

03.5-5 THE STRUCTURE OF A Hg(II) COMPLEX OF ADENINE N(1)-OXIDE. By M. Damodara Poojary and H. Manohar, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India.

The structure basically consists of a dimeric unit with a centre of symmetry involving two HgCl_2 and two adenine N(1)-oxide molecules.

Adenine N(1)-oxide acts as a bridging bidentate ligand coordinating through N(7) and O(1). The chloride ions link up metal ions to give a polymeric structure. Mercury has a distorted square-pyramidal coordination geometry with O(1) occupying the axial position. Three chloride ions and N(7) atom constitute the base. Hg(II) is indirectly linked to the N(6) atom through a N-H...Cl hydrogen bond.

On the basis of the present structural observations it is suggested that during Hg-DNA complexation, Hg interacts directly with N(6) by releasing a proton at pH ~9.0, thus resulting in a chelate. Earlier models, on the other hand, have implicated N(3) and O(4) atoms of thymidine as binding sites for Hg in DNA. Interesting features of the structure in relation to Hg-DNA interaction will be discussed.

Crystal data : $\text{Hg}(\text{C}_5\text{H}_5\text{N}_5\text{O})\text{Cl}_2$, monoclinic, $P2_1/n$, $a = 6.685(1)$, $b = 11.798(2)$, $c = 10.155(1)\text{\AA}$, $\beta = 100.22(1)^\circ$, $Z = 4$, 1912 observed reflections measured by diffractometer, $R = 0.074$.

03.5-6 X-RAY STRUCTURE OF (AQUO)(5'-PHOSPHOPYRIDOXYLIDENEGLYCINATO)COPPER(II) TRIHYDRATE. By S.P. Sudhakara Rao and H. Manohar, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India and R. Bau, Department of Chemistry, University of Southern California, Los Angeles, California 90089-1062, U.S.A.

The role of metal ions in nonenzymatic pyridoxal-dependent reactions of α -amino acids has been examined by a number of studies in solution. Metal-pyridoxylideneamino acid complex is an intermediate in such a reaction, the metal serving as a trap for the preformed Schiff base of pyridoxal and amino acid. The title compound crystallizes in space group $P1$ with $a = 8.394$, $b = 9.819$, $c = 10.884\text{\AA}$, $\alpha = 101.85$, $\beta = 97.48$, $\gamma = 112.60^\circ$ and $Z = 2$. The structure was solved by heavy atom method and refined by least squares to $R = 0.064$ for 1464 observed reflections.

Cu(II) ion has a square pyramidal coordination geometry. Three donor atoms from the terdentate Schiff base ligand (phenolic O, imine N and carboxylate O) and a water O constitute the base (M-L distances: 1.9-2.0 \AA). The axial site is occupied by a phosphate O of a neighbouring molecule (M-O = 2.31 \AA), resulting in a polymeric structure. Unlike in bis(pyridoxylidene-glycinato)nickel(II) complex (Rao and Manohar, XV Natl. Seminar on Crystallography, Bangalore, 1984), the ligand is nearly planar. These observations can be correlated with the lower and higher activities of Ni(II) and Cu(II) ions in nonenzymatic reactions.

03.5-7 CRYSTAL AND MOLECULAR STRUCTURE OF 7-BENZYLAMINO-2-METHYLMERCAPTO THIAZOLO[5,4-d]PYRIMIDINE. By A. De, R. Ghosh and P. Roychowdhury, Department of Physics (X-Ray Lab.), University College of Science, 92, A.P.C. Road, Calcutta-700009, INDIA.

