04. ATOMIC SCALE MECHANISM AND CHEMICAL PROPERTIES

04.6-7 HYDROGEN-BOND RESEARCH USING THE CAMBRIDGE STRUCTURAL DATABASE. Robin Taylor and Olga Kennard, Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

Analysis of data in the Cambridge Structural Database provides detailed information about the basic factors governing hydrogen bond geometry. H...A distances can be correlated with the nature and crystallographic environment of the donor and acceptor groups - for example, R$_3$N+H...O bonds are found to be shorter than H$_3$N-H...O bonds. Donor and acceptor angles have an energetic preference for linearity or near-linearity, particularly when the H...A distance is short. There is a slight preference for hydrogen bonding in the directions of sp$^2$ lone pairs, but it is arguable whether a similar preference exists for sp$^3$ lone pairs. Donor and acceptor valence bonds appear to be lengthened by hydrogen-bond formation, but this may be an artefact of librational freedom. Hydrogen bonds involving C-H donors or the 3-centre ("bifurcated") arrangement are more common than previously supposed.

04.6-8 CRYSTAL STRUCTURE OF $\text{Mg}^{2+}\text{AsO}_4$ COMPOUNDS AND HYDROGEN BONDING ($\text{Mg}^{2+} = \text{Mg}, \text{Mn}, \text{Ni}, \text{Cu}$ and $\text{Zn}$). By M. Chiadni and D. Tran Quí, Laboratoire de Cristallographie, C.N.R.S., associé à l'U.M.S.G., 166 X, 38042 - Grenoble Cedex, France.

Acidic orthoarsenate $\text{Mg}^{2+}\text{AsO}_4$ compounds ($\text{Mg}^{2+} = \text{Mg}, \text{Mn}, \text{Ni}, \text{Cu}$ and $\text{Zn}$) have been prepared and single crystal grown. X-ray data show that all the series members belong to space group $\text{P}2_1\text{c}$ and have very close unit cell parameters suggesting normally isomorphism between these salts. Crystal structure of $\text{CuHg(AsO}_4)\text{H}_2\text{O}$ ($a = 5.98(1)$, $b = 17.38(1)$, $c = 10.00(1)$) has been established including hydrogen positions and refined to a final $R$ factor 3.9% for 2356 reflections. The structure consists of $\text{CuHg-AsO}_4$ chain parallel to $a$-axis. $\text{D}_2\text{O}$ octahedra and $\text{AsO}_4$ tetrahedra are linked together by oxygen corners sharing. Hydrogen localizations confirm the existence of biacidic and tricarboxylic groups : $\text{AsO}_2(\text{OH})_2$ and $\text{AsO}(\text{OH})_3$.

It was also observed that the triacidic $\text{AsO}(\text{OH})_3$ orientation with respect to $\text{CuHg-AsO}_4$ chain is significantly different in $\text{CuHg(AsO}_4)\text{H}_2\text{O}$ crystal structure and in that of $\text{CuHgl(AsO}_4)\text{H}_2\text{O}$ ($a = 5.89(5)$, $b = 7.82(4)$, $c = 8.60(5)$, $\alpha = 98.17(1)$, $\beta = 97.62(3)$ and $\gamma = 98.64(10)$) has been established including hydrogen positions and refined to a final $R$ factor 3.9% for 2356 reflections. The structure consists of $\text{CuHg-AsO}_4$ chain parallel to $a$-axis. $\text{D}_2\text{O}$ octahedra and $\text{AsO}_4$ tetrahedra are linked together by oxygen corners sharing. Hydrogen localizations confirm the existence of biacidic and tricarboxylic groups : $\text{AsO}_2(\text{OH})_2$ and $\text{AsO}(\text{OH})_3$.

In acid salts of dicarboxylic acids $\text{H}_2\text{Y}$ we should expect the anion in $\text{MMY}$ to have one carboxyl group ionized, the other not. In this case the carboxyl groups are linked by H bonds, which are essentially non-symmetric; they are called $A$-type bonds [Speakman, Structure and Bonding (1972) 12, 141]. However, frequently another variant is found in which inter-carboxyl H bonds lie across crystallographic symmetry elements; according to Speakman they are classified as $B$-type bonds.

Acid salts of mono-tartaric acid display a wide variety of H-bond patterns. We already reported the mixed A/B type of $\text{KHC}_4\text{H}_4\text{O}_6\text{H}_2\text{O}$ [Kroon & Kanters, Acta Cryst. (1972) B28, 714] and the B-type acid salt $\text{NaH}_3\text{(C}_4\text{H}_4\text{O}_6)$ [Blankensteijn, Neerman, Ouwkerk & Kroon, Coll. Abstracts E.C.N. B (1983) 161].

We now have solved the crystal structure of the supersacid salt of composition $\text{Na}_2\text{(C}_4\text{H}_4\text{O}_6)$, which also appears to be of a mixed A/B type and that of $\text{LiH}_2\text{C}_4\text{H}_4\text{O}_6\text{H}_2\text{O}$ with unusual cyclic $A$-bonded carboxyl dimer formation.