$BaCu_2S_2$ is a representative of a chalcogenide group with the $ThCr_2Si_2$—type layer structure. The way of synthesizing the tetragonal modification of $BaCu_2S_2$ with: $a=3.909$, $c=12.655$Å parameters has been suggested in the paper (Saeki M., Onoda M., Nozaki H., Mater. Res. Bull., 1988, 23, 4, 603); a crystal structure determination of $BaCu_2S_2$ obtained by another way and compounds with potassium and rubidium inserted into this structure was undertaken in our work (Saveliyeva M., V., Alekseev V. I. et al., Izv. SO AN SSSR. Rhim. Sek. 1990, 1, 123-125).

For X-Cu-M-S system (X=K, Rb, Cs, M=Fe, Mn, Zn) we have managed to obtaina series of compounds with general formula $X_2Cu_3MS_4$ (X=K, Rb, Cs, M=Fe) one of them-$K_2Cu_3FeS_4$ is known (Dobrovolskaya M. G. et al. Zap. Un. Min. Soc., 1981, 4, 468-473) as mineral Murunskit, however without any structure investigations. For X=K, Rb, Cs, M=Mn, Zn we have obtained compounds with a general formula $XCuMnS_2$. In both cases the structure supposes to be of the $ThCr_2Si_2$-type, that is typical for transition metal chalcogenides $AM_2X_2$ (A=K, Rb, Cs, M=Co; A=K, M=Ni, X=S, Se) (Huan G. et al., Eur. J. Solid State Inorg. Chem., 1989, 26, 193). All samples were prepared in the atmosphere of $CS_2$ at $900\pm50°C$ from $Cu_2O$, the corresponding metal oxide ($ZnO$, $Fe_2O_3$, $MnO_2$) and $Rb_2CO_3$, $Cs_2CO_3$, $KHCO_3$, which were taken in definite stoichiometry. Chemical composition of the products was estimated by chemical and powder X-ray diffraction analysis. A granulometric investigation of particles was carried out on a SK laser micron sizer "PRO — 7000". The melting points of compounds were determined by DTA method. The temperature variations of resistivity were measured by conventional four-probe technique on pressed pellets sintered at 850°C.

The proximity of the tetragonal unit cell parameters of samples and appearences of their diffraction patterns (DRON-UM1, R= 192mm, CuKα-radiation, Ni-filter, Si-external standard) indicates a retaining of the $ThCr_2Si_2$-type structure.

**PS-08.04.45** CRYSTAL STRUCTURE OF TETRAPOTASSIUM PENTA-MOLYBDODISELENIUM(IV) DIHYDRATE $K_4NaSe^{IV}Mo_5O_{21}$ $2H_2O$

By S.W. Zhang⁻, G.Q. Huang⁻ and M.C. Shao, Department of Chemistry, Peking University, Beijing, 100871, P.R.China

Selenium is one of the essential elements and is required for almost all forms of life. Some heteropolyanions of selenium are described but a few crystal structure information is available.

The structure of the Strandberg-type heteropolymolybdate of selenium $K_4NaSe^{IV}Mo_5O_{21}$ $2H_2O$ has been determined by the single-crystal X-ray method.

Crystal data:
Monoclinic, space group $P-2_1/n$, $a=9.851(2)$, $b=23.224(5)$, $c=10.456(3)$Å, $\beta=114.13(2)°$, $V=2183.1$Å$^3$, and Z=4. The structure was refined by full-matrix least squares to R=0.069 for 2845 reflexions with Fo>5 σ (F)

The $[Se^{IV}Mo_5O_{21}]^{4-}$ anion has the distinguishable pentagonal molybdate framework of $MoO_6$ octahedra, which are joined together through four sharing of edges and one corner sharing approximating a plane to form a $Mo_5O_{21}$ pentagon. The two $Se^{IV}O_3$ trigonal pyramids are situated so that the $Mo_5O_{21}$ pentagon is capped on both sides of the plane.

**PS-08.04.46** CRYSTAL STRUCTURE OF A REMARKABLE POLY-METALLATE OXYGEN CLUSTER $[H_{20}Mo_{57}Fe^{II}_6O_{188}(NO)_6(H_2O)_{18}(MoO)_3]^{6-}$

By G.Q. Huang,⁻ S.W. Zhang, and M.C. Shao, Department of Chemistry, Peking University, Beijing, 100871, P.R. China

Understanding the driving force for the formation of high nuclearity clusters is still a formidable challenge. We recently reported the structure with the largest polymetallate cluster involving mixed valence molybdenum and vanadium(IV) or iron(III) (Zhang, Huang, Shao & Tang, J. Chem. Soc., Chem. Commun., (1993), 1, 37). Here is another remarkable cluster structure with mixed valence molybdenum and iron(II). They may give an indication about the possible mechanism of formation of the polymolybdate.

