	1	4	41.758	41.761	2.1614	1
2	1	4	42.275	42.257	2.1361	1
$\bar{4}$	1	4		42.278		
$\bar{6}$	0	4	43.074	43.087	2.0983	6

^a1L, lower than 1.

the peak full-width at half maximum, the usual quadratic function in $\tan \theta$ was used. Unit cell and instrument parameters were allowed to vary from time to time during the refinement process. The final Rietveld refinement using 1531 F_{obs} was carried out in the angular range 7–100° (2θ). It

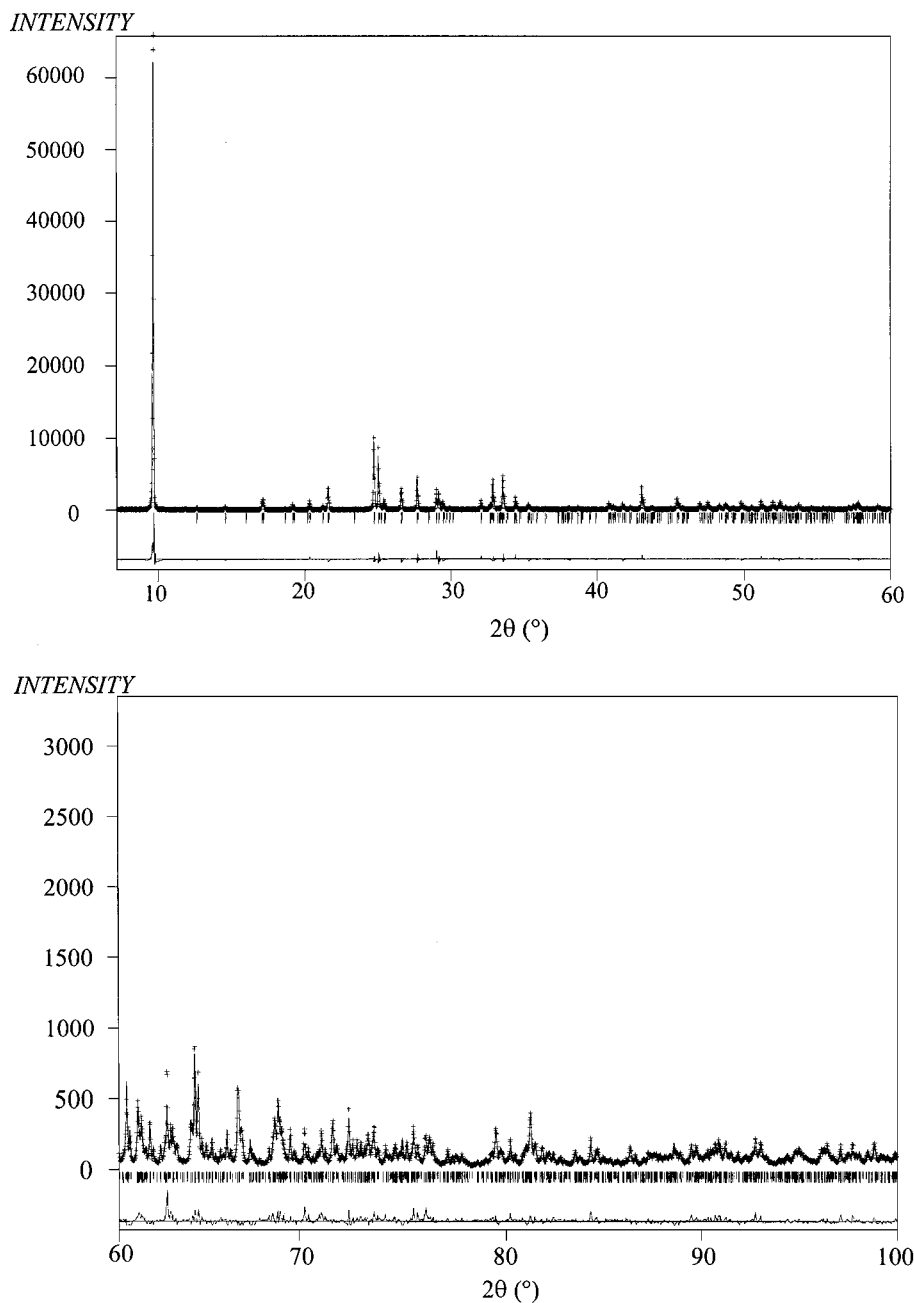


FIG. 1. The final Rietveld plot for $(C_2H_{10}N_2)[Mo_5O_{16}]$. The observed data are shown by the crosses; the calculated pattern is displayed by the solid line; the lower curve is a plot of the difference, observed minus calculated. All intensities were multiplied by 20 in the second part of the pattern.

involved the following parameters: one scale factor, 37 atomic coordinates, one overall isotropic temperature factor, one zero point and four cell parameters, three half-width parameters, two asymmetry factors, two parameters to define the θ -dependent pseudo-Voigt profile shape function, five coefficients to describe the functional dependence of the background, and one preferred orientation factor. Figure 1 shows the final fit obtained between calculated and observed patterns. It corresponds to satisfactory crystal

structure model indicators ($R_F = 0.061$ and $R_B = 0.088$) and profile factors ($R_p = 0.126$ and $R_{wp} = 0.175$). Details of the refinement are summarized in Table 2. Final atomic parameters are given in Table 3. Selected bond distances and angles are listed in Table 4.

$(C_4H_{12}N_2)[Mo_5O_{16}]$. Diffraction data collection was carried out with a Siemens SMART system using a three-circle diffractometer equipped with a CCD bidimensional

TABLE 2
Crystallographic Data for (C₂H₁₀N₂)[Mo₅O₁₆]

Empirical formula	C ₂ H ₁₀ Mo ₅ N ₂ O ₁₆
Chemical formula weight (g mol ⁻¹)	797.80
Calculated density (g.cm ⁻³)	3.571
Experimental density (g.cm ⁻³)	3.608(5)
Crystal system	Monoclinic
Space group	<i>P</i> 2/ <i>n</i>
<i>a</i> (Å)	15.801(1)
<i>b</i> (Å)	5.5878(4)
<i>c</i> (Å)	9.3743(7)
β (°)	116.321(6)
<i>V</i> (Å ³)	741.90(7)
Figures of merit	<i>M</i> ₂₀ = 93; <i>F</i> ₃₀ = 119(0.0041, 62)
<i>Z</i>	2
Radiation (Å)	1.5418
2 θ range (°)	7–100
No. reflections	1531
No. atoms	13
No. structural parameters	39
<i>R</i> _p	0.126
<i>R</i> _{wp}	0.175
<i>R</i> _B	0.088
<i>R</i> _F	0.061

detector. A total of 6246 intensities were collected at room temperature. The data were corrected for Lorentz and polarization effects and absorption corrections were applied by means of the SADABS program (20). The scattering factors and anomalous dispersion corrections were taken from the “International Tables for X-ray Crystallography” (21). The structure was solved in the *C*2/*c* (No. 15) space group. All calculations were performed with the SHELXTL program (22). Molybdenum atoms were first located using

TABLE 3
Positional Parameters and Their Standard Deviations for (C₂H₁₀N₂)[Mo₅O₁₆] (Overall Isotropic Temperature Factor = 0.59(6)Å²)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Mo(1)	0.2500	0.642(1)	−0.2500
Mo(2)	0.4266(3)	0.1673(8)	0.0508(4)
Mo(3)	0.3954(3)	0.2861(8)	−0.3094(4)
O(1)	0.332(2)	−0.175(5)	−0.113(2)
O(2)	0.353(2)	0.311(5)	−0.113(2)
O(3)	0.507(2)	0.381(4)	0.160(3)
O(4)	0.297(2)	0.551(5)	−0.395(3)
O(5)	0.487(2)	0.139(4)	−0.120(2)
O(6)	0.317(2)	0.077(5)	−0.408(3)
O(7)	0.376(2)	0.123(4)	0.162(2)
O(8)	0.539(2)	−0.315(5)	−0.583(2)
N	0.349(1)	−0.236(4)	−0.641(2)
C	0.2981(9)	−0.448(3)	0.747(3)

TABLE 4
Selected Bond Distances (Å) and Angles (°) for (C₂H₁₀N₂)[Mo₅O₁₆]

Within MoO ₆ octahedra			
Mo(1)–O(1) ^a	1.70(2)	O(1) ^a –Mo(1)–O(1) ^b	106(2)
Mo(1)–O(1) ^b	1.70(2)	O(1) ^a –Mo(1)–O(2)	87(2)
Mo(1)–O(2)	2.42(3)	O(1) ^a –Mo(1)–O(2) ^c	165(2)
Mo(1)–O(2) ^c	2.42(3)	O(1) ^a –Mo(1)–O(4)	107(2)
Mo(1)–O(4)	1.89(3)	O(1) ^a –Mo(1)–O(4) ^c	92(2)
Mo(1)–O(4) ^c	1.89(3)	O(1) ^b –Mo(1)–O(2)	165(2)
		O(1) ^b –Mo(1)–O(2) ^c	87(2)
		O(1) ^b –Mo(1)–O(4)	92(2)
		O(1) ^b –Mo(1)–O(4) ^c	107(2)
		O(2)–Mo(1)–O(2) ^c	81(2)
		O(2)–Mo(1)–O(4)	78(2)
		O(2)–Mo(1)–O(4) ^c	79(2)
		O(2) ^c –Mo(1)–O(4)	79(2)
		O(2) ^c –Mo(1)–O(4) ^c	78(2)
		O(4)–Mo(1)–O(4) ^c	149(3)
Mo(2)–O(1)	2.49(3)	O(1)–Mo(2)–O(2)	80(2)
Mo(2)–O(2)	1.66(2)	O(1)–Mo(2)–O(3)	171(2)
Mo(2)–O(3)	1.71(3)	O(1)–Mo(2)–O(5)	80(2)
Mo(2)–O(5)	2.20(3)	O(1)–Mo(2)–O(5) ^d	72(1)
Mo(2)–O(5) ^d	2.11(3)	O(1)–Mo(2)–O(7)	87(2)
Mo(2)–O(7)	1.59(3)	O(2)–Mo(2)–O(3)	104(2)
		O(2)–Mo(2)–O(5)	73(2)
		O(2)–Mo(2)–O(5) ^d	140(2)
		O(2)–Mo(2)–O(7)	110(2)
		O(3)–Mo(2)–O(5)	92(2)
		O(3)–Mo(2)–O(5) ^d	100(2)
		O(3)–Mo(2)–O(7)	100(3)
		O(5)–Mo(2)–O(5) ^d	75(1)
		O(5)–Mo(2)–O(7)	166(3)
		O(5) ^d –Mo(2)–O(7)	97(2)
Mo(3)–O(2)	2.22(2)	O(2)–Mo(3)–O(3) ^e	80(2)
Mo(3)–O(3) ^e	2.43(3)	O(2)–Mo(3)–O(4)	80(2)
Mo(3)–O(4)	2.04(3)	O(2)–Mo(3)–O(5)	69(2)
Mo(3)–O(5)	1.91(2)	O(2)–Mo(3)–O(6)	95(2)
Mo(3)–O(6)	1.65(3)	O(2)–Mo(3)–O(8) ^f	161(2)
Mo(3)–O(8) ^f	1.75(3)	O(3) ^e –Mo(3)–O(4)	81(2)
		O(3) ^e –Mo(3)–O(5)	77(2)
		O(3) ^e –Mo(3)–O(6)	172(2)
		O(3) ^e –Mo(3)–O(8) ^f	83(2)
		O(4)–Mo(3)–O(5)	144(2)
		O(4)–Mo(3)–O(6)	92(2)
		O(4)–Mo(3)–O(8) ^f	104(2)
		O(5)–Mo(3)–O(6)	107(2)
		O(5)–Mo(3)–O(8) ^f	100(2)
		O(6)–Mo(3)–O(8) ^f	103(2)
		Within organic cation	
N–C	1.53(3)	N–C–C ^g	105(2)
C–C ^g	1.50(3)		
		Most likely hydrogen bonds	
N ... O(4) ^h	3.01(3)	N ... O(7) ⁱ	2.88(3)
N ... O(6)	3.01(3)	N ... O(8)	2.83(5)

Note. Symmetry codes: ^a*x*, 1 + *y*, *z*; ^b $\frac{1}{2}$ − *x*, 1 + *y*, − $\frac{1}{2}$ − *z*; ^c $\frac{1}{2}$ − *x*, *y*, − $\frac{1}{2}$ − *z*; ^d1 − *x*, −*y*, −*z*; ^e1 − *x*, 1 − *y*, −*z*; ^f1 − *x*, −*y*, −1 − *z*; ^g $\frac{1}{2}$ − *x*, *y*, − $\frac{3}{2}$ − *z*; ^h*x*, −1 + *y*, *z*; ⁱ*x*, *y*, −1 + *z*.

TABLE 5

Crystal Data and Structure Refinement for $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{Mo}_5\text{O}_{16}]$

Empirical formula	$\text{C}_4\text{H}_{12}\text{Mo}_5\text{N}_2\text{O}_{16}$
Formula weight	823.86
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 23.3997(3)$ Å $\alpha = 90^\circ$ $b = 5.6222(1)$ Å $\beta = 115.960(1)^\circ$ $c = 14.4131(2)$ Å $\gamma = 90^\circ$
Volume, Z	$1704.83(4)$ Å ³ , 4
Density (calculated)	3.210 g·cm ⁻³
Density (measured)	$3.242(5)$ g·cm ⁻³
Absorption coefficient	3.663 mm ⁻¹
$F(000)$	1552
Crystal size	$0.16 \times 0.1 \times 0.04$ mm
θ range for data collection	1.94 to 30.87°
Limiting indices	$-33 \leq h \leq 26$, $-8 \leq k \leq 8$, $-20 \leq l \leq 20$
Reflections collected	6246
Independent reflections	2492 [$R(\text{int}) = 0.0301$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2492/0/124
Goodness-of-fit on F^2	0.877
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0208$, $wR_2 = 0.0495$
R indices (all data)	$R_1 = 0.0256$, $wR_2 = 0.0514$
Extinction coefficient	0.00088(5)
Largest diff. peak and hole	0.964 and -1.355 e·Å ⁻³

the direct methods analysis. Remaining nonhydrogen atoms were found by successive difference Fourier maps. Hydrogen atoms were located using geometrical constraints. The

TABLE 6

Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å²) for $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{Mo}_5\text{O}_{16}]$

Atom	x	y	z	U (eq)
Mo(1)	0.0000	0.6396(1)	0.2500	0.009(1)
Mo(2)	0.0538(1)	1.1691(1)	0.4795(1)	0.009(1)
Mo(3)	0.0929(1)	0.2825(1)	0.1907(1)	0.010(1)
O(1)	0.0240(1)	0.8277(3)	0.3546(1)	0.014(1)
O(2)	0.0100(1)	1.3280(3)	0.3553(1)	0.012(1)
O(3)	0.0846(1)	0.5429(3)	0.2720(1)	0.012(1)
O(4)	0.0666(1)	1.3927(3)	0.5674(1)	0.016(1)
O(5)	0.0480(1)	0.1094(3)	0.0598(1)	0.012(1)
O(6)	0.1284(1)	1.1156(3)	0.4884(2)	0.017(1)
O(7)	0.1669(1)	0.3361(4)	0.1984(2)	0.023(1)
O(8)	0.1069(1)	0.0535(3)	0.2740(2)	0.021(1)
N	0.1850(1)	0.7481(4)	0.4249(2)	0.019(1)
C(1)	0.2068(1)	1.5917(5)	0.5166(2)	0.024(1)
C(2)	0.2369(1)	-0.2007(6)	0.3936(2)	0.026(1)
H(0A)	0.1708(1)	0.8859(4)	0.4389(2)	0.023
H(0B)	0.1523(1)	0.6779(4)	0.3721(2)	0.023
H(1A)	0.2188(1)	1.4379(5)	0.5001(2)	0.029
H(1B)	0.1724(1)	1.5673(5)	0.5359(2)	0.029
H(2A)	0.2215(1)	-0.0918(6)	0.3355(2)	0.031
H(2B)	0.2498(1)	-0.3469(6)	0.3724(2)	0.031

Note. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

refinement with anisotropic thermal parameters for all atoms except H gives $R_1(F_o) = 0.021$ and $wR_2(F_o)^2 = 0.049$ for 2212 reflections [$I > 2\sigma(I)$] and 124 parameters. Crystallographic data and final atomic parameters with equivalent temperature factors are given in Tables 5 and 6, respectively. Bond distances and angles are listed in Table 7.

TABLE 7

Selected Bond Lengths (Å) and Angles (°) for $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{Mo}_5\text{O}_{16}]$

Within MoO_6 octahedra			
Mo(1)–O(1)	1.722(2)	O(1)–Mo(1)–O(1) ^a	104.25(12)
Mo(1)–O(1) ^a	1.722(2)	O(1)–Mo(1)–O(3) ^a	103.52(8)
Mo(1)–O(3) ^a	1.941(2)	O(1) ^a –Mo(1)–O(3) ^a	96.32(8)
Mo(1)–O(3)	1.941(2)	O(1)–Mo(1)–O(3)	96.32(8)
Mo(1)–O(2) ^b	2.262(2)	O(1) ^a –Mo(1)–O(3)	103.52(8)
Mo(1)–O(2) ^c	2.262(2)	O(3) ^a –Mo(1)–O(3)	147.48(10)
		O(1)–Mo(1)–O(2) ^b	164.01(8)
		O(1) ^a –Mo(1)–O(2) ^b	89.40(7)
		O(3) ^a –Mo(1)–O(2) ^b	82.83(7)
		O(3)–Mo(1)–O(2) ^b	72.01(7)
		O(1)–Mo(1)–O(2) ^c	89.40(7)
		O(1) ^a –Mo(1)–O(2) ^c	164.00(8)
		O(3) ^a –Mo(1)–O(2) ^c	72.01(7)
		O(3)–Mo(1)–O(2) ^c	82.83(7)
		O(2) ^b –Mo(1)–O(2) ^c	78.50(9)
Mo(2)–O(4)	1.715(2)	O(4)–Mo(2)–O(6)	103.33(9)
Mo(2)–O(6)	1.719(2)	O(4)–Mo(2)–O(2)	101.75(8)
Mo(2)–O(2)	1.857(2)	O(6)–Mo(2)–O(2)	105.71(9)
Mo(2)–O(5) ^d	1.987(2)	O(4)–Mo(2)–O(5) ^d	100.44(8)
Mo(2)–O(5) ^e	2.220(2)	O(6)–Mo(2)–O(5) ^d	98.35(8)
Mo(2)–O(1)	2.513(2)	O(2)–Mo(2)–O(5) ^d	142.23(8)
		O(4)–Mo(2)–O(5) ^e	96.88(8)
		O(6)–Mo(2)–O(5) ^e	158.95(8)
		O(2)–Mo(2)–O(5) ^e	75.39(7)
		O(5) ^d –Mo(2)–O(5) ^e	71.91(8)
		O(4)–Mo(2)–O(1)	173.15(8)
		O(6)–Mo(2)–O(1)	82.76(8)
		O(2)–Mo(2)–O(1)	79.27(7)
		O(5) ^d –Mo(2)–O(1)	75.33(7)
		O(5) ^e –Mo(2)–O(1)	76.76(6)
Mo(3)–O(8)	1.692(2)	O(8)–Mo(3)–O(7)	102.21(10)
Mo(3)–O(7)	1.712(2)	O(8)–Mo(3)–O(3)	100.67(9)
Mo(3)–O(3)	1.938(2)	O(7)–Mo(3)–O(3)	101.17(9)
Mo(3)–O(5)	1.968(2)	O(8)–Mo(3)–O(5)	99.19(8)
Mo(3)–O(2) ^b	2.215(2)	O(7)–Mo(3)–O(5)	104.50(9)
Mo(3)–O(4) ^f	2.431(2)	O(3)–Mo(3)–O(5)	143.17(8)
		O(8)–Mo(3)–O(2) ^b	98.49(8)
		O(7)–Mo(3)–O(2) ^b	159.23(9)
		O(3)–Mo(3)–O(2) ^b	73.16(7)
		O(5)–Mo(3)–O(2) ^b	73.46(7)
		O(8)–Mo(3)–O(4) ^f	176.85(9)
		O(7)–Mo(3)–O(4) ^f	80.85(9)
		O(3)–Mo(3)–O(4) ^f	79.30(7)
		O(5)–Mo(3)–O(4) ^f	79.23(7)
		O(2) ^b –Mo(3)–O(4) ^f	78.46(6)

TABLE 7—Continued

Within organic cation			
N-C(1) ^f	1.480(4)	C(1) ^f -N-C(2) ^g	112.0(2)
N-C(2) ^g	1.498(4)	N ^g -C(1)-C(2) ^h	110.7(2)
C(1)-C(2) ^h	1.515(4)	N ^e -C(2)-C(1) ^h	109.7(2)
N-H(0A)	0.90	C(1) ^f -N-H(0A)	109.2(2)
N-H(0B)	0.90	C(2) ^g -N-H(0A)	109.2(2)
		C(1) ^f -N-H(0B)	109.20(14)
		C(2) ^g -N-H(0B)	109.2(2)
		H(0A)-N-H(0B)	107.9
C(1)-H(1A)	0.97	N ^g -C(1)-H(1A)	109.5(2)
C(1)-H(1B)	0.97	N ^g -C(1)-H(1A)	109.5(2)
		C(2) ^h -C(1)-H(1A)	109.5(2)
		N ^g -C(1)-H(1B)	109.50(14)
		C(2) ^h -C(1)-H(1B)	109.5(2)
		H(1A)-C(1)-H(1B)	108.1
C(2)-H(2A)	0.97	N ^e -C(2)-H(2A)	109.7(2)
C(2)-H(2B)	0.97	C(1) ^h -C(2)-H(2A)	109.7(2)
		N ^e -C(2)-H(2B)	109.7(2)
		C(1) ^h -C(2)-H(2B)	109.7(2)
		H(2A)-C(2)-H(2B)	108.2
Most likely hydrogen bonds			
H(0A) ... O(6)	1.944(3)		
H(1A) ... O(3)	1.779(3)		

Note. Symmetry transformations used to generate equivalent atoms: ^a -x, y, -z + 1/2; ^b -x, y - 1, -z + 1/2; ^c x, y - 1, z; ^d x, -y + 1, -z + 1/2; ^e -x, y + 1, -z + 1/2; ^f x, -y + 2, z - 1/2; ^g x, y + 1, z; ^h -x + 1/2, -y + 3/2, -z + 1.

DESCRIPTION OF THE STRUCTURES AND DISCUSSION

The structure of both compounds can be described from [Mo₅O₁₆]²⁻ layers perpendicular to the (101)* and to the *a** axes for (C₂H₁₀N₂)[Mo₅O₁₆] and (C₄H₁₂N₂)[Mo₅O₁₆], respectively (Fig. 2). The vectorial relationships between the two unit cells are the following: **a**₁ = (**a**₂ - **c**₂)/2, **b**₁ = **b**₂, and **c**₁ = (-**a**₂ - **c**₂)/2.

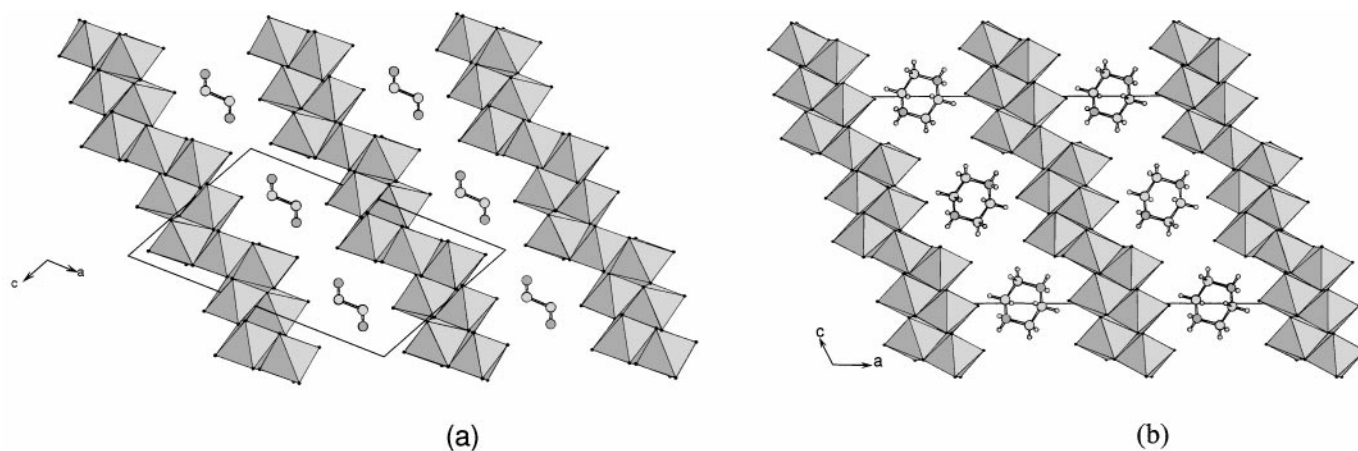


FIG. 2. View of the structures of (C₂H₁₀N₂)[Mo₅O₁₆] (a) and of (C₄H₁₂N₂)[Mo₅O₁₆] (b) and relationship between the two monoclinic unit cells.

[Mo₅O₁₆]²⁻ layers have already been found in the cesium pentamolybdate described by Gatehouse and Miskin (23). It could moreover be noted that the cesium salt is isostructural with the piperazine pentamolybdate. The [Mo₅O₁₆]²⁻ layers could be described from an infinite strip of ReO₃-type which is five octahedra wide and one octahedron deep. Every strip is connected to two neighboring ones by sharing octahedron edges to form a “staggered sheet” as shown in Fig. 3. In both structures, each octahedron is distorted with distances lying between 1.59(3) and 2.49(3) Å for (C₂H₁₀N₂)[Mo₅O₁₆] and between 1.692(2) and 2.513(2) Å for (C₂H₁₀N₂)[Mo₅O₁₆]. In most cases, Mo(VI) octahedra have two short, two medium, and two long molybdenum–oxygen bonds. It is not observed for Mo(2)O₆ octahedron of (C₂H₁₀N₂)[Mo₅O₁₆] but this structure was determined by conventional X-ray powder diffraction and it could be explained by a lower precision of the data. The two short distances are in *cis* position and correspond to two terminal oxygen atoms [Mo(3)O₆], one terminal and one linking oxygen atom [Mo(2)O₆], or two linking oxygen atoms [Mo(1)O₆]. It could be noted that Mo(1)O₆ shares all its vertices with neighboring octahedra. Amine cations are located between the layers and are connected to the oxygen atoms of the molybdate units via hydrogen bonds. The most likely hydrogen bonds are listed in Tables 4 and 7 for ethylenediamine and piperazine compounds, respectively.

These two pentamolybdates belong to a [Mo_nO_{3n+1}]²⁻ (*n* odd) series of layered molybdates. With *n* = 5, only the structure of Cs₂Mo₅O₁₆ has been reported in the literature and (C₂H₁₀N₂)[Mo₅O₁₆] and (C₄H₁₂N₂)[Mo₅O₁₆] are the first representatives of the series with an organic template. With *n* = 7, several molybdates have been synthesized: Cs₂[Mo₇O₂₂] (23) and Tl₂[Mo₇O₂₂] (24) first, with organic cations (4-4'-H₂bpy)[Mo₇O₂₂]·H₂O (9) and (NH₃CH₃)₂[Mo₇O₂₂] (25) more recently. The existence of a layered trimolybdate [Mo₃O₁₀]²⁻ was not reported but the relationship between the “predicted” layered [Mo₃O₁₀]²⁻ and

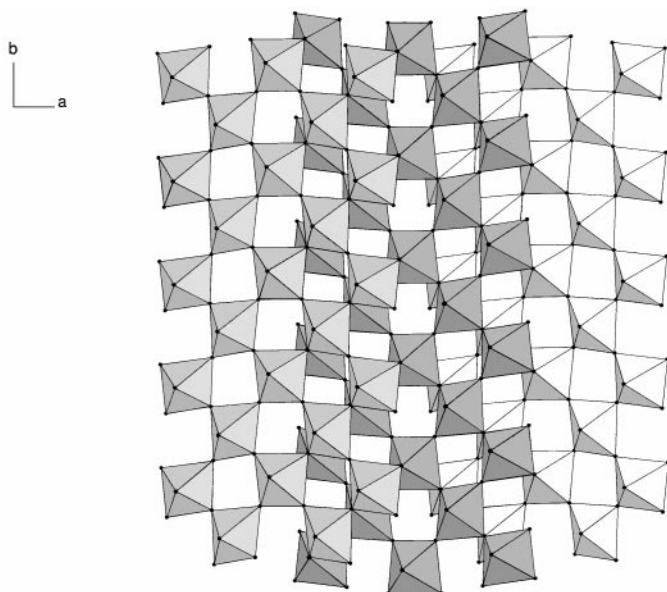


FIG. 3. View of the $[\text{Mo}_5\text{O}_{16}]^{2-}$ layers as an edge sharing stacking of five membered ReO_3 blocks.

the real chain $[\text{Mo}_3\text{O}_{10}]^{2-}$ found in $\text{Cs}_2\text{Mo}_3\text{O}_{10}$ has been evidenced by Gatehouse and Miskin (23). Members of this series with higher n values were not reported up to now but their synthesis is in progress by using linear long chain amines.

REFERENCES

1. R. C. Haushalter and L. A. Mundi, *Chem. Mater.* **4**, 31 (1992) and references therein.
2. F. Arnaud-Neu and M. J. Schwing-Weill, *Bull. Soc. Chim. Fr.* **12**, 3225 (1973).
3. F. Arnaud-Neu and M. J. Schwing-Weill, *Bull. Soc. Chim. Fr.* **12**, 3233 (1973).
4. F. Arnaud-Neu and M. J. Schwing-Weill, *J. Less-Common Met.* **36**, 71 (1974).
5. W. Bensch, P. Hug, R. Emmenegger, A. Reller, and H. R. Oswald, *Mater. Res. Bull.* **22**, 447 (1987).
6. M. I. Khan, Q. Chen, and J. Zubieta, *Inorg. Chim. Acta* **213**, 325 (1993).
7. Y. Xu, L.-H. An, and L.-L. Koh, *Chem. Mater.* **8**, 814 (1996).
8. W. T. A. Harrison, L. L. Dussack, and A. J. Jacobson, *Acta Crystallogr. C* **52**, 1075 (1996).
9. P. J. Zopf, R. C. Haushalter, and J. Zubieta, *Chem. Commun.* 321 (1997).
10. D. Hagman, C. Zubieta, D. J. Rose, J. Zubieta, and R. C. Haushalter, *Angew. Chem. Int. Ed. Engl.* **36**, 873 (1997).
11. P. J. Zopf, R. C. Haushalter, and J. Zubieta, *Chem. Mater.* **9**, 2019 (1997).
12. P. J. Zopf, C. J. Warren, R. C. Haushalter, and J. Zubieta, *Chem. Commun.* 1543 (1997).
13. N. Guillou and G. Férey, *J. Solid State Chem.* **132**, 224 (1997).
14. N. Guillou, G. Férey, and M. S. Whittingham, *J. Mater. Chem.* **8**, 2277 (1998).
15. A. Boulouf and D. Louër, *J. Appl. Crystallogr.* **24**, 987 (1991).
16. A. D. Mighell, C. R. Hubbard, and J. K. Stalick, "NBS*AIDS80: A Fortran Program for Crystallographic Data Evaluation." *NBS Tech Note 1141*, 1980. [NBS*AIDS83 is an expanded version of NBS*AIDS80.]
17. A. Le Bail, H. Duroy, and J. L. Fourquet, *Mater. Res. Bull.* **23**, 447 (1988).
18. J. Rodriguez-Carvajal, in "Collected Abstracts of Powder Diffraction Meeting, Toulouse, France," p. 127, 1990.
19. A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, and G. Polidori, *J. Appl. Cryst.* **27**, 435 (1994).
20. G. M. Sheldrick, SADABS, unpublished.
21. "International Tables for X-ray Crystallography." Kluwer Academic, Dordrecht, 1991.
22. G. M. Sheldrick, SHELXTL, "Siemens Analytical X-ray Instruments," 1994.
23. B. M. Gatehouse and B. K. Miskin, *Acta Crystallogr. B* **31**, 1293 (1975).
24. P. Tolédano, M. Touboul, and P. Herpin, *Acta Crystallogr. B* **32**, 1859 (1976).
25. P. Y. Zavalij and M. S. Whittingham, *Acta Crystallogr. C* **53**, 1374 (1997).