The crystal structure of the compound has been determined from three dimensional X-ray diffraction data for 2478 unique reflections, collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromatised $\text{MoK}\alpha$ radiation with a crystal of dimensions 0.40x0.28x0.13 mm. The crystal data are: $\text{C}_{13}\text{H}_{12}\text{N}_4\text{S}_2$, $M_r = 288.399$, monoclinic, space group $P2_1/a$, $a = 8.745(2)$, $b = 13.230(8)$, $c = 11.728(2)\text{\AA}$, $\beta = 94.06(2)^\circ$, $V = 1353.5\text{\AA}^3$, $Z = 4$, $D_m = 1.43$, $D_x = 1.42$ Mg m^{-3} , $\mu = 0.37\text{mm}^{-1}$ for $\text{MoK}\alpha$ ($\lambda = 0.7107\text{\AA}$). The positions of the sulphur atoms were located from a Patterson synthesis and its phases were used to compute a difference Fourier synthesis which enabled the location of the other non-hydrogen atoms. All the hydrogen atoms were located from a subsequent difference Fourier synthesis. The structure was refined by the full-matrix least-squares (Busing, Martin and Levy, 1962) to a R of 0.035 for 1788 'observed' reflections [$I \geq 3\sigma(I)$] with all hydrogen atom parameters included in the final cycles of refinement.

03.5-8 STUDIES ON NUCLEOBASES AND THEIR DERIVATIVES: CRYSTAL STRUCTURES OF 1-((S)-2,3-DIHYDROXYPROPYL)URACIL ($\text{C}_7\text{H}_{10}\text{N}_2\text{O}_4$), 5-BROMO, 1-((S)-2,3-DIHYDROXYPROPYL)URACIL ($\text{C}_7\text{H}_9\text{N}_2\text{O}_4\text{Br}$) AND ARPRINOCID (9-(2-CHLORO-6-FLUOROBENZYL)ADENINE, $\text{C}_{12}\text{H}_9\text{N}_5\text{FCl}$) By

P. Thomas Muthiah and S.K. Mazumdar, Crystallography Division, Saha Institute of Nuclear Physics, Bidhannagar, Calcutta-64, India.

1-((S)-2,3-dihydroxypropyl)uracil (structure I) crystallizes in the space group $P2_12_12_1$ with $a = 4.719(1)$, $b = 8.882(1)$, $c = 19.768(3)\text{\AA}$ and $z = 4$; the structure was solved by direct method and refined to $R = 0.036$. 5-Bromo, 1-((S)-2,3-dihydroxypropyl)uracil (structure II) crystallizes in the space group $P1$ with $a = 6.175(2)$, $b = 7.453(2)$, $c = 5.205(1)\text{\AA}$, $\alpha = 100.00(2)$, $\beta = 102.58(3)$, $\gamma = 83.74(3)^\circ$ and $z = 1$. The structure was solved by heavy atom method and refined to $R = 0.050$. The propyl side chain is extended in these two compounds and the related aliphatic nucleoside analogues - 9-((S)2,3-dihydroxypropyl)adenine (SDPA) and 9-((RS)2,3-dihydroxypropyl)adenine (RSDPA). (G.S.D. King and L. Sengier, J. Chem. Res. (M), 1501 (1981)). The two hydroxy groups are trans with respect to each other in structures II and in SDPA, but gauche in structure I and RSDPA. In structure I, the plane defined by C(1'), C(2') and C(3') also contains O(3') and makes an angle of 70.7° with the uracil plane. In structure II, the plane defined by C(1'), C(2') and C(3') makes an angle of 97.3° with the uracil and the two hydroxy oxygen lies on

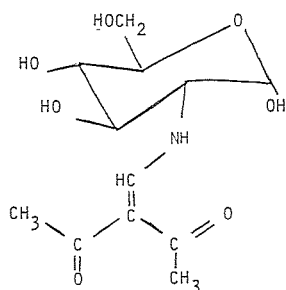
opposite sides of the plane of the propyl chain. In SDPA, the plane defined by the side chain carbon atoms makes an angle of 70° with the adenine plane where as in RSDPA, it makes an angle of 86° and also contains O(3'). Thus the molecular conformation observed is determined more by packing considerations and ease of hydrogen bond formation than by intrinsic molecular properties.

Arprinocid crystallizes in the space group $P1$ with $a = 7.967(2)$, $b = 11.251(4)$, $c = 7.484(2)$ Å and $\alpha = 93.03(2)$, $\beta = 111.36(2)$, $\gamma = 72.58(3)$ and $z = 2$. The structure was solved direct method and refined to $R = 0.105$. Each molecule participates in two types of A:A pairing simultaneously-through pairs of N(6)-H...N(1) and N(6)-H...N(7) hydrogen bonds about the two inversion centres.