Crystal data:
Hexagonal, space group P-6₃/mmc, $a=23.868(5)$Å, $c=27.521(12)$Å, $V=13577$Å$^3$ and Z=2. The structural parameters have been refined to convergence R =0.058 for 2067 reflexions with Fo>4.0 σ (F).

The interesting cluster consists of three 17-molybdate subunits related to each other by a three-fold axis; the cluster centre sits on a special position with 6m2 crystallographic symmetry, and each individual subunit has internal $C_{2v}$ symmetry.

Each subunit contains fifteen $MoO_6$ octahedra and two $MoO_6(NO)$ pentagonal bipyramids in which the oxidation state of Mo atom is 5+; three subunits are connected by six $Fe^{II}O_6$ octahedra and six $MoO_6$ octahedra linked by six bridging water molecules and three bridging oxygen atoms. In central cavity, there are 12 water molecules, which are situated around $\overline{6}$ fold axis and coordinated to six molybdate and six iron(II) respectively; moreover, these 12 water molecules are linked to each other by hydrogens bonding to form two six-membered rings.

There are still two four-coordination Mo atom occupying the six outer cavities of the cluster with 1/3 probability. Such occupancies for Mo atoms can be explained by the fact that the anion with high negative is stablized by two $(MoOH)^{5+}$ groups and the cavity is a good room to accommodate the tetrahedra.

**PS-08.04.47** MIXED VALENT MOLYBDENUM PHOSPHATES INVOLVING Mo(V).

By A. Leclaire⁎, M.M. Borel, A. Grandin and B. Raveau. CRISMAT, CNRS-URA1318, Caen France.

A large series of molybdenum phosphates has been isolated during these last ten years with a molybdenum valency ranging from III to VI. In most of these phosphates, molybdenum exhibits an octahedral coordination. The different valences can be present in the same framework leading to compound with a mixed valency for molybdenum. The most frequent mixed valences involve Mo(III) and Mo(IV). They have been synthesized and studied principaly by R.C.Haushalter and al., by Lii and al. and by the authors. In these compounds each valency has generally its own well defined sitting, for instance in $NaMo_2P_4O_{14}$ the two independant sites for molybdenum contain respectively Mo(III) and Mo(IV). In the other hand very few mixed valent molybdenum phosphates involving Mo(V) have been synthesized. Only six kinds of frameworks corresponding to the phosphates : $AMo_2P_2O_{10}$ $xH_2O$ and $Cs_6Mo_7P_7O_{37}$ $H_2O$ characterized by the mixed valences Mo(IV)/Mo(V) $Cs_3Mo_4P_4O_{22}$ and $Rb_3Mo_4P_4O_{22}$ and $AMo_3P_3O_{16}$ and $KMo_3P_2O_{14}$ characterized by the mixed valency Mo(V)/(Mo(VI)) are known up to now. This rarity may be related to the particular configuration of Mo(V) which tends to form molybdenyl ions and would prevent a delocalisation of the electrons in the structure.

The first mixed valent molybednum phosphate involving Mo(IV) and Mo(V) isolated by R.C. Haushalter and al. using hydrothermal synthesis was $NH_4Mo_2P_2O_{10}$ $H_2O$. This compound is isotypic with leucophosphite, it exhibits tetraoctahedral units built up from two edge-sharing $Mo(IV)O_6$ octahedra which share also one of their corners with one $Mo(V)O_6$ octahedron. These units are linked together by $PO_4$ tetrahedra. The polyhedra delimit large intersecting tunnels. We have synthesized by solid state chemistry isotypic compounds

$RbMo_2P_2O_{10}(1-x)$ $H_2O$ and $CsMo_2P_2O_{10}$. The main difference between these compounds is the filling of the tunnel by the alcaline ions and water.

$K_3Mo_4P_4O_{22}$ $H_2O$ exhibits also a leucophosphite structure but the tetraoctahedral units are built up from one $Mo(III)O6$ octahedron sharing one edge with one $Mo(IV)O_6$ octahedron and each of them sharing also one corner with one $Mo(V)O6$ octahedron. So this compound has not realy a mixed valency $Mo(IV)/Mo(V)$ but $Mo(III)/Mo(IV)/Mo(V)$. The $Mo(III)$ and the $Mo(IV)$ are spread randomly over the two edge-sharing octahedra. We obtained a new mixed valent monophosphate containing also tetraoctahedral units : $Cs_6Mo_7P_7O_{37}$ $H_2O$. In these units the edge sharing octahedra contain $Mo(IV)$ and the other ones $Mo(V)$. Beside the tetraoctahedral units the framework exhibits trioctahedral units containing only $Mo(V)$ in which two octahedra share one edge and share also one of their common oxygen atoms with the third octahedron of the unit.

