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Mo^V–Mo^{VI} cationic ordering in the layered molybdate $(C_2H_{10}N_2)[Mo_4O_{12}]$

Nathalie Guillou,[a] Gérard Férey*[a] and M. Stanley Whittingham[b]

[a] *Institut Lavoisier, UMR CNRS C0173, Université de Versailles Saint-Quentin-en-Yvelines, 45, Avenue des Etats-Unis, 78035 Versailles cedex, France. E-mail: guillou@chimie.uvsq.fr and Gerard.Ferey@chimie.uvsq.fr*

[b] *Department of Chemistry and Materials Research Center, State University of New York at Binghamton, Binghamton, New York 13902-6000. E-mail: stanwhit@mail.binghamton.edu*

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The mixed valence Mo^V–Mo^{VI} layered tetramolybdate $(C_2H_{10}N_2)[Mo_4O_{12}]$ has been hydrothermally synthesized (180 °C, 3 weeks, autogenous pressure). It crystallizes in the monoclinic system (space group *C*2) with $a=11.4090(2)$, $b=11.8227(2)$, $c=10.2305(1)$ Å, $\beta=117.549(1)°$ and $Z=4$ at 20 °C. The structure was solved from single crystal X-ray diffraction data. Full matrix anisotropic least-squares techniques led to a conventional $R_1(F_o)$ factor of 0.044 [$wR_2(F_o^2)=0.107$] for 2885 reflections [$I>2\sigma(I)$]. Its structure consists of $[Mo_4O_{12}]^{2-}$ layers perpendicular to the c^* axis, made up of an ordered organization of isolated tetrameric Mo^V clusters linked by edges to tetrameric Mo^{VI} ones. Ethylenediamine cations are located between the inorganic layers and ensure the connectivity of the structure *via* hydrogen bonds.

Introduction

Hydrothermal synthesis has been widely used for obtaining zeolitic materials, especially templated metal phosphates. In this way, reduced molybdenum phosphates with octahedral and tetrahedral frameworks have been reported by Haushalter and Mundi.[1] Molybdates are of much interest, especially in the fields of catalysis and of intercalation chemistry. Furthermore, secondary and ternary molybdates(VI) are also well known for their photochromic properties.[2–4] More recently, some organic–inorganic compounds constructed from molybdenum(VI) oxide and containing diamine have been reported.[5–13] The influence of the templating agent as well as the acidity have been demonstrated by the wide range of the structures obtained. On the other hand, Guo *et al.*[14] have reported the use of tetramethylammonium ion as a templating agent in the synthesis of molybdates, and in the formation of a new mixed valence Mo^V–Mo^{VI} layered compound, $(NMe_4)Mo_{4-\delta}O_{12}$. However, single crystals of this compound could not be obtained and its structure was solved *ab initio* from powder diffraction. Owing to the large effects of preferred orientation, location of Mo^V and Mo^{VI} in the tetramethylammonium molybdate was not possible. Furthermore, the chemical formula, $(NMe_4)Mo_{4-\delta}O_{12}$ ($\delta\approx0.2$), was not in agreement with their measured oxidation state of 5.5. During the investigation of the MoO_3–ethylenediamine–H_2O system, single crystals of the mixed Mo^V–Mo^{VI} layered tetramolybdate, $(C_2H_{10}N_2)[Mo_4O_{12}]$, were isolated. Here, we report the synthesis and the crystal structure of this mixed valence molybdate.

Experimental

Synthesis

Crystals of $(C_2H_{10}N_2)[Mo_4O_{12}]$ were obtained hydrothermally from a mixture of 1 g of MoO_3 (Aldrich, 99.5%+), 0.23 ml of ethylenediamine (Aldrich, 99%+) and 5 ml of H_2O. The reaction was performed (180 °C, 3 weeks, autogenous pressure) in a sealed hydrothermal bomb fitted with a 23 ml Teflon liner. The liner was filled to 20% of its volume with starting materials before heating. The pH decreased from 10 to 7 during the reaction. The dark brown sheet shaped crystals obtained, mixed with the already described fibrillar colorless crystals of $(C_2H_{10}N_2)[Mo_3O_{10}]$,[6, 13] were then separated from the bulk. TGA measurements, performed under an oxygen flow, showed a weight loss of 9.33% occurring between 275 and 500 °C . This result is in good agreement with the theoretical value for the loss of the ethylenediamine (9.78%). The resulting product is the orthorhombic molybdenum oxide MoO_3.

Structure determination

Diffraction data collection was carried out with a Siemens SMART system using a three-circle diffractometer equipped with a CCD bidimensional detector. A total of 5141 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.[15] The scattering factors and anomalous dispersion corrections were taken from ref. 16. All calculations were performed with the SHELXTL program.[17] Owing to the similarity between the powder patterns of our compound and that described by Guo *et al.*,[14] the first attempts to solve the structure were undertaken in the centrosymmetric space group *C*2/*m* used for $(NMe_4)Mo_{4-\delta}O_{12}$.[14] The two independent molybdenum coordinates proposed by Guo *et al.*[14] were used as the starting model. Fourier calculations were then performed to complete the model but did not give satisfactory results. Attempts to solve the structure were then undertaken in the two non-centrosymmetric space groups *C*2 and *Cm*. The structure was solved in the *C*2 space group (no. 5) while attempts to solve it in the *Cm* space group failed. The four independent molybdenum atoms were first located using direct methods analysis. Remaining non-hydrogen atoms were found by successive difference Fourier maps. Hydrogen atoms were located using geometrical constraints. The refinement with anisotropic thermal parameters for all atoms except H gives $R_1(F_o)=0.044$ and $wR_2(F_o^2)=0.107$ for 2885 reflections [$I>2\sigma$(I)] and 184 parameters. Crystallographic data and final atomic parameters with equivalent temperature factors are given in Table 1 and 2, respectively. Bond distances and angles are listed in Table 3.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater.*

Table 1 Conditions of data measurements and structure refinement for $(C_2H_{10}N_2)[Mo_4O_{12}]$

Empirical formula	$C_2H_{10}Mo_4N_2O_{12}$
Formula weight	637.88
Temperature/K	293(2)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	*C*2
Unit cell dimensions	
a/Å	11.4090(2)
b/Å	11.8227(2)
c/Å	10.2305(1)
β/°	117.549(1)
Volume/Å^3, *Z*	1223.48(3), 4
D_c/g cm^{-3}	3.463
Absorption coefficient/mm^{-1}	4.073
F(000)	1200
Crystal size/mm	0.180 × 0.050 × 0.005
Theta range for data collection/°	3.45–32.50
Limiting indices	$-17 \leqslant h \leqslant 13$, $-15 \leqslant k \leqslant 17$, $-14 \leqslant l \leqslant 14$
Reflections collected	5141
Independent reflections	3773 ($R_{int} = 0.0583$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3773/1/184
Goodness-of-fit on F^2	0.945
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0441$, $wR_2 = 0.1073$
R indices (all data)	$R_1 = 0.0602$, $wR_2 = 0.1108$
Absolute structure parameter	0.3(2)
Extinction coefficient	0.0017(2)
Largest diff. peak and hole/e Å^{-3}	1.259 and −2.392

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters^a (Å^2 × 10^3) for $(C_2H_{10}N_2)[Mo_4O_{12}]$

Atom	*x*	*y*	*z*	U_{eq}
Mo(1)	9841(1)	7884(1)	1512(1)	8(1)
Mo(2)	8158(1)	2599(1)	1582(1)	8(1)
Mo(3)	8101(1)	5790(1)	1505(1)	8(1)
Mo(4)	9810(1)	1086(1)	1556(1)	8(1)
O(1)	7940(8)	10964(8)	1098(11)	8(2)
O(2)	9645(8)	6058(8)	1405(9)	12(2)
O(3)	9653(6)	9345(10)	1235(7)	14(2)
O(4)	6248(8)	6037(8)	901(11)	12(2)
O(5)	8005(7)	7558(7)	974(9)	8(2)
O(6)	11165(8)	7629(9)	962(11)	11(2)
O(7)	9734(8)	2732(10)	1332(11)	15(2)
O(8)	8049(6)	4292(10)	1222(7)	14(2)
O(9)	8656(9)	5906(8)	3351(9)	19(2)
O(10)	10646(9)	7804(8)	3373(9)	19(2)
O(11)	8612(8)	2635(8)	3391(9)	18(2)
O(12)	10735(8)	908(7)	3393(9)	17(2)
N(1)	6708(10)	9145(11)	1750(10)	25(3)
N(2)	8256(9)	5610(8)	5800(10)	21(2)
C(1)	7581(12)	9045(11)	3310(13)	34(3)
C(2)	13020(11)	−615(11)	5725(10)	24(2)
H(1A)	7076(39)	8812(63)	1249(10)	37
H(1B)	6571(65)	9873(11)	1504(19)	37
H(1C)	5941(32)	8812(61)	1535(18)	37
H(2A)	8578(74)	5797(13)	5186(66)	32
H(2B)	8834(60)	5801(13)	6716(23)	32
H(2C)	7499(17)	5975(8)	5544(84)	32
H(1D)	8356(12)	9509(11)	3554(13)	40
H(1E)	7873(12)	8265(11)	3526(13)	40
H(2D)	13850(11)	−1012(11)	6034(10)	29
H(2E)	12433(11)	−829(11)	4715(10)	29

^{a} U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

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Description of the structure and discussion

The structure of ethylenediamine tetramolybdate $(C_2H_{10}N_2)[Mo_4O_{12}]$ is similar to that of $(NMe_4)Mo_{4-\delta}O_{12}$,[14] but exhibits Mo^V–Mo^{VI} cationic ordering. It consists of $[Mo_4O_{12}]^{2-}$ layers perpendicular to the *c** axis (Fig. 1) constructed of distorted Mo^VO_6 and $Mo^{VI}O_6$ octahedra. $[Mo_4O_{12}]^{2-}$ layers (Fig. 2) are built up from the connection of tetrameric units Mo_4O_{16} (Fig. 3) built up of two Mo^{VI} and two Mo^V edge-sharing molybdenum octahedra. These tetrameric units are connected by sharing edges to form infinite double zigzag chains running parallel to the *a* axis, each tetrameric unit being rotated by 90° with regard to its neighbour. These chains are connected together by sharing MoO_6 octahedra corners to form the $[Mo_4O_{12}]^{2-}$ layers. The structure exhibits channels delimited by eight polyhedra along the [101] direction as shown in Fig. 2. Ethylenediammonium cations are located between the layers and ensure the connectivity of the structure by hydrogen bonds (Fig. 4). One amine group of the diamine points directly toward the centre of the square window whose aperture is 2.6 Å.

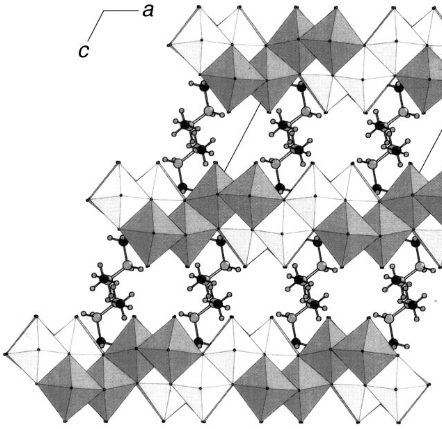

Fig. 1 Projection of the structure of $(C_2H_{10}N_2)[Mo_4O_{12}]$ along the *b* axis; Mo^V and Mo^{VI} octahedra are represented in dark and light grey, respectively.

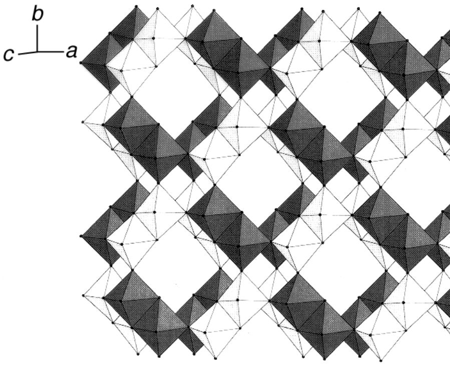

Fig. 2 Polyhedral represention of the $[Mo_4O_{12}]^{2-}$ layers.

The formula $(C_2H_{10}N_2)[Mo_4O_{12}]$ deduced from the

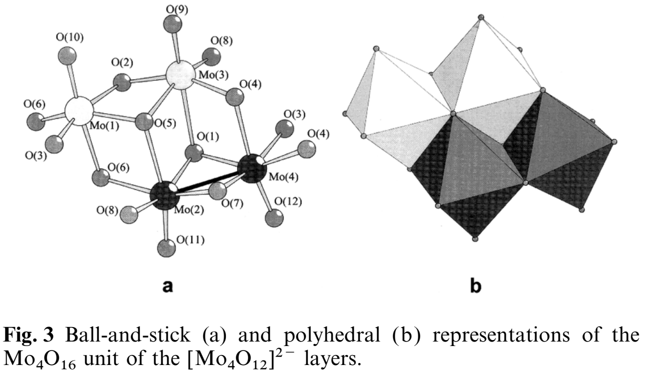

Fig. 3 Ball-and-stick (a) and polyhedral (b) representations of the Mo_4O_{16} unit of the $[Mo_4O_{12}]^{2-}$ layers.

Table 3 Principal interatomic distances (Å) and angles (°) for $(C_2H_{10}N_2)[Mo_4O_{12}]$

