

PS-08.04.04 THE CRYSTAL STRUCTURE OF Mg-FILLOWITE. By Z. S. MA, N. C. Shi and H. WANG. X-Ray laboratory, China University of Geosciences, Beijing 100083, China.

Mg-fallowite was discovered in a muscovite pegmatite in Northwestern Qinghe County, Altay Prefecture, Uygur Autonomous Region of Xinjiang, China. The chemical formula is:  $(\text{Na}_{1.52}\text{K}_{0.01})_{1.52}\text{Ca}_{1.07}(\text{Al}_{0.52}\text{Zn}_{0.7}\text{Fe}_{0.2}\text{Mg}_{1.5}\text{Mn}_{4.06})_{8.98}\text{P}_{20}\text{O}_{64}$ , the ideal formula is  $\text{Na}_2\text{Ca}(\text{FeMg}_2\text{Mn}_4)_7(\text{PO}_4)_8$ . A crystal 0.2 × 0.2 × 0.3 mm in size was selected and mounted on RASA-11S, Rigaku 4-circle automated diffractometer, with MoK $\alpha$  radiation, a graphite monochromator, a  $2\theta$ - $\omega$  scan, the scanning constant of  $\Delta\omega = 1.26 + 0.5 \tan\theta$ , a speed of  $8^\circ/\text{min}$ . 6391 diffractions were collected in the range of  $3^\circ < 2\theta < 65^\circ$ , of which 3951  $[F > 3\sigma |F|]$  were used for structure refining. Space group was  $R\bar{3}$ ,  $a = 15.143(3)$ ,  $c = 43.192(2)$  Å,  $\gamma = 120^\circ$ ,  $V = 8573.6 \text{ \AA}^3$ ,  $Z = 18$ ,  $D_x = 3.42 \text{ g/cm}^3$ . The structure was solved by direct method (SHELXS-76). After cations were located, the coordinates of oxygen were obtained by Fourier synthesis. Atomic coordinates, occupancy, isotropic and anisotropic temperature factor refinements were carried out, which finally led to a reduction of R to 0.084. There are 3 sets of Na, 1 set of Ca, 3 sets of Mg, 1 set of Fe, 7 sets of Mn, 6 sets of P and 24 sets of O, forming 21 kinds of coordination polyhedra, in an asymmetric unit. It consists of three kinds of polyhedral clusters. Every cluster included 2 cations along c axis. They were indicated as I, II, III polyhedral clusters. The determination of the structure indicated that Mg atoms occupy an independent crystallochemical position and its crystallochemical formula is  $\text{Na}_2\text{CaMg}(\text{Fe, Mg, Mn})_6(\text{PO}_4)_8$ . It is different from the formula of fallowite, which is  $\text{Na}_2\text{Ca}(\text{Fe, Mn})_7(\text{PO}_4)_8$ .

PS-08.04.05 THE CRYSTAL STRUCTURE OF  $\alpha$ -DAWSON MIXED-VALENCE OCTADECATUNGSTOPERCHLORATE. By Jie Liu\*, Ming-Qin Chen and Yue-Fang Huang, Research Center of analysis & measurement, Fudan University, Shanghai, P.R.China, 200433; Si-San Zhu, Xiao-Qun Shi, Bin Yue and Yi-Dong Gu, Chemistry Department of Fudan University.

The "heteropoly blue"  $[\text{n-Bu}_4\text{N}]_3[\text{Cl}_2\text{W}^{VI}\text{W}^{V}\text{O}_{62}]$  is so far the first reported tungstate which contains two chlorine atoms as heteroatoms. This makes the structure rather unique in our serial work on iso- and hetero-tungstate and significant in the study of redox properties.

Observed (calculated) element analysis showed as follows: C, 11.88(11.29); N, 1.01(0.82); H, 2.18(2.12);  $\text{WO}_3$ , 81.34(81.87). The crystal structure was determined on an ENRAF-NONIUS CAD4 diffractometer with a micro VAX II computer. The compound crystallized in space group P, with  $a = 15.676(3)$  Å,  $b = 16.315(4)$  Å,  $c = 15.062(2)$  Å,  $\alpha = 62.26(1)^\circ$ ,  $\beta = 121.35(2)^\circ$ ,  $\gamma = 118.74(2)^\circ$ ,  $V = 2762.5 \text{ \AA}^3$ ,  $d = 3.123 \text{ g/cm}^3$ . Total 10093 reflections up to  $\theta = 25^\circ$  were collected. 6384 reflections with  $I > 3\sigma(I)$  were used in direct methods to locate most tungsten atoms. All the other atoms except hydrogen ones were found on the difference Fourier map. Full matrix least square refinements led to the final R factor of 0.039.

