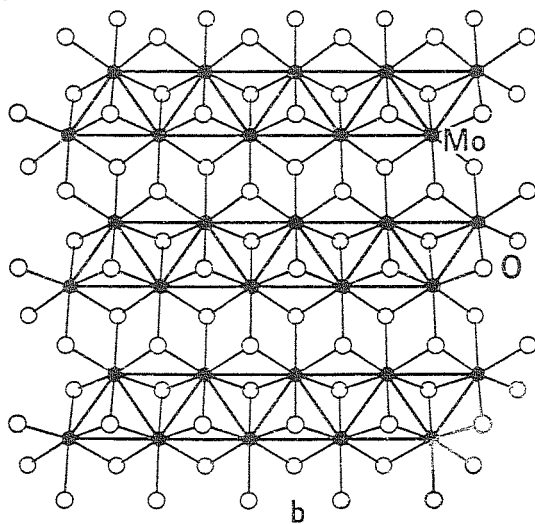


09.5-14 SYNTHESIS AND CRYSTAL STRUCTURES OF SEVERAL NEW TERNARY MOLYBDENUM OXIDES CONTAINING Mo-Mo BONDING. C.C. Torardi, Central Research and Development Dept., E.I. du Pont de Nemours and Co., Inc., Experimental Station, Wilm., DE 19898 USA.

Four new compounds in the family of ternary molybdenum oxides with extended and localized metal-metal bonding arrangements have been prepared. These phases incorporate an alkali metal with molybdenum in an average oxidation state of +4 or less. They are synthesized by hydrothermal reaction of aqueous MOH solution (M=Li, Na, or K) with MoO<sub>3</sub> and Mo at temperatures between 500-700°C. Na<sub>1.17</sub>(4)Mo<sub>2</sub>O<sub>4</sub> is monoclinic, C2/m, with a=12.253(2), b=2.881(1), c=4.945(1) Å, and β=103.23(2)° (R=0.026, R<sub>w</sub>=0.030). Na<sub>0.90</sub>(2)Mo<sub>2</sub>O<sub>4</sub> is orthorhombic, Pnma, with a=4.923(1), b=2.879(1), and c=12.060(2) Å (R=0.017, R<sub>w</sub>=0.022). K<sub>0.7</sub>(1)Mo<sub>2</sub>O<sub>4</sub> is monoclinic, C2/m, with a=14.670(15), b=2.890(3), c=4.945(6) Å, and β=97.55(9)° (R=0.070, R<sub>w</sub>=0.072). Li<sub>2</sub>MoO<sub>3</sub> is rhombohedral, R3m, with a=5.738(1), and c=61.325(15) Å (R=0.035, R<sub>w</sub>=0.034). The structure of the Li and Na compounds is related to that of NaFeO<sub>2</sub> with metal atom layers alternating with oxygen atom layers with sequence ...O-Mo-O-M-O-Mo-O.... All metal atoms in the sodium compounds are located in octahedral sites between close-packed oxide layers. In the potassium phase, the O-atom layers are shifted to give trigonal prismatic sites in which the K atoms reside. Within the Mo-atom layers of Na<sub>1.17</sub>Mo<sub>2</sub>O<sub>4</sub>, Na<sub>0.90</sub>Mo<sub>2</sub>O<sub>4</sub>, and K<sub>0.7</sub>Mo<sub>2</sub>O<sub>4</sub>, the molybdenum atoms are moved from the center of their octahedral sites towards neighboring Mo atoms to create infinite double chains oriented parallel with the b axis. Mo-Mo bonding occurs along the chains (~2.88 Å) and across the chains (~2.55 Å) as seen in the figure (Mo atoms and Mo-Mo bonds are shaded).



Metal-metal bonding in Li<sub>2</sub>MoO<sub>3</sub> is more complicated with two different types of molybdenum-atom layers present, one with partially occupied molybdenum sites. Trigonal clusters of Mo atoms is the dominant structural feature in both types of layers. The structures of these novel materials will be presented.

09.5-15 CRYSTAL AND MOLECULAR STRUCTURE OF N-ALKYLAMMONIUM HEPTAMOLYBDATES. By P. Román<sup>a</sup>, A. Luque<sup>a</sup>, J. M. Gutiérrez-Zorrilla<sup>a</sup> and A. Vegas<sup>b</sup>. <sup>a</sup>Departamento de Química Inorgánica, UPV/EHU, Apartado 644, 48080 Bilbao, Spain. <sup>b</sup>Instituto de Química Inorgánica "Elhuyar", CSIC, Serrano 113, 28006 Madrid, Spain.

Three new heptamolybdates of n-alkylammonium have been synthesized, with the general formula: (BH)<sub>6</sub>[Mo<sub>7</sub>O<sub>24</sub>].3H<sub>2</sub>O, where B = n-butyl-, n-pentyl- and n-hexyl-amine, hereafter abbreviated as BUTMO, PENTMO and HEXMO, respectively.

Thermogravimetric studies show that the compounds contain three water molecules. Ir spectra indicate that the organic bases are protonated and the polyanion presents the well-known infrared spectrum for heptamolybdates in solid state.

The crystal structure analysis of these compounds shows that all of them are isostructural. The compound BUTMO crystallizes in poor quality specimen to be studied as single crystal, but it has been determined in powder samples.

Crystal data for PENTMO are: (C<sub>5</sub>H<sub>14</sub>N)<sub>6</sub>[Mo<sub>7</sub>O<sub>24</sub>].3H<sub>2</sub>O. a = 17.085(2), b = 31.344(4), c = 11.487(12) Å, β = 93.04(3)°, V = 6143(6) Å<sup>3</sup>, Z = 4, P2<sub>1</sub>/n, D<sub>x</sub> = 1.77, D<sub>0</sub> = 1.78(1) Mg/m<sup>3</sup>, R = 0.059 and R<sub>w</sub> = 0.066 for 5526 observed reflexions.

The structure solution confirms that the compound contains discrete [Mo<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> anions, (C<sub>5</sub>H<sub>14</sub>N)<sup>+</sup> cations and water molecules, connected through hydrogen bonds.

The distinguishing features of compound PENTMO are its extensive hydrogen bonding. The cations, and the water molecules are positioned so as to be able to form hydrogen bonds with either molybdate oxygen atoms or water oxygen atoms. The proposed strong hydrogen bonding interactions appear to stabilize the structure. Some of these hydrogen bonds can play an important role in the possible photocromism of this compound. (Y. Ohashi et al., Bull. Chem. Soc. Jpn., 1982, 55, 1254-1260).

The Mo<sub>6</sub> octahedra within the polyanion are distorted and the distortion has been evaluated using different equations. (P. Román et al. Transition Met. Chem., 1986, 11, 143-150).