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 KOH solution (K=Li, Na, or K) with MoO$_3$ and Mo at temperatures between 500-700°C. Na$_{1.17}$Mo$_2$O$_{4}$ is monoclinic, C2/m, with a=12.253(2), b=2.881(1), c=4.965(1) Å, and β=103.23(2)° (R=0.026, R$_p$=0.030). Na$_{2}$Mo$_3$O$_{12}$ is orthorhombic, Pnma, with a=6.292(1), b=2.879(1), and c=12.060(2) Å (R=0.017, R$_p$=0.022). K$_2$M$_{1153}$Mo$_{14}$O$_{4}$ is monoclinic, C2/m, with a=14.67(15), b=2.890(3), c=4.945(6) Å, and β=97.55(9)° (R=0.070, R$_p$=0.072). Li$_2$MoO$_4$ is rhombohedral, R3m, with a=5.738(1) Å, and c=6.325(15) Å (R=0.035, R$_p$=0.034). The structure of the Li and Na compounds is related to that of NaFeO$_2$ with additional layers alternating with oxygen atom layers sequence ...O-Mo-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$_{1.17}$Mo$_2$O$_{4}$, Na$_{2}$Mo$_3$O$_{12}$, and K$_2$M$_{1153}$Mo$_{14}$O$_{4}$, 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$_2$MoO$_4$ 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.

Three new heptamolybdates of n-alkylammonium have been synthesized, with the general formula: (3R)$_n$(Mo$_7$O$_{24}$)$_3$H$_2$O, where B = n-butyl-, n-pentyl- and n-hexyl-amine, hereafter abbreviated as BUTH, PENTH and HEXH, respectively. Thermogravimetric studies show that the compounds contain three water molecules. As spectra indicate that the organic bases are protonated and the polyoxoanion 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 PENTH crystallizes in poor quality specimen to be studied as single crystal, but it has been determined in powder samples.

Crystal data for PENTH are: (C$_{6}$H$_{14}$N)$_{3}$(Mo$_{7}$O$_{24}$)$_{3}$H$_{2}$O. a = 17.068(2), b = 31.344(1), c = 12.48(12) Å, β = 92.94(3)°. V = 6143(6) Å$^3$, Z = 4. P$_{2_1}$2$_1$2$_1$. D$_c$ = 1.77. D$_x$ = 1.78(1) g/cm$^3$, P = 0.089 and Rw = 0.064 for 5526 observed reflections.

The structure solution confirms that the compound contains discrete [Mo$_{7}$O$_{24}$]$^{3+}$ anions. (C$_{6}$H$_{14}$N)$_{3}^{+}$ cations and water molecules, connected through hydrogen bonds.

The distinguishing features of compound PENTH 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 photoreactivity of this compound. (T. Ohashi et al., Bull. Chem. Soc. Jpn. 1982, 55, 1284-1260).

The MoO$_4$ octahedra within the polyoxoanion are distorted and the distortion has been evaluated using different equations. (P. Roman et al. Transition Met.Chem., 1986, 11, 143-150).