The polyanion shows a  $\alpha$ -Dawson structure (Dawson, B. (1953). Acta Cryst. 6, 113) consisting of two  $\text{ClW}_6\text{O}_{21}$  "half-units" with a pseudo point symmetry  $3/m$  (see figure 1). Each "half-unit" has a central distorted  $\text{ClO}_4$  tetrahedron sharing corners with three edge-sharing polar  $\text{WO}_6$  octahedra and six alternately edge- and corner-sharing equatorial ones. It also can be described that the anion frame is constructed of two well known Keggin structures of  $[\text{XW}_{12}\text{O}_{40}]^{n-}$  (Pope, M. T. (1972). Inorg. Chem. 11, 1973) by removing a  $\text{W}_3\text{O}_{12}$  ring formed by three corner-sharing  $\text{WO}_6$  octahedra from each  $[\text{XW}_{12}\text{O}_{40}]^{n-}$  and then connecting the two residues together via six oxygen atoms which lie on a mirror plane.

The oxygen atoms in  $\text{ClO}_4$  tetrahedra can be divided into two types: those each shared by two equatorial  $\text{WO}_6$  octahedra with Cl-O bond lengths (1.42-1.47 Å) being consistent with 1.41-1.48 Å in other  $\text{ClO}_4$  groups (taken from "International Tables for X-ray Crystallography", 1962, Vol III), and those each shared by three polar  $\text{WO}_6$  octahedra, with Cl-O

distances (1.49 and 1.55 Å) being somewhat longer due to the large liganacy of this kind of oxygen atoms. Infrared spectrum shows the characteristic stretching vibration band of Cl(VII)-O at  $1091.3 \text{ cm}^{-1}$ . All these observations support the presence of Cl(VII).

The crystals exhibit an unique blue color of W(V), confirming the existence of mixed valences. A cyclic voltammogram reveals that the reduction of W(VI) to W(V) is irreversible, in agreement with the fact that the crystal turns more and more to dark blue on exposure to air and in contrast to the reversible redox property of  $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$  (Pope, M. T. (1967). Inorg. Chem. 6, 1147). The W-O bond lengths extend from 1.59 to 2.54 Å, which is wider than 1.85-2.35 Å in  $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$  (Dawson, B. (1953). Acta Cryst. 6, 113), showing considerable structural distortion. The presence of two different valences of tungsten atoms and the asymmetric distribution of the paramagnetic electron over the whole anion may account for this distortion. The further investigation on the redox property and the utilization of the title compound is of considerable interest.

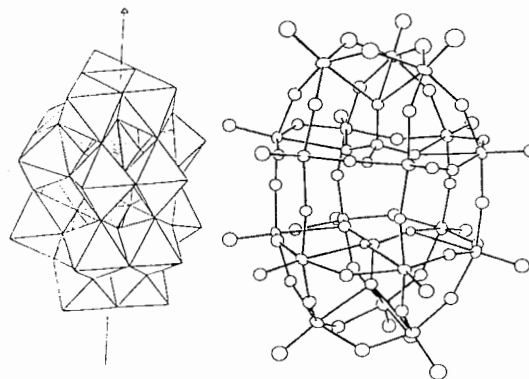


Figure 1. The structure of the anion  $[\text{Cl}_2\text{W}_{18}\text{O}_{62}]^{3-}$ .

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MERCURIOUS HALIDES by Erahama D. Sharma, Chemistry Departments, Cal State Univ. L.A. Los Angeles, 90032 & L.A. Pierce College, Woodland Hills, CA 91371, U.S.A.

