

09.4-05 THE STRUCTURES OF SOME TETRAHEDRAL ZINC COMPLEXES. By G.W. Smith, BP Research Centre, Sunbury-on-Thames, UK.

The structure of basic zinc acetate, like its beryllium analogue, is known to have molecular symmetry 4_3m (Koyama and Saito, Bull. Chem. Soc. Japan (1954) 27 112) but no other structures have been reported in the intervening years. As part of an exploratory program into the chemical and structural properties of this interesting range of compounds several basic zinc carboxylates have been prepared and their crystal structures are being investigated. The structure of basic zinc t-butylacetate $Zn_4O((CH_3)_3C.CH_2.CO_2)_6$ which crystallises in space group $P2_1/n$ was refined to $R=0.086$. Unlike basic zinc acetate where molecular symmetry is fixed by crystal symmetry there are no symmetry requirements imposed on the molecule. Different orientations of the trimethyl groups destroy the overall molecular symmetry. However the molecules do adopt a form of close packing. The four zinc atoms form a nearly regular tetrahedron around the central oxygen atom with Zn-Zn distances of 3.15-3.18Å. The Zn-O distances inside the tetrahedron have a mean distance of 1.942Å and are not statistically different from the distances to the twelve oxygen atoms of the carboxylate groups where the mean is 1.944Å. There are no significant differences between the two C-O distances in each of the six butylacetate groups, which are linked to the edges of the tetrahedron, indicating that resonance is occurring. Structural details of basic zinc β -chloro pivalate $Zn_4O((CH_3)_2(CH_2Cl).C.CO_2)_6$ currently under investigation will also be reported.

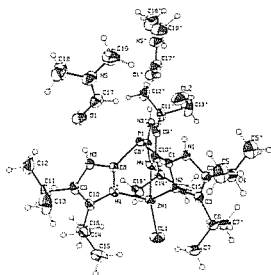
The compound crystallizes in space group $Pnma$ with $a = 10.323(5)$, $b = 18.648(9)$, $c = 22.220(15)$ Å and $Z = 4$. The crystal and molecular structure has been determined and refined to a final agreement factor $R = 0.037$ for the 2361 reflections ($CuK\alpha$ radiation) having $1 > 3\sigma(I)$.

The Zn(II) coordination sphere is similar to that of Zn in carbonic anhydrase; the N atoms of the three substituted imidazole rings and one of the chloride ions are coordinated to Zn in an approximately tetrahedral configuration. A discussion of the structure and of the results of several model-building experiments will be presented.

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09.4-06 CRYSTAL STRUCTURE OF AN ACTIVE-SITE MODEL FOR CARBONIC ANHYDRASE: [TRIS-2(4,5-DIISOPROPYLIMIDAZOLYL)PHOSPHINE]DICHLOROZINC(II). $2[N,N$ -DIMETHYLFORMAMIDE]. By R.J. Read and M.N.G. James, MRC Group in Protein Structure and Function, Department of Biochemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2H7.

The active site of the enzyme carbonic anhydrase includes a Zn(II) atom, which is coordinated to the N atoms of three histidine residues and to a solvent molecule (Kannan et al., Proc. Natl. Acad. Sci. USA 72: 51-55 [1975], Liljas et al., Nature New Biol. 235:1-7 [1972]). The title compound was synthesized as a structural analogue to this portion of the carbonic anhydrase active site and, in fact, it shows a small catalytic activity toward CO_2 hydration. (Brown et al., submitted to J. Am. Chem. Soc.)



09.4-07 TWO CD(II) WITH DIFFERENT COORDINATION NUMBERS IN THE CRYSTAL STRUCTURE OF HEXAMETHYLENETETRAMINE-CADMIUM IODIDE-WATER (2/3/4). By Thomas C.W. Mak, Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong.

As part of our investigation of the coordination properties of hexamethylenetetramine, $(CH_2)_6N_4$, we have prepared the title compound and determined its crystal structure. Crystals of stoichiometry $2(CH_2)_6N_4 \cdot 3CdI_2 \cdot 4H_2O$ are monoclinic, space group $P2_1/c$, with $a=8.114(1)$, $b=10.482(2)$, $c=19.133(2)$ Å, $\beta=107.06(4)^\circ$, $Z=2$. The structure was solved by direct methods using 3404 diffractometer measured ($MoK\alpha$) observed reflections and refined by full-matrix anisotropic least-squares to $R=0.042$.

The hexamethylenetetramine molecule makes full use of its four nitrogen lone pairs: N(1) and N(4) are coordinated to Cd(1) and Cd(2), respectively; and N(2) and N(3) accept protons from water oxygen atoms O(1) and O(2), respectively. Atom Cd(1) is situated at a center of symmetry and octahedrally coordinated by N(1), O(1), I(1), and atoms related to them by the inversion center. The configuration around Cd(2) is distorted tetrahedral, with coordination sites occupied by N(4), I(1), I(2) and I(3). Zigzag chains composed of Cd(1) coordination octahedra, Cd(2) coordination tetrahedra, and hexamethylenetetramine groups are cross-linked by hydrogen bonds involving water molecules to form a three-dimensional network.