

08.2-56 CRYSTAL STRUCTURE OF PIPERAZINE HEXACHLORODICUPRATE (II). By A. Daoud, Laboratoire de Chimie du Solide, E.N.I.S., Sfax, Tunisie, and D. Tran Qui, Laboratoire de Cristallographie, C.N.R.S., associé à l'U.S.M.G. 166X, 38042 Grenoble Cedex, France.

Magnetic study of the title compound $C_4H_{12}N_2Cu_2Cl_6$ (HCCP) has suggested a 1-D interaction behavior probably due to copper chain. However, no orbital interpretation and exchange parameter have been proposed or calculated owing to the lack of structural data. In order to understand this exchange parameter, single crystals of this complex were grown into suitable size for X-Ray experiment and its crystal structure has been determined using heavy atom method.

HCCP crystallizes in triclinic system, space group $P\bar{1}$; the lattices parameters are:

$a = 6.081(3)$, $b = 7.041(3)$, $c = 7.971(3)\text{\AA}$,
 $\alpha = 81.14(6)$, $\beta = 79.80(3)$ and $\gamma = 68.951(7)$,
 with $Z = 2$.

Least squares refinements of the structure were carried out to conventional and weighted R-factors, respectively 0.023 and 0.026 for 1535 reflections ($AgK\alpha$). The structure of HCCP consists of (Cu_2Cl_6) polyhedra weakly linked together by edge sharing to form an infinite chain along the a axis. The Cu^{2+} coordination is a square pyramid with four short and one long Cu-Cl distances (2.265(2) to 2.321(2) \AA and 2.606(2) \AA). The stability of copper chain is found to be ensured by short hydrogen bonding N-H...Cl.

08.2-57 ADAMANTYLAMINE AS GUEST MOLECULE IN CLATHRASILS. By H. Gies and B.-S. Zhang, Mineralogisches Institut der Universität, D 23 Kiel, FRG.

In recent years clathrate compounds with three different silica frameworks have been synthesized (Gerke et al., Z. Anorg. Allg. Chem. (1983), submitted). In the presence of adamantylamine as structure-determining guest molecule the dodecasil 1H framework is stabilized.

The crystal structure of that compound, $34SiO_2 \cdot 3M^{12} \cdot 12M^{20}$, has been refined in space group $P6/mmm$ with $a = 13.825\text{\AA}$ and $c = 11.189\text{\AA}$ and 767 symmetry independent reflexions to residual values of $R = 0.168$ and $R_w = 0.099$.

SiO₂ - framework: The silica framework consists of hexagonal layers of pentagondodecahedra ($[5^{12}]$ cages) which are stacked in $\bar{A}A$ sequence. This produces two additional types of cages $[4^3 5^6 6^3]$ cages and $[5^{12} 6^8]$ cages the later housing the adamantylamine guest molecule. The Si-O distances are short (1.532 \AA -1.605 \AA ; $\bar{d} = 1.565\text{\AA}$); according to Hill and Gibbs (Acta Cryst. (1979), B35, 25) this correlates with the large Si-O-Si angles (166°-180°; $\bar{\alpha} = 171.4^\circ$). These values differ significantly from the average angles and distances found in silica polymorphs (144°, 1.608 \AA respectively) but are in good agreement with those found in previously investigated clathrasils.

Guest Molecules: The $[5^{12}]$ cage and the $[4^3 5^6 6^3]$ cage (with $V = 97\text{\AA}^3$ each) can be occupied only by very small guest molecules like M^{12} , $M^{12} = O_2$, N_2 , Ar from the atmospheric air; the big $[5^{12} 6^8]$ cage ($V = 348\text{\AA}^3$) contains the adamantylamine guest molecule.

A difference Fourier synthesis $\rho(\text{obs}) - \rho(\text{Si}, O, \text{calc})$ shows that the guest molecules in the small cage are highly orientationally disordered; for the adamantylamine

guest molecule in the $[5^{12} 6^8]$ cage only four crystallographically different orientations are found. Fig. 1 shows the very good geometrical fit of the guest molecule in the cage, consistent with the very mild conditions for synthesis: aqueous solution of silica acid, adamantylamine, 160°C.

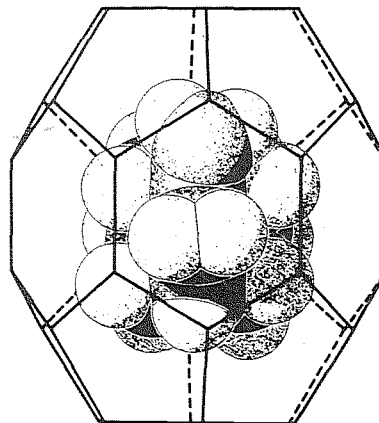


Fig. 1: Adamantylamine in the $[5^{12} 6^8]$ cage

08.2-58 THE CRYSTAL STRUCTURE OF Ga-ORTHO-PHOSPHATE. By N.M. Mustafaev, I.R. Amiraslanov, T.Z. Kulieva, G.S. Teimurov, Kh.S. Mamedov, Institute of Inorganic and Physical Chemistry, the Academy of Sciences of the Azerbaijan SSR, Narimanov prospect, 29, Baku, 370143, USSR.

The object of investigation was single crystals obtained by hydrothermal synthesis in the system $Ga_2O_3 - P_2O_5 - H_2O$ in the form of hexagonal prisms.

The cell parameters determined from photographic records and refined on automated "Syntex P2₁" single-crystal diffractometer are:

$a = 9.048\text{\AA}$, $c = 16.718\text{\AA}$,
 $V = 1185.278\text{\AA}^3$, and the space group is $P6_3$.

Three-dimensional data of 911 independent reflections were collected using the same diffractometer. The $P6_3$ space group

was established taking into account a systematically absent reflections and using Patterson analysis. The structure has been solved by a heavy atom method. The coordinates of the heavy atoms were used for calculating successive ordinary and difference electron density syntheses from which the light atoms are localized. The bases of the structure are dimers made up from two Ga- octahedra and three PO_4 - tetrahedra which are characteristic structural elements in mixed frameworks of some silicates and phosphates. The composition of one dimer is expressed by formula