Late Prof. J. Donohue assigned me to study Hg-Hg bond as he was intrigued by the non-constancy of the length as one compared the bonds in crystals of  $\text{Hg}_2\text{F}_2$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{Hg}_2\text{Br}_2$  &  $\text{Hg}_2\text{I}_2$ . If he had any clue he never told me. This was a stroke of GENIUS to assign a problem in crystal structure to a graduate student at a place where the facilities in '56 were as primitive as they come (I was not a novice). The problem involved solving for one Z parameter for Hg & I in the space group  $I 4/m 2/m 2/m$ . After hundreds of twins, which haunt me in ways more than one, a single crystal was obtained & diffraction data obtained which was processed using the sophisticated concept of ANAMOLOUS DISPERSION without much improvement. The Hg-Hg length has a range from 251 pm to 272 pm in the series (A.F. Wells (1984), Structural Inorganic Chemistry, 5th ed., Clarendon Press: Oxford, p. 1157) and the stretching frequencies are in the range  $185 \text{ cm}^{-1}$  &  $113 \text{ cm}^{-1}$  (J.R. Durig, K.K. Lau, G. Nagarajan, M. Walker, J. Bragin (1969) J. Chem. Phys. 50, 2130). These experimental observations substantiate the differing nature of the Hg-Hg bond in the series. For  $\text{Hg}_2\text{F}_2$  the chemical reaction with water to give hydrolysis clarifies the IONIC nature of the Hg to F bonding & the colorless clear crystals. In the rest the color gradation allows us to invoke CHARGE TRANSFER (H. B. Gray, An Intro. to Atomic & Molecular Structure (1973), Benjamin, San Francisco, p. 169-170). The absorption of visible light in the 350-400 nm range gives the red-brown color to  $\text{Hg}_2\text{I}_2$ . This is the right

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energy that separates the bonding & antibonding orbitals if one likens the formation of Hg dimer moiety to H<sub>2</sub> on the ground that Hg<sup>2+</sup> has the configuration [Xe] 4f<sup>14</sup> 5d<sup>10</sup> 6s<sup>1</sup>. Details of the semiquantitative calculations will be presented.

**PS-08.04.07 TERNARY NIOBIUM CHALCOGENIDE HALIDES: PREPARATION AND CHARACTERIZATION OF Nb<sub>3</sub>SI<sub>7</sub> AND (Nb<sub>3</sub>SI<sub>7</sub>)<sub>2</sub>NbI<sub>5</sub>.** By J. Lin\* and G. J. Miller, Department of Chemistry and Ames Laboratory-USDOE, Iowa State University, USA.

It has been shown that most of the Nb<sub>3</sub>YX<sub>7</sub> (Y = Chalcogen, X = Halogen) compounds adopt the Nb<sub>3</sub>X<sub>8</sub> layer structure (G. J. Miller, unpublished). The niobium atoms fill 3/8 of the octahedral holes of a close packed array of anions to form sandwich-type layers. A basic structural feature of this layer is that the niobium atoms form triangular clusters by sharing octahedral edges. All of these compounds crystallize in either hexagonal or trigonal symmetry depending upon the stacking sequences of the layers. In the Nb-S-I system, in addition to the hexagonal phase, an orthorhombic Nb<sub>3</sub>SI<sub>7</sub>, as well as a new compound, (Nb<sub>3</sub>SI<sub>7</sub>)<sub>2</sub>NbI<sub>5</sub>, were found.

All of the compounds were synthesized from elemental materials and characterized by single crystal X-ray diffraction. The crystals of (Nb<sub>3</sub>SI<sub>7</sub>)<sub>2</sub>NbI<sub>5</sub> were always found as twins, so the structure was refined with a twin program SFLS. The twin operation is (-1 0 0, 0 1 0, 1/6 0 1).

The anion array in the orthorhombic Nb<sub>3</sub>SI<sub>7</sub> structure is cubic close packing. The niobium atoms occupy the octahedral holes in the sequence [AcBa<sup>+</sup>CbAc<sup>+</sup>BaCb<sup>+</sup>Ac]. A, B and C, a, b and c, as well as a<sup>+</sup>, b<sup>+</sup> and c<sup>+</sup> represent, respectively, the anion arrays, niobium arrays 5/8 filled and 1/8 filled sites of octahedral holes. The niobium triangular clusters in this structure are formed either within or between layers of metal atoms. The whole structure is also layered, but the sheets are buckled and run perpendicular to the  $\vec{c}$  axis.

