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-fillowite was discovered in a muscovite pegmatite in Northwestern Qinghe County, Altay Prefecture, Uygur Autonomous Region of Xinjiang, China. The chemical formula is:

$(Na_{1.92}K_{0.01})_{1.93}Ca_{1.07}(Al_{0.03}Zn_{0.07}Fe_{3.89}Mg_{1.84}Mn_{4.08})_{9.89}P_{5.95}O_{24}$, the ideal formula is $Na_2Ca(FeMg_2Mn_4)_7(PO_4)_6$. A crystal $0.2 \cdot 0.2 \cdot 0.3mm$ in size was selected and mounted on RASA-IIS, Rigaku 4-circle automated diffractometer, with MoKα radiation, a graphite monochromator, a $2\theta-\omega$ scan, the scanning constant of $\triangle\omega=1.26+0.5\tan\theta$, a speed of $8°/min$. 6391 diffractions were collected in the range of $3° < 2\theta < 65°$, 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, $\gamma=120°$, $V=8573.6Å^3$, $Z=18$, $Dx=3.42 g/cm^3$. 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 $Na_2CaMg(Fe,Mg,Mn)_6(PO_4)_6$. It is different from the formula of fillowite, which is $Na_2Ca(Fe,Mn)_7PO_4)_6$.

PS-08.04.05 THE CRYSTAL STRUCTURE OF α-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" $[n-Bu_4N]_3[Cl_2W^V_2W^{VI}_{17}O_{62}]$ 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); 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 $P\bar{1}$ with $a=15.676(3)$Å, $b=16.315(4)$Å, $c=15.062(2)$Å, $\alpha=62.26(1)°$, $\beta=121.35(2)°$, $\gamma=118.74(2)°$, $V=2762.5Å^3$, $d_c=3.123 g/cm^3$. Total 10093 reflections up to $\theta=25°$ 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 α-Dawson structure (Dawson,B.(1953). Acta Cryst. 6,113) consisting of two ClW_9O_{31} "half-units" with a pseudo point symmetry 3/m (see figure 1). Each "half-unit" has a central distorted ClO_4 tetrahedron sharing corners with three edge-sharing polar 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 $[XW_{12}O_{40}]^{n-}$ (Pope,M.T.(1972). Inorg.Chem. 11,1973) by removing a W_3O_{12} ring formed by three corner-sharing WO_6 octahedra from each $[XW_{12}O_{40}]^{n-}$ and then connecting the two residues together via six oxygen atoms which lie on a mirror plane.

The oxygen atoms in ClO_4 tetrahedra can be divided into two types: those each shared by two equatorial WO_6 octahedra with Cl-O bond lengths (1.42-1.47Å) being consistent with 1.41-1.48Å in other ClO_4 groups (taken from "International Tables for X-ray Crystallography",1962,Vol III), and those each shared by three polar WO_6 octahedra, with Cl-O

distances (1.49 and 1.55Å) being somewhat longer due to the large ligancy of this kind of oxygen atoms. Infrared spectrum shows the characteristic stretching vibration band of Cl(VII)-O at 1091.3 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 $[P_2W_{18}O_{62}]^{6-}$ (Pope,M.T.(1967). Inorg.Chem. 6,1147). The W-O bond lengths extend from 1.59 to 2.54Å, which is wider than 1.85-2.35Å in $[P_2W_{18}O_{62}]^{6-}$ (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.
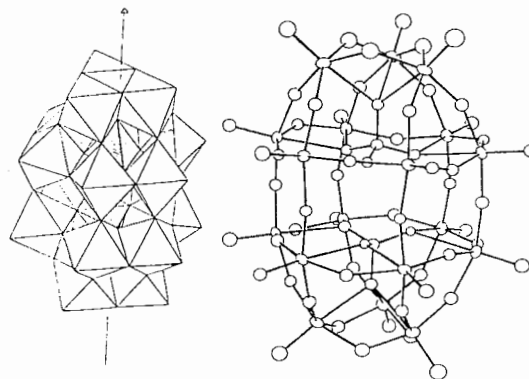

Figure 1. The structure of the anion $[Cl_2W_{18}O_{62}]^{3-}$

PS-08.04.06

MERCUROUS HALIDES by Brahama 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 Hg_2F_2, Hg_2Cl_2, Hg_2Br_2 & Hg_2I_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 251pm 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 cm^{-1} & 113 cm^{-1}(J.R.Durig, K.K.Lau,G. Nagarajan, M.Walker, J.Bragin(1969) J. Chem. Phys.<u>50</u>, 2130). These experimental observations substantiate the differing nature of the Hg--Hg bond in the series. For Hg_2F_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 350-400nm range gives the red-brown color to Hg_2I_2. This is the right