Within MoO_6 octahedra			
Mo(1)—O(10)	1.691(8)	Mo(1)—O(5)	1.943(8)
Mo(1)—O(3)	1.748(12)	Mo(1)—O(2)	2.168(10)
Mo(1)—O(6)	1.864(8)	Mo(1)—O(6$^{\mathrm{I}}$)	1 2.264(10)
O(10)—Mo(1)—O(3)	101.6(4)	O(6)—Mo(1)—O(2)	84.4(4)
O(10)—Mo(1)—O(6)	103.7(4)	O(5)—Mo(1)—O(2)	73.5(3)
O(3)—Mo(1)—O(6)	99.6(4)	O(10)—Mo(1)—O(6$^{\mathrm{I}}$)	169.0(4)
O(10)—Mo(1)—O(5)	105.1(4)	O(3)—Mo(1)—O(6$^{\mathrm{I}}$)	89.4(3)
O(3)—Mo(1)—O(5)	96.6(3)	O(6)—Mo(1)—O(6$^{\mathrm{I}}$)	72.8(4)
O(6)—Mo(1)—O(5)	143.2(4)	O(5)—Mo(1)—O(6$^{\mathrm{I}}$)	74.6(3)
O(10)—Mo(1)—O(2)	89.4(4)	O(2)—Mo(1)—O(6$^{\mathrm{I}}$)	79.9(3)
O(3)—Mo(1)—O(2)	166.9(3)		
Mo(2)—O(11)	1.675(8)	Mo(2)—O(8)	2.029(12)
Mo(2)—O(7)	1.936(8)	Mo(2)—O(6$^{\mathrm{III}}$)	2.060(8)
Mo(2)—O(1$^{\mathrm{II}}$)	1.983(10)	Mo(2)—O(5$^{\mathrm{IV}}$)	2.322(9)
O(11)—Mo(2)—O(7)	108.2(4)	O(1$^{\mathrm{II}}$)—Mo(2)—O(6$^{\mathrm{III}}$)	86.9(3)
O(11)—Mo(2)—O(1$^{\mathrm{II}}$)	103.9(4)	O(8)—Mo(2)—O(6$^{\mathrm{III}}$)	87.7(3)
O(7)—Mo(2)—O(1$^{\mathrm{II}}$)	93.6(4)	O(11)—Mo(2)—O(5$^{\mathrm{IV}}$)	165.4(3)
O(11)—Mo(2)—O(8)	97.9(4)	O(7)—Mo(2)—O(5$^{\mathrm{IV}}$)	86.3(3)
O(7)—Mo(2)—O(8)	83.0(4)	O(1$^{\mathrm{II}}$)—Mo(2)—O(5$^{\mathrm{IV}}$)	76.0(4)
O(1$^{\mathrm{II}}$)—Mo(2)—O(8)	157.9(4)	O(8)—Mo(2)—O(5$^{\mathrm{IV}}$)	82.0(3)
O(11)—Mo(2)—O(6$^{\mathrm{III}}$)	94.2(4)	O(6$^{\mathrm{III}}$)—Mo(2)—O(5$^{\mathrm{IV}}$)	71.3(3)
O(7)—Mo(2)—O(6$^{\mathrm{III}}$)	156.7(4)		
Mo(3)—O(9)	1.697(8)	Mo(3)—O(4)	1.931(8)
Mo(3)—O(8)	1.791(12)	Mo(3)—O(5)	2.150(9)
Mo(3)—O(2)	1.839(8)	Mo(3)—O(1$^{\mathrm{IV}}$)	2.370(10)
O(9)—Mo(3)—O(8)	103.1(4)	O(8)—Mo(3)—O(5)	157.9(3)
O(9)—Mo(3)—O(2)	100.0(4)	O(2)—Mo(3)—O(5)	75.9(4)
O(8)—Mo(3)—O(2)	97.0(4)	O(4)—Mo(3)—O(5)	81.5(3)
O(9)—Mo(3)—O(4)	97.7(5)	O(9)—Mo(3)—O(1$^{\mathrm{IV}}$)	168.1(4)
O(8)—Mo(3)—O(4)	98.5(4)	O(8)—Mo(3)—O(1$^{\mathrm{IV}}$)	86.7(3)
O(2)—Mo(3)—O(4)	153.1(4)	O(2)—Mo(3)—O(1$^{\mathrm{IV}}$)	85.3(3)
O(9)—Mo(3)—O(5)	98.8(4)	O(4)—Mo(3)—O(1$^{\mathrm{IV}}$)	73.8(3)
O(5)—Mo(3)—O(1$^{\mathrm{IV}}$)	72.0(3)		
Mo(4)—O(12)	1.690(8)	Mo(4)—O(4$^{\mathrm{V}}$)	2.040(8)
Mo(4)—O(7)	1.957(12)	Mo(4)—O(3$^{\mathrm{II}}$)	2.079(12)