Recently we have isolated compounds with a $Mo(V)/Mo(VI)$ valency. Three of them ($NaMo_3P_3O_{16}$, $AgMo_3P_3O_{16}$ and $KMo_3P_2O_{14}$) have their different valency well located, the two others $Cs_3Mo_4P_4O_{22}$ and $Rb_3Mo_4P_4O_{22}$ have the $Mo(V)$ and the $Mo(VI)$ spread randomly over the same sitting. In $NaMo_3P_3O_{16}$ and in $AgMo_3P_3O_{16}$ the two $Mo(V)O_6$ octahedra have each their own sitting while the $Mo(VI)$ is surrounded by a triangular bipyramid of oxygen allowing the formulation $AMo_2^V{}_{octa}Mo^{VI}{}_{bipy}P_3O_{16}$. In $KMo_3P_2O_{14}$ layer structure one observes one octahedral site for $Mo(V)$ and the two $Mo(VI)$ are respectively loctated in an octahedron and a bipyramid allowing the formulation $KMo^V{}_{octa}Mo^{VI}{}_{octa}Mo^{VI}{}_{bipy}P_2O_{14}$. In spite of their same formula and their same basic units $Mo_2P_2O_{15}$ forming similar $[Mo_2P_2O_{13}]_\infty$ layers, $Cs_3Mo_4P_4O_{22}$ and $Rb_3Mo_4P_4O_{22}$ exhibit dissimilar frameworks principally due to different way of stacking the layers.

It is worth pointing out that in the compounds we synthesized, the mixed valency of molybdenum involving $Mo(V)$ arises only when the frameworks exhibit polyoctahedral units built up from edge sharing or/and corner sharing octahedra. One observes also that the molybdenyl oxygen of the octahedron is never shared with another polyhedron.

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**PS-08.04.48** STUDY ON THE LAW OF MINUTE CHANGE IN CRYSTAL STRUCTURE. By Zhang Hanqing, Institute of Mineral Deposits of Chinese Academy of Geological Sciences, He Zhuwen and Xu Li, China University of Science and Technology

The crystal structure varies minutely with the change of its composition and the environ ments which it is situated in. Those changes could be indicated in different ways Researchers previously proposed a lot of expressing methods when they compared these structures, such as unit cell parameters, volume of lattice cell, bond lengths and bond angles, deformation of ligands, the changes of thermal parameters of each ion, and so on. Based on the study of the minute variation of some type structures in recent years, the authors find that: (1) The change of coordinates of characteristic ions or of the relative value of each parameter can be used to indicate the law of minute change in crystal structure; (2) On condition that the space group is unchanging, no matter how the tiny the change of crystal structure is, the ligand form can become different but the symmetry of ligand can be unchanged. In this paper, we discuss the law of the minute change in crystal structure, taking the examples spinel, wurtzite, nickeline, rutile, calcite, and pyrite type structure etc.

Spinel ($AB_2O_4$) The space group of spinel is $Fd{-}3m$. In its crysl structure, the $O^-$ ion cumulate and arrange closely with each other, and produce tetrahedral and octahedral voids . A ions occupy the tetrahedral voids with coordinates $(1/4, 1/4, 1/4)$ . B ions are located in the $(3/8, 5/8, 3/8)$ octahedral. The coordinates of $O^-$ ion are $(u, u, u)$ . Because of the special sites of A and B ions, their symmetry and coordinates are not changing when composition, temperature and pressure vary. However, $O^-$ ions may move along the 3 axes (i.e.u will possess different values) .Thus, $AO_4$ tetrahedral and $BO6$ octahedral will react differently. The four $O^-$ ions will move (in or out) along the four A−O directions of an $AO_4$ tetrahedron at the same time, and still form a regular tetrahedron, only the ligand size will change. The six $O^-$ ions of a $BO_6$ octahedron will move along the [111] direction of the unit cell simultaneously. Thus the regular octahedron will distort and become a flat tened or elongared trigonal anti−prism.The relation between each parameter and the U value is as indicaled in the block diagram (fig.1) . From this we can see that there are two mutate points ($u=0.375$ and $u=0.3875$) which influence the crystal structure as the u value is changing. So, the structure can be divided into five regions, the main characters of each and is as in figure 1.

Conclusion: (1) The coordination polyhedron of ions suited in structure can be used to discuss the law of minute change in crystal structure; (2) The move of ions in crystal structure should follow the symmetry rules of the space group; (3) The form and size of ligand in stucture can change, but its symmetry is constant.That is to say, the minute change in crystal structure is the adjusted result of form and size of each ligand.The law of munite change in crystal structure can be reflected from the locus of ion movement.