METAL-ORGANIC COMPOUNDS

The Layered Methylammonium Molybdate (NH3CH3)2[Mo7O22] from X-ray Powder Data

Peter Y. Zavalij and M. Stanley Whittingham

Materials Research Center, State University of New York at Binghamton, Binghamton, NY 13902-6016, USA. E-mail: zavalij@binghamton.edu

Abstract

Hydrothermally prepared bis(methylammonium) heptamolybdate(VI) crystallizes in the monoclinic system (space group $C2/c$). Its structure was solved by conventional X-ray powder diffraction using the initial model of the molybdenum oxide layer from the known $Tl_2Mo_7O_{22}$ structure. The molybdenum coordination polyhedra are significantly distorted octahedra which form layers parallel to the bc plane. The methylammonium cations are incorporated between the layers.

Comment

This work originated from a systematic investigation of the hydrothermal interaction of molybdenum oxide with methyl-substituted ammonium as the template cation (Whittingham, Li, Guo & Zavalij, 1994), as was performed previously for tungsten oxide (Zavalij *et al.*, 1996). Two of our previous works describe the two extreme members: hexagonal ammonium molybdenum oxide (Guo, Zavalij & Whittingham, 1995) and tetramethylammonium molybdenum oxide, $[N(CH_3)_4][Mo_4O_{12}]$ (Guo, Zavalij & Whittingham, 1994a). Trimethylammonium hydroxide always reduced molybdic acid (2:1 ratio) under hydrothermal conditions (473 K, pH 1–5.5) to the monoclinic form of MoO_2. Dimethylammonium hydroxide (2:1, 473 K, pH 3.5) yields $[NH_2(CH_3)_2][Mo_6O_{20}].2H_2O$, obtained previously by Toraya, Marumo & Yamase (1984) after one year of decomposition of the precipitate obtained by the reaction of $Na_2[MoO_4]$ and $(CH_3)_2NCS_2$. Methylammonium hydroxide forms (2:1, 473 K, pH 3.5) the purple bronze $[NH_4][Mo_3O_9]$, previously syn-
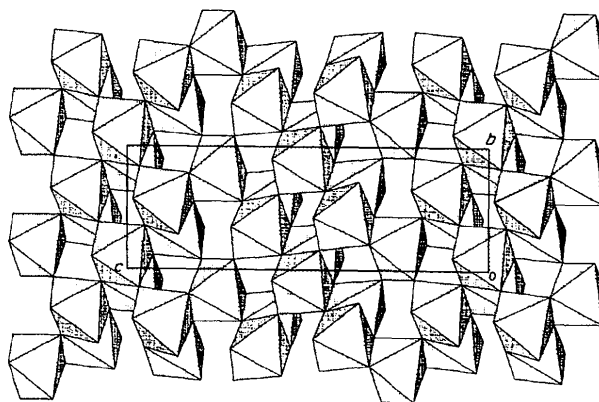

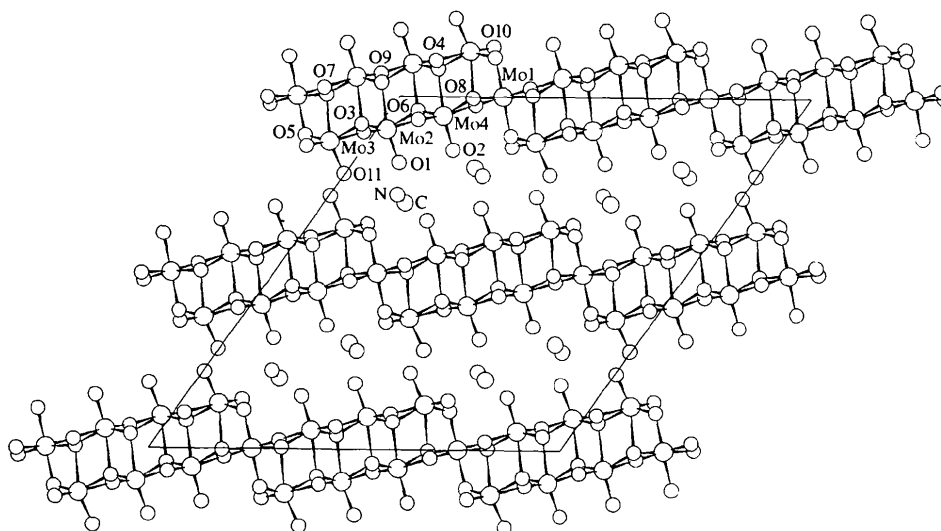Fig. 1. Octahedral representation of the $[Mo_7O_{22}]^{2-}$ layer in the bc plane.

