

08.2-7 SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW NON-CENTROSYMMETRIC  $\beta$ -OCTAMOLYBDATE. By P. Román<sup>a</sup>, J. M. Gutiérrez-Zorrilla<sup>a</sup>, M. Martínez-Ripoll<sup>b</sup>, and S. García-Blanco<sup>b</sup>. <sup>a</sup>Departamento de Química Inorgánica, UPV/EHU, Apartado 644.48080 Bilbao, Spain. <sup>b</sup>UEI de Cristalografía, Instituto Rocasolano, CSIC, Serrano 119, 28006 Madrid, Spain.

Four compounds with the general formula:  $(3\text{-MepyH})_x(3\text{-EtpyH})_{4-x}[\text{Mo}_8\text{O}_{26}] \cdot n\text{H}_2\text{O}$  ( $x = 0-4$ ;  $n = 0, 1$ ) have been prepared. Three of them are isostructural ( $x = 0, 2, 4$ ;  $n = 0$ ) and crystallize in the monoclinic system, space group  $P2_1/n$ ,  $Z = 2$ . Parameters for the compound  $x = 4$  are  $a = 13.652(2)$ ,  $b = 10.887(1)$ ,  $c = 13.759(1)$  Å.  $\beta = 90.87(1)^\circ$ ,  $V = 2044(4)$  Å<sup>3</sup>,  $D_x = 2.53$ ,  $D_o = 2.54(1)$  Mg/m<sup>3</sup>. Only slight differences in cell dimensions have been observed when  $x = 0$  or 2.

A non isomorphous compound with the formula  $(3\text{-MepyH})_3(3\text{-EtpyH})[\text{Mo}_8\text{O}_{26}] \cdot \text{H}_2\text{O}$  (**1**) ( $x = 3$ ;  $n = 1$ ) crystallizes in the triclinic system, space group  $P\bar{1}$ ,  $Z = 2$ ,  $a = 10.918(1)$ ,  $b = 10.985(3)$ ,  $c = 18.991(2)$  Å,  $\alpha = 97.19(2)$ ,  $\beta = 91.45(2)$ ,  $\gamma = 107.30(2)^\circ$ ,  $V = 2152.8(7)$  Å<sup>3</sup>,  $D_x = 2.456$ ,  $D_o = 2.456(1)$  Mg/m<sup>3</sup>,  $R = 0.055$  and  $R_w = 0.073$  for 6277 observed reflexions.

Thermo gravimetric studies show that the isostructural compounds are anhydrous while the non isomorphous compound contains one water molecule. Ir spectra indicate that the organic bases are protonated and the polyanion presents the well-known infrared spectrum for  $\beta$ -octamolybdates in solid state.

The distinguishing features of compound (**1**) are its non-centrosymmetric polyanion and its extensive hydrogen bonding. The asymmetric unit contains three independent 3-methylpyridinium and one 3-ethylpyridinium cations, one water molecule and the  $\beta$ -octamolybdate anion.

The planar cations are oriented to permit hydrogen bonds with either molybdate oxygen atoms or water oxygen atoms. Four different types of hydrogen bonds have been found:  $\text{N-H} \cdots \text{O}$ ;  $\text{N-H} \cdots \text{Ow}$ ;  $\text{Ow-Hw} \cdots \text{O}$ ; and  $\text{C-H} \cdots \text{O}$ .

The  $\text{MoO}_6$  octahedra are distorted and the degree of distortion has been estimated using different equations (P. Román et al. Transition Met. Chem., in press).

08.2-8 STRUCTURES OF THREE SODIUM-CALCIUM-GERMANATES. F. Nishi, Saitama Institute of Technology, 1690, Fusaiji, Okabe, Saitama  $\mp$ 369-02, and Y. Takéuchi, Department of Geological Sciences, Nihon University, Sakurajousui 3-25-40, Setagaya-ku, Tokyo  $\mp$ 156, Japan

Three new crystalline phases in the  $\text{Na}_2\text{O-CaO-GeO}_2$  system were synthesized at around 1500 K and their crystal structures have been studied based on single-crystal diffraction intensities. They include (1) a cubic phase,  $a = 15.626(3)$  Å,  $\text{Pa}\bar{3}$ ,  $\text{Na}_{1.5}\text{Ca}_{1.5}\text{Ge}_3\text{O}_{12}$ ,  $Z = 16$ , (2) a rhombohedral phase,  $a = 10.788(2)$ ,  $c = 13.460(2)$  Å,  $R\bar{3}m$ ,  $\text{Na}_{3.0}\text{Ca}_{1.5}\text{Ge}_3\text{O}_{12}$ ,  $Z = 6$ , and (3) a trigonal phase,  $a = 10.780(2)$ ,  $c = 13.449(2)$  Å,  $P\bar{3}21$ ,  $\text{Na}_{2.5}\text{Ca}_{1.5}\text{Ge}_3\text{O}_{12}$ ,  $Z = 6$ . The structure of the cubic phase has a marked feature that it consists of twelve-membered rings of  $\text{GeO}_4$  tetrahedra (Fig. 1). Although a similar ring of  $\text{SiO}_4$  tetrahedra has been reported in  $\text{Na}_2\text{CaSi}_3\text{O}_{12}$  (Fischer and Tillmanns, Z. Krist. 166, 245, 1984), the ring in structure (1) is considerably distorted compared to the reported silicate ring. The remaining two phases contain six-membered rings of  $\text{GeO}_4$  tetrahedra and they are based on a structural scheme which is basically similar with that of the structures of sodium calcium silicates reported by Ohsato, Maki and Takéuchi (Acta Cryst., C41, 1575, 1985; Ohsato, Takéuchi and Maki, Acta Cryst., C42, 934, 1986). There are, however, notable differences between germanates (2,3) and the silicates. Firstly, splittings, which were found only for a symmetrical set of oxygen atoms in the silicates, occur for more than a set of oxygen atoms in our germanates. Secondly, a new site for Na, which is missing in the silicates, has been found in our structures.

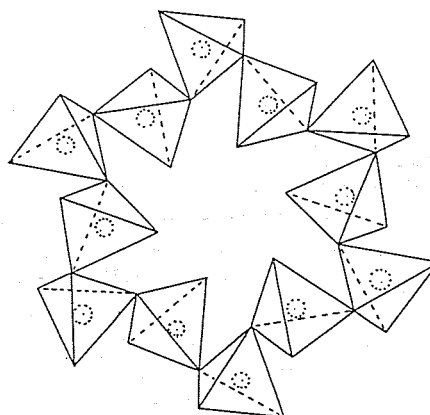


Fig. 1. The configuration of the 12-membered ring of  $\text{GeO}_4$  tetrahedra in the cubic phase, viewed down  $[1 \bar{1} 1]$ .