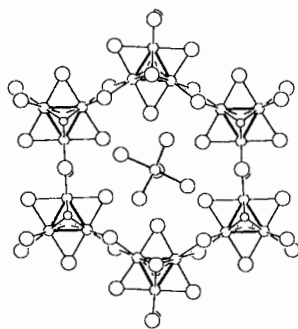


Fig. 1. Projection of the (Nb<sub>3</sub>SI<sub>7</sub>)<sub>2</sub>(NbI<sub>5</sub>) structure along  $\vec{c}$ .

In the monoclinic (Nb<sub>3</sub>SI<sub>7</sub>)<sub>2</sub>NbI<sub>5</sub> structure, the niobium atoms form the triangular cluster via sharing octahedral faces and each cluster connects with three other clusters by sharing edges to form a layer with large hexagonal holes, as shown in Fig. 1. The whole framework is constructed by stacking these layers one over another along  $\vec{c}$  to achieve a channel-like structure. The isolated NbI<sub>5</sub> molecules with trigonal bipyramidal geometry sit at the positions between the layers along the channels. We should point out that in the solid state, NbI<sub>5</sub> occurs with the niobium atoms in octahedral coordination and dimerized into Nb<sub>2</sub>I<sub>10</sub> cluster. The

trigonal bipyramidal coordination of niobium is known in the gas phase of NbCl<sub>5</sub> and in some niobium oxides. Extended Hückel band calculations show that this geometry increases the energy gap between the HOMO and LUMO, so as to reduce the electron transfer from the framework to NbI<sub>5</sub> molecules.

**PS-08.04.08 STRUCTURAL CHANGES IN ISOSTOICHIOMETRIC SERIES OF ALKALI LANTHANUM NITRATES.** By A.G.Vigdorchik\*, Yu.A.Malinovsky, Institute of Crystallography Russian Acad. of Sci., Leninsky pr.59, Moscow, 117333, Russia.

Our investigation was performed in the course of a systematic study of alkali rare-earth nitrates and is devoted to an analysis of the structural crystal-chemical characteristics of isostoichiometric series of alkali lanthanum nitrates A<sub>2</sub>[La(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)<sub>2</sub>]·nH<sub>2</sub>O, where A = Cs, Rb, NH<sub>4</sub>, K. Such a comparative analysis shows how far the nature of the alkali metals influences the structure of these compounds. The Cs, Rb, and ammonium compounds have similar values of the unit cell parameters. We can note their similarity both in the structure of the rare-earth complexes and in the packing of these complexes in the structure. The only essential difference lies in the absence of water molecules outside the coordination sphere of the La atoms in the cesium compound. The channels in which the alkali ions lie have approximately equal dimensions. The cavities adequate for the Cs atoms are too ample for the smaller Rb<sup>+</sup> and NH<sub>4</sub><sup>+</sup> ions. This circumstance determines the possibility of water getting into the intraframework cavities of the rubidium and ammonium compounds. The ammonium ion tends to form hydrogen bonds. They join the ammonium ions and the molecules of intermolecular water to form the chains along Y axis. That is why the ammonium ions are fixed in one position, while the Rb atoms occupy statistically two independent positions. The organization of the structure of K<sub>2</sub>[La(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)<sub>2</sub>] is quite different as the ionic radii of cesium, ammonium and rubidium are too large in comparison with potassium.

**PS-08.04.09 CRYSTAL STRUCTURE OF FERROELECTRIC KGeOPO<sub>4</sub> CRYSTALS.** By N.I.Sorokina\*, I.A.Verin, V.I.Simonov, Institute of Crystallography, Moscow, Russia; V.I.Voronkova, V.K.Yanovskii, Physics Department, Moscow State University, Russia.

Single crystals of KGeOPO<sub>4</sub> (KGP) which belong to the family of ferroelectric and nonlinear optical compounds of the KTiOPO<sub>4</sub> (KTP) type have been obtained. Their dielectric susceptibility has been measured and their crystal structure has been studied. The ferroelectric phase transition temperature for KGP is 785°C which is close to the temperature of incongruent melting of this compound at 805°C. Besides, relaxation phenomena due to a high ionic electroconductivity are observed. The KGP crystals at room temperature have the polar sp.gr. Pna2<sub>1</sub> with the following unit cell parameters: a=12.6013(10), b=6.3051(5), c=10.0031(8) Å. Our X-ray structural study (an "Enraf-Nonius" autodiffractometer, AgK<sub>α</sub>-radiation,