Fig. 2. View of the structure of $(NH_3CH_3)_2[Mo_7O_{22}]$ along the b axis.

thesized by decomposition of the silver molybdate at 623 K and 500 bar (5.0 × 10^7 Pa) (Range, Bauer & Klement, 1990). However, using methylammonium chloride leads to the formation of a new compound, $(NH_3CH_3)_2[Mo_7O_{22}]$, the structure of which is reported here.

The structure of the title compound belongs to an $[Mo_nO_{3n+1}]^{2-}$ series of molybdates and has an Mo_7O_{22} layer with the same structure as those of the caesium (Gatehouse & Miskin, 1975) and thallium heptamolybdates(VI) (Tolédano, Touboul & Paulette, 1976), two other representatives of the series with $n = 7$. The molybdenum coordination polyhedra are significantly distorted octahedra. Each shares two edges and three corners with five others. Sharing edges, the octahedra form a zigzag chain along the c axis (Fig. 1), with an Mo1 octahedron in each bend of the chain. By sharing corners, these chains form 'stair-like' sheets (Fig. 2) parallel to the bc plane. The methylammonium cations fill the space between the 'steps' of the sheets in such a way that the ammonium group forms hydrogen bonds with the layers [N$\cdots$O 2.78 (3)–2.88 (3) Å]. Unlike $[N(CH_3)_4][Mo_4O_{12}]$, molybdenum in the methylammonium compound is in its highest oxidation state, +6. However, it can be reduced easily under X-rays or direct sunlight, changing color from white to blue.
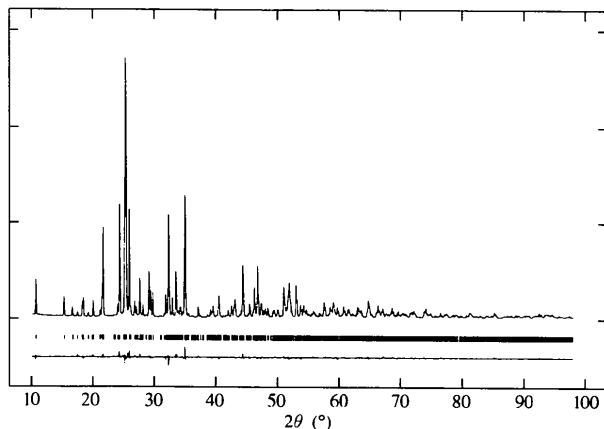

Fig. 3. Comparison of observed and calculated intensities for $(NH_3CH_3)_2[Mo_7O_{22}]$. The difference pattern appears below.

Experimental

The title compound was prepared by the hydrothermal treatment of NH_3CH_3Cl and H_2MoO_4 in a 4:1 molar ratio acidified to pH 1.0 with HCl. The reaction mixture was heated in a Teflon-lined Parr reactor for 4 d at 473 K. A white crystalline powder resulted. Use of a 2:1 molar ratio leads to a mixture of the title compound with hexagonal $MoO_3.0.55H_2O$ (Guo, Zavalij & Whittingham, 1994b).