The authors thank Prof. E. De Clercq for kindly supplying compound I and Drs G.V. Downing and I. Shinkai for a gift of Compound III. This work forms a part of the Ph.D. thesis of P. Thomas Muthiah. ("Crystallographic studies on some derivatives of nucleic acid bases and their complexes", Thesis, Univ. Calcutta, September 1983).

03.5-9 STRUCTURE OF 2-((2,2-DIACETYLVINYL)AMINO)-2-DESOXY- α -D-GLUCOPYRANNOSE, $C_{12}H_{19}NO_7$. By M. J. Diáñez, A. López-Castro & R. Marquez. Depto. de Optica y Sección de Física del Depto. de Investigaciones Físicas y Químicas de la Universidad de Sevilla. Centro Coordinado del C.S. I.C., Sevilla, Spain.

As a part of structural studies on enamino-esters and ketones "enaminones" the crystal structure of the title compound of formula

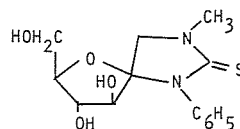


has been determined from X-Ray diffractometer data. A large number of substituted ethylenes are known where the C=C bond is significantly longer than in ethylene and the deviation from the planarity is quite appreciable (Abrahamsson, Rehnberg, Liljefors & Sandstrom. 1974; Ammon & Wheeler, 1975; Ammon, 1976; Adhikesavatu

& Venkatesan, 1981, 1982). The two main factors which determine the geometry of a push-pull system are conjugation (push-pull effect) and steric strain in the planar state. In this paper we report our findings on the molecular geometry. Crystal are monoclinic, $P2_1$ with $a = 12.495(4)$, $b = 4.632(2)$, $c = 12.394(3)$, $\beta = 93.9^\circ(1)$, $V = 715.6 \text{ \AA}^3$, $Z = 2$, $D_m = 1.33 \text{ Mg m}^{-3}$, $D_x = 1.34 \text{ Mg m}^{-3}$, $\lambda(\text{MoK}\alpha) = 0.7106 \text{ \AA}$, $\mu(\text{MoK}\alpha) = 0.13 \text{ mm}^{-1}$, $F(000) = 308$, $T = 300^\circ\text{K}$. The structure was solved by direct methods and refined by full-matrix least squares to $R = 0.052$ for 1317 reflections with $1/2\sigma(I_o)$. Bond lengths and angles of the glucopyranose group are in good agreement with accepted values. As in other structure, one of the O-C bond is slightly longer than the other one, and that is due to the anomeric effect. Results of the X-Ray analysis confirm that there is extensive electron delocalization involving the donor (N-sugar ring) and acceptor (acetyl groups). Because of the delocalization, the acceptor part of the molecule assumes a carbonion-like structure. The acetyl groups adopt an EZ conformation.

03.5-10 THE CRYSTAL AND MOLECULAR STRUCTURE OF (2R,3R,4S)-6-PHENYL-3,4-DIHYDROXY-2-HYDROMETHYL-8-METHYL-7-THIOXO-1-OXA-6,8-DIAZASPIRO-(4,4)-NONANE. By E. Moreno, A. López-Castro & R. Marquez. Depto. de Optica y Sección de Física del Depto. de Investigaciones Físicas y Químicas de la Universidad de Sevilla. Centro Coordinado del C.S.I.C., Sevilla, Spain.

The title compound has recently been synthesized in Organic Chemistry Dept. of Sevilla University. The compound of formula



was obtained by cyclation of 3-phenyl-1,3-dihydro-1-methyl-4-(D-lyxotetritol-1-yl)-2H-imidazole-2-thione, obtained by reaction of 1-amino-1-desoxy-D-fructose and phenyl-isothiocyanate. Crystals are tetragonal, space group $P4_12_1$ with 8 molecules in the unit cell of dimensions $a = b = 11.255(3)$, $c = 24.829(7)$ Å, $V = 3145.2 \text{ \AA}^3$, $D_x = 1.24 \text{ Mg m}^{-3}$, $D_m = 1.23$, $T = 300^\circ\text{K}$, $\mu(\text{MoK}\alpha) = 0.23 \text{ mm}^{-1}$, $F(000) = 1248$. The structure has been solved by direct methods from 2033 dif-