Mo(4)—O(1$^{\mathrm{II}}$)	1.967(8)	Mo(4)—O(4$^{\mathrm{IV}}$)	2.229(10)
O(12)—Mo(4)—O(7)	103.0(4)	O(1$^{\mathrm{II}}$)—Mo(4)—O(3$^{\mathrm{II}}$)	83.4(3)
O(12)—Mo(4)—O(1$^{\mathrm{II}}$)	107.8(4)	O(4$^{\mathrm{V}}$)—Mo(4)—O(3$^{\mathrm{II}}$)	86.8(3)
O(7)—Mo(4)—O(1$^{\mathrm{II}}$)	93.5(4)	O(12)—Mo(4)—O(4$^{\mathrm{IV}}$)	169.9(4)
O(12)—Mo(4)—O(4$^{\mathrm{V}}$)	100.3(4)	O(7)—Mo(4)—O(4$^{\mathrm{IV}}$)	85.5(4)
O(7)—Mo(4)—O(4$^{\mathrm{V}}$)	89.4(4)	O(1$^{\mathrm{II}}$)—Mo(4)—O(4$^{\mathrm{IV}}$)	76.6(3)
O(1$^{\mathrm{II}}$)—Mo(4)—O(4$^{\mathrm{IV}}$)	150.3(4)	O(4$^{\mathrm{V}}$)—Mo(4)—O(4$^{\mathrm{IV}}$)	74.2(4)
O(12)—Mo(4)—O(3$^{\mathrm{III}}$)	90.9(3)	O(3$^{\mathrm{II}}$)—Mo(4)—O(4$^{\mathrm{IV}}$)	80.4(3)
O(7)—Mo(4)—O(3$^{\mathrm{II}}$)	166.0(3)		
Between molybdenum atoms:			
Mo(2)—Mo(4)	2.6076(10)	Mo(1)—Mo(3)	3.1711(10)
Within organic cation:			
N(1)—C(1)	1.443(14)	C(1)—C(2$^{\mathrm{VIII}}$)	1.494(14)
N(2)—C(2$^{\mathrm{VI}}$)	1.47(2)		
N(1)—H(1A)	0.89	N(1)—H(1C)	0.89
N(1)—H(1B)	0.89		
C(1)—N(1)—H(1A)	109.5(6)	C(1)—N(1)—H(1C)	109.5(6)
C(1)—N(1)—H(1B)	109.5(7)	H(1A)—N(1)—H(1C)	109.5
H(1A)—N(1)—H(1B)	109.5	H(1B)—N(1)—H(1C)	109.5
N(2)—H(2A)	0.89	N(2)—H(2C)	0.89
N(2)—H(2B)	0.89		
C(2$^{\mathrm{VI}}$)—N(2)—H(2A)	109.5(5)	C(2$^{\mathrm{VI}}$)—N(2)—H(2C)	109.5(6)
C(2$^{\mathrm{VI}}$)—N(2)—H(2B)	109.5(5)	H(2A)—N(2)—H(2C)	109.5
H(2A)—N(2)—H(2B)	109.5	H(2B)—N(2)—H(2C)	109.5
C(1)—H(1D)	0.97	C(1)—H(1E)	0.97
N(1)—C(1)—C(2$^{\mathrm{VII}}$)	114.6(9)	N(1)—C(1)—H(1E)	108.6(7)
N(1)—C(1)—H(1D)	108.6(7)	C(2$^{\mathrm{VII}}$)—C(1)—H(1E)	108.6(7)
C(2$^{\mathrm{VII}}$)—C(1)—H(1D)	108.6(7)	H(1D)—C(1)—H(1E)	107.6
C(2)—H(2D)	0.97	C(2)—H(2E)	0.97
N(2$^{\mathrm{V}}$)—C(2)—C(1$^{\mathrm{VIII}}$)	111.1(9)	N(2$^{\mathrm{V}}$)—C(2)—H(2E)	109.4(5)
N(2$^{\mathrm{V}}$)—C(2)—H(2D)	109.4(6)	C(1$^{\mathrm{VIII}}$)—C(2)—H(2E)	109.4(6)
C(1$^{\mathrm{VIII}}$)—C(2)—H(2D)	109.4(7)	H(2D)—C(2)—H(2E)	108.0
Most likely hydrogen bonds			
H(1A)—O(7)	1.92(6)	H(2A)—O(9)	1.92(7)
H(1B)—O(1)	2.21(6)	H(2B)—O(2)	1.93(4)
H(1C)—O(7$^{\mathrm{VI}}$)	1.82(6)	H(2C)—O(12$^{\mathrm{IX}}$)	2.19(7)

Symmetry transformations used to generate equivalent atoms: I $-x+2,y,-z$; II $x,y-1,z$; III $x-1/2,y-1/2,z$; IV $-x+3/2,y-1/2,-z$; V $x+1/2,y-1/2,z$; VI $x-1/2,y+1/2,z$; VII $-x+2,y+1,-z+1$; VIII $-x+2,y-1,-z+1$; IX $x-1/2,y+1/2,z+1$.

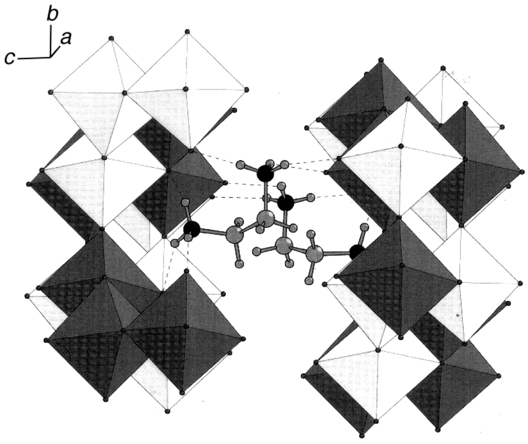

Fig. 4 View of the connection of the $[Mo_4O_{12}]^{2-}$ layers *via* hydrogen bonds shown by dotted lines.

structure determination indicates an oxidation state of 5.5 for Mo. Bond valence calculations[18] show that Mo(1) and Mo(3) are Mo^{VI} while Mo(2) and Mo(4) are Mo^{V}. The Mo(2)–Mo(4) distance of 2.608(1) Å is characteristic of a metal–metal distance between two Mo^{V}.[1] The two Mo^{V} octahedra have one short, four medium and one long molybdenum–oxygen bond with values between 1.675(8) and 1.690(8) Å, 1.936(8) and 2.079(12) Å, and 2.229(10) and 2.370(10) Å, respectively. There is only one terminal oxygen which corresponds to the short distance. As already observed for the reduced molydenum phosphates, the short Mo=O distance and the much longer Mo–O distance are in *trans* position.[1] The two Mo^{VI} octahedra have two short, two medium, and two long molybdenum–oxygen bonds with values between 1.691(8) and 1.791(12) Å, 1.839(8) and 1.943(8) Å and 2.060(8) and 2.322(9) Å, respectively. The two short distances are in *cis* position as already observed in numerous structures of amine molybdates,[5–13] and correspond to the terminal oxygen atom and the oxygen atom which ensures the connectivity of the chains within the layers.

Comparison between $(NMe_4)Mo_{4-\delta}O_{12}$ and $(C_2H_{10}N_2)[Mo_4O_{12}]$

Both structures have essentially the same inorganic skeleton. However, in the title compound the organic cation carries a charge of +2, whereas in the NMe_4 compound the organic cation only carries a charge of +1. Thus, there must be some additional charge compensation in the NMe_4 compound. In the NMe_4 compound[14] the formula should correspond to $(NMe_4)Mo_{4+\delta}O_{12}$ with δ around +0.2, not −0.2 as originally stated. The formula may also be written as $(NMe_4)Mo_4O_{12-\Delta}$, suggesting some possible oxygen vacancies. Alternatively, the charge compensation might be due to protons, leading to a formula $(NMe_4)H_xMo_4O_{12}$ where $x \leqslant 1$.[14]. These alternatives could not be differentiated by a powder Rietveld study. However, based on the similar structure exhibited by $(C_2H_{10}N_2)[Mo_4O_{12}]$ it seems probable that protons are the charge compensating ions in the NMe_4 salt. The Mo^{V}–Mo^{VI} ordering seen in the title compound was not observed in the earlier NMe_4 compound Rietveld study because of the structural complexity. The unusual cationic order in the title compound leads to a very interesting arrangement of edge sharing tetrameric clusters of Mo^{VI} linked by edges to tetrameric clusters of Mo^{V}.

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