Crystal data

$(NH_3CH_3)_2[Mo_7O_{22}]$
$M_r = 1087.7$

Cu $K\alpha_1$, $K\alpha_2$ radiation
$\lambda = 1.540562, 1.544390$ Å

Monoclinic
$C2/c$
$a = 23.0801 (2)$ Å
$b = 5.51742 (6)$ Å
$c = 19.5747 (2)$ Å
$\beta = 122.9297 (4)°$
$V = 2092.22 (4)$ Å^3
$Z = 4$
$D_x = 3.415$ Mg m^{-3}
D_m not measured

$\mu = 35.93$ mm^{-1}
$T = 293$ K
Powder
Specimen shape: flat sheet
25 × 25 × 1 mm
White

Data collection

Scintag XDS2000 diffractometer
ω/θ scans
Specimen mounting: packed powder pellet

Specimen mounted in reflection mode
$2\theta_{min} = 7$, $2\theta_{max} = 100°$
Increment in $2\theta = 0.02°$

Refinement

Refinement on I_{net}
$R = 0.038$
$R_p = 0.047$
$R_{wp} = 0.064$
$R_{exp} = 0.029$
$2\theta_{min} = 10.0$, $2\theta_{max} = 98.1°$
Increment in $2\theta = 0.02°$
Excluded region(s): the region below 10° 2θ was excluded because both the intensity and its uncertainty for the low-angle 200 reflection are much greater than for other reflections and caused unstable refinement
Profile function: pseudo-Voigt

1087 reflections
92 parameters
H atoms not located
$(\Delta/\sigma)_{max} = 0.10$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}
Extinction correction: none
Preferred orientation correction: Marsh–Dollase, [100] axis, $R_0 = 0.837 (1)$ (Dollase, 1986)
Scattering factors from $GSAS$ (Larson & Von Dreele, 1990)

Table 1. *Fractional atomic coordinates and isotropic displacement parameters (Å^2)*

	x	y	z	U_{iso}
Mo1	1/2	0.1222 (6)	1/4	0.0172 (13)
Mo2	0.42137 (11)	0.0709 (5)	0.47848 (15)	0.0139 (10)
Mo3	0.39143 (10)	0.4778 (5)	0.09769 (12)	0.0182 (8)
Mo4	0.04787 (11)	0.1033 (4)	0.13800 (15)	0.0170 (11)
O1	0.3380 (6)	0.100 (3)	0.3998 (9)	0.0165 (9)
O2	0.1302 (7)	0.159 (2)	0.2142 (10)	0.0165 (9)
O3	0.0648 (7)	0.150 (2)	0.4524 (10)	0.0165 (9)
O4	0.4139 (8)	0.160 (2)	0.0331 (11)	0.0165 (9)
O5	0.4076 (6)	0.208 (2)	0.1705 (10)	0.0165 (9)
O6	0.0374 (6)	0.382 (2)	0.0725 (9)	0.0165 (9)
O7	0.0223 (6)	0.419 (3)	0.2051 (9)	0.0165 (9)
O8	0.4980 (6)	0.439 (2)	0.3169 (8)	0.0165 (9)
O9	0.4463 (7)	0.377 (2)	0.4187 (10)	0.0165 (9)
O10	0.1154 (6)	0.224 (2)	0.3579 (9)	0.0165 (9)
O11	0.3112 (6)	0.423 (3)	0.0147 (8)	0.0165 (9)
N	0.7122 (7)	-0.014 (3)	0.3451 (9)	0.016 (4)
C	0.7310 (11)	0.156 (3)	0.3028 (15)	0.016 (4)

Table 2. *Selected bond lengths (Å)*

Mo1—O7^i	1.67 (2)	Mo3—O11	1.700 (15)
Mo1—O7^{ii}	1.67 (2)	Mo3—O5	1.953 (15)
Mo1—O5	1.89 (2)	Mo3—O3^{vii}	1.99 (2)
Mo1—O5^{iii}	1.89 (2)	Mo3—O8^{viii}	2.171 (15)
Mo1—O8	2.200 (14)	Mo3—O4	2.38 (2)
Mo1—O8^{iii}	2.200 (14)	Mo4—O2	1.69 (2)

Mo2—O1	1.70 (2)	Mo4—O9"	1.72 (2)
Mo2—O4^{iv}	1.73 (2)	Mo4—O6	1.933 (14)
Mo2—O3^v	1.959 (15)	Mo4—O8"	1.93 (2)
Mo2—O6"	2.00 (2)	Mo4—O3^{viii}	2.23 (2)
Mo2—O6^{vi}	2.29 (2)	Mo4—O7	2.438 (15)
Mo2—O9	2.30 (2)	N—C	1.46 (3)
Mo3—O10^{vii}	1.668 (14)		

Symmetry codes: (i) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $1 - x, y, \frac{1}{2} - z$; (iv) $x, -y, \frac{1}{2} + z$; (v) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (vi) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (vii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (viii) $-x, y, \frac{1}{2} - z$.

The powder diffraction pattern was indexed in a monoclinic system using the Ito method from *CSD* software (Akselrud *et al.*, 1993). The systematic absences among *hkl* and *h0l* reflections lead to the possible space groups *Cc* and *C2/c*. The centrosymmetric space group *C2/c* was chosen and confirmed later during the crystal structure determination. The cell dimensions together with the 7.3% weight loss at 583 K for the reaction

$$(NH_3CH_3)_xMoO_{3+\frac{x}{2}} \xrightarrow{(T^\circ, O_2)} MoO_3$$
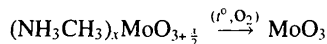
allowed us to determine the exact composition as $(NH_3CH_3)_2$-$[Mo_7O_{22}]$. Only two molybdates were known with the same composition: $Cs_2Mo_7O_{22}$ (Gatehouse & Miskin, 1975) and $Tl_2Mo_7O_{22}$ (Tolédano, Touboul & Paulette, 1976). Their symmetry appears to be the same and their cell dimensions are very similar to those of the methylammonium compound. This fact allowed us to use the atomic coordinates from the Tl compound as a starting model in the Rietveld refinement. The positions of the remaining atoms were located from the difference Fourier map after least-squares profile fitting of the known atomic parameters. The N atom in the methyl-ammonium cation differs from the C atom by having much shorter contacts with neighboring O atoms due to hydrogen bonding (N···O 2.8 *versus* C···O 3.2 Å). The final Rietveld refinement (Fig. 3) was performed using *GSAS* (Larson & Von Dreele, 1990). Individual isotropic atomic displacement parameters were refined only for Mo atoms and a single parameter was used for the O atoms and atoms of the methyl-ammonium cation. A surface roughness absorption correction (Suortti, 1972) was applied.

Data collection: *DMS* software from Scintag. Cell refinement: *CSD* (Akselrud *et al.*, 1993). Data reduction: *CSD*. Program(s) used to refine structure: *CSD*, *GSAS* (Larson & Von Dreele, 1990). Molecular graphics: *POLIEDRI* (Pilati, 1990), *INSIGHTII* (Biosym Technologies, 1995). Software used to prepare material for publication: *CSD*, *GSAS*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1181). Services for accessing these data are described at the back of the journal.

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Potassium Diaqua(ethylenediamine-tetraacetato)ytterbate(III) Pentahydrate

Narumi Sakagami, Jun-ichi Homma, Takumi Konno† and Ken-ichi Okamoto

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan. E-mail: okamoto@staff.chem.tsukuba.ac.jp

Abstract

The Yb atom in the title compound, $K[Yb(C_{10}H_{12}N_2O_8)$-$(H_2O)_2].5H_2O$, is eight-coordinate through two N and four O atoms in edta, and two water O atoms, where edta denotes ethylenediaminetetraacetate. The geometry around the Yb atom is influenced by the size and electrostatic properties of the countercations.

Comment

The crystal structures of several lanthanide–edta (Ln–edta) complexes (where edta denotes ethylenediamine-tetraacetate) have been reported and it has been suggested that the coordination numbers of the complexes depend on the changing ionic radii; a ten-coordinate complex for La (Lind, Lee & Hoard, 1965), nine-coordinate complexes for La (Hoard, Lee & Lind, 1965; Nakamura, Kurisaki, Wakita & Yamaguchi, 1995), Nd

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† Current address: Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan.