

04.5-10 'POLAR FLATTENING'; THE EFFECTIVE VAN DER WAALS SHAPES OF ATOMS BONDED TO A CARBON ATOM. By S. C. Nyburg and C. H.

Faerman, Department of Chemistry, University of Toronto, Toronto, Canada, M5S 1A1.

Using a fairly small number of crystal structures, it was shown (Nyburg and Szymański, J. Chem. Soc., Chem. Commun. (1968) p.669) that the non-bonding effective shape of a fluorine atom bound to another halogen atom was flattened at the pole. More recently, similar flattening was demonstrated for Cl, Br and I and for N in RCN (Nyburg, Acta Cryst. (1979) A35, 641).

We have now used the Cambridge Structure Data Base to retrieve all the non-bonded distances X...X where X is bound to a carbon atom for X = F, Cl, Br, I, O, S, Se and N. In most cases there is such a wealth of data that one can restrict consideration to cases where the angles C(1)-X(1)...X(2) and X(1)...X(2)-C(2) are within 10° of each other. Halving these X(1)...X(2) distances gives a reliable measure of the effective radius of X over a large range of angles measured from the pole. All the atoms studied show the same kind of flattening at the pole.

Many of the so-called 'short contacts' reported in the literature are due to this flattening and thus do not signify the presence of any unusually strong interatomic attraction.

04.6-1 THE CRYSTAL STRUCTURE OF TETRAAQUA BIS-

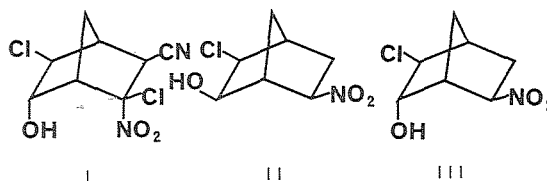
HYDROGEN MALEATE, NICKEL(II) by M.P. Gupta, A.T.H. Lenstra and H.J. Geise, Department of Chemistry (U.I.A.), Universiteitsplein 1, B-2610 Wilrijk, Belgium.

The crystal structure of title compound has been re-determined (earlier unpublished work of Gupta, M.P. and Sahu, R.D., 1982) using 1366 reflections upto $\theta(M) = 27^\circ$. The crystals are triclinic with $a = 7.309(5)$, $b = 9.751(2)$, $c = 5.170(2)$ Å, $\alpha = 105.97(1)$, $\beta = 87.12(1)$, $\gamma = 117.05(1)$ space group $P\bar{1}$ $Z = 1$, $D_c = 1.91 \text{ Mg m}^{-3}$, $D_m = 1.89 \text{ Mg m}^{-3}$. The X-ray data were refined by least square using all the reflections and the refinement converged to conventional $R = 0.030$, weighted $R_w = 0.036$. In the crystal, the maleate anions are not planar: the skeletal carbon atoms are in one plane but the end carboxyl groups are rotated out of the carbon atoms plane by 2.5° and 2.8° . The metal, at a centre of symmetry, is sixfold co-ordinated in a distorted octahedron by oxygen atoms with average Ni - O distance of 2.057 Å , two of the oxygen atoms belonging to the water molecules and one to the anion. The structure is held together by metal-oxygen linkages, van der Waals contacts and hydrogen bonds. There is an interesting scheme of a bifurcated three-center donor hydrogen bond. All the hydrogen atoms in the asymmetric unit of the unit cell were located from a difference Fourier map.

04.6-2 HYDROGEN BONDING BETWEEN NITRO AND HYDROXY GROUPS IN NORBORNYL SYSTEMS

By J.C.A. Boeyens, L. Denner and J.P. Michael Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa.

Nitro and hydroxy groups on the 2 and 6 positions of the norbornyl system adopt conformations which are determined by hydrogen bonding interaction between them. The hydrogen bonds in I, II and III have been studied by means of X-ray crystallography and spectroscopy.



An interesting intramolecular hydrogen bond exists in I. The general case for 1,3-nitroalcohols is probably one in which the functional groups are too remote for interaction. However, in the case of I, the nitro and hydroxy groups are restricted to close proximity by the norbornyl skeleton, allowing for sufficient interaction. This hydrogen bond is not bifurcated and persists in solution. A normal intermolecular hydrogen bond is present in the structure of II, whereas a bifurcated hydrogen bond is found in the structure of III. The orientations of both the hydroxy and nitro groups differ considerably, but this has been rationalised by structure analysis and force-field calculations.

04.6-3 CRYSTAL STRUCTURES OF TETRAETHYLAMMONIUM FLUORIDE-WATER (4/11) AND TETRAETHYLAMMONIUM ACETATE TETRAHYDRATE. 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 organic salt hydrates, we have determined the crystal structures of the title compounds.

Crystals of $4\text{Et}_4\text{N}^+\text{F}^- \cdot 11\text{H}_2\text{O}^*$ are orthorhombic, space group $Pna2_1$, with $a = 16.130(3)$, $b = 16.949(7)$, $c = 17.493(7)$ Å, and $Z = 4$. The structure was solved by direct methods and refined to $R_p = 0.091$ (F and O atoms anisotropic; C, N and H atoms isotropic) for 2278 observed $\text{MoK}\alpha$ data. Prominent in the structure are infinite chains of edge-sharing $(\text{H}_2\text{O})_4\text{F}^-$ tetrahedra extending parallel to the a axis. The chains are laterally linked, in both the b and c axial directions, by bridging water molecules to give a three-dimensional hydrogen-bonded anion/water framework. The ordered Et_4N^+ cations occupy the voids in two open channel systems running in the b and c directions.

Compound $\text{Et}_4\text{N}^+\text{OAc}^- \cdot 4\text{H}_2\text{O}$ crystallizes in space group $P\bar{1}$, with $a = 12.327(2)$, $b = 17.196(6)$, $c = 8.753(3)$