**08.2—56    CRYSTAL STRUCTURE OF PIPERAZINE HEXA-CHLORODICUPRATE (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 P1; the lattices parameters are:

a = 6.081(3), b = 7.041(3), c = 7.971(3)Å, α = 81.14(6), β = 79.80(3) and γ = 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 (AgKα). 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) Å and 2.606(2) Å). The stability of copper chain is found to be ensured by short hydrogen bonding N-H...Cl.

A differenceFourier synthesis $\rho$(obs)-$\rho$(Si,0, 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.
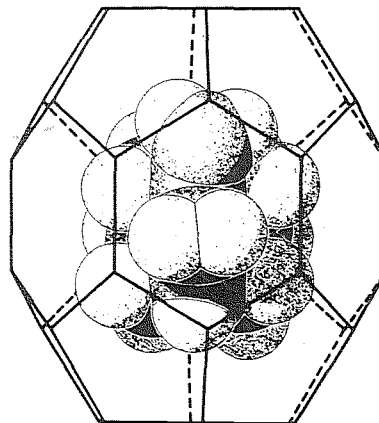


Fig. 1: Adamantylamine in the $5^{12}6^8$ cage

**08.2—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 stabilised. The crystal structure of that compound, $34SiO_2.3M^{12}.2M^{12'}.2M^{20}$, has been refined in space group P/6mmm with a=13.825Å and c=11.189Å and 767 symmetry independent reflexions to residual values of R=0.168 and $R_w$=0.099.

$SiO_2$ - framework: The silica framework consists of hexagonal layers of pentagondodecahedra ($[5^{12}]$cages) which are stacked in ĀA sequence. This produces two additional types of cages $[4^35^66^3]$cages and $[5^{12}6^8]$ cages the later housing the adamantylamine guest molecule. The Si-O distances are short (1.532Å-1.605Å; d̄=1.565Å); according to Hill and Gibbs (Acta Cryst.(1979),B35,25) this correlates with the large Si-O-Si angles(166°-180°; X̄=171.4°).These values differ significantly from the average angles and distances found in silica polymorphs (144°, 1.608Å respectively) but are in good agreement with those found in previously investigated clathrasils.

Guest Molecules: The $[5^{12}]$ cage and the $[4^35^66^3]$cage (with V≈97Å³ 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≈348Å³) contains the adamantylamine guest molecule.

**08.2—58    THE CRYSTAL STRUCTURE OF Ga-ORTHOPHOSPHATE. 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 $P2_1$" single-crystal diffractometer are: a= 9.048Å, c=16.718Å, V= 1185.278Å³, 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

$Ga_2O_6[PO_4]_3$. The dimers stringed on an two-hold axes form continuous chains along the Z axis in which the filled octahedra and the empty trigonal prisms are situated alternately. All the structure consists of a totality of indicated chains connected with each other by octahedra forming unique framework of the composition $Ga(PO_4)_2$ with large-scale spaces. It is not difficult to notice that the obtained motive as composed from Ga- octahedra and $PO_4$ - tetrahedra carries a negative

charge equal to - 3 for compensation of which positive cations are required. The crystal chemistry analysis of interatomic distances indicates that such positive cations can be only protons transforming free terminal oxygen atoms of phosphate groups into hydroxylic ions. Thus, by taking into account the hydrogen atoms and the water molecules the presence of which in the structure is also confirmed by DT analysis and which are statistically arranged in the above indicated vacancies, the structural formula can be expressed as $GaH_3(PO_4)_2$ 2,5 $H_2O$.

and Ho form zigzag chains along the axis b being connected through the general rib with the nearest symmetrically equivalent polyhedra. Such chains of Ho- polyhedra form step (zigzag) layers, parallel to planes (001),being connected by general oxygen summits between them. The layers of Ho-polyhedra being associated by general summits and ribs of Na-polyhedra, B- tethedra and hydrogen bonds between them, form the framework structure of sodium and holmium borates.

**08.2–59    THE CRYSTAL STRUCTURE OF SODIUM AND HOLMIUM BORATE.** By G.G.Jafarov, G.K.Abdullayev. The Institute of Inorganic and Physical Chemistry of the Academy of Sciences,Azerbaijan SSR, Baku, USSR.

Sodium and holmium borate $NaHo[BO_2(OH)_2]OH$ was obtained under hydrothermal conditions in the system $HO_2O_3-Na_2O-H_2O$ at 400 C. The crystals are

transparent and are of lemon-yellow colour. The habitus of the crystals changes from shortly prismatic to isometric. The crystal structure was determined by single-crystal X-ray analysis (diffractometer, Mo radiation, 890 reflections, least squares refinement with anisotropic approximation, R=0,083). The cell dimensions are: a=5,142(2), b=6,434(4), c= 6,155(3)Å, $\beta$ = 114,7(2), $Z$ = 2, dx=5,07 g/cm³, space group $P2_1/m$. The structure has been

solved by the heavy atom method. The coordinations of Ho atoms have been determined from Patterson map. The localization of the remaining atoms (Na, O and B) was carried out from Fourier and difference electron density synthesis. The crystal structure of sodium and holmium borate consists of isolated$[BO_2(OH)_2]^{3-}$

tetrahedra (B-O,1,480- 1,524Å) and coordination polyhedra of metallic cations. The sodium cations are inside the distorted bicapped trigonal prisms formed by two O atoms and six OH groups (Na-O 2,204-2,613Å). The holmium cations are also inside the distorted eight coordinated polyhedra formed by four oxygen atoms and four OH groups. (Ho- O 2,322-2,686,Å) Na

**08.2–60    STRUCTURAL ANALYSIS OF SUBSTITUTED BARIUM HOLLANDITES.** By R.W. Cheary, J. Kwiatkowska and J. Hodge. School of Physics & Materials, New South Wales Institute of Technology, Sydney, N.S.W. 2007, Australia.

The structures of a number of polycrystalline barium hollandites have been determined by x-ray and neutron diffraction using the Rietveld method. The purpose of this work is to establish the structural conditions required for the successful immobilisation of radioactive waste within this group of compounds. In cesium substituted hollandites

(viz $[Ba_xCs_y][Al_{2x+y}Ti_{8-2x-y}]O_{16}$) the structural parameters for titanium,aluminium and oxygen do not change significantly with the level of cesium substitution. The only significant change occurs in the z parameter which defines the average Cs/Ba position. This increases with the level of Cs substitution indicating that these ions tend to occupy a more central location with respect to their coordinating oxygen ions. An analysis of the (Cs/Ba)-O bond length suggests a possible limit of structural stability corresponding to 0.25 cesium ions per unit cell. Electron microprobe results indicate that the level of cesium substitution is constrained by the condition that the total volume occupied per unit cell the cesium and barium remains substantially constant. Barium hollandites containing varying proportions and types of 3⁺ ions on the octahedral sites have also been examined (viz $Ba_x[M_{2x}Ti_{8-2x}]O_{16}$, M = Al, Ga, Fe and Ti to determine how these affect the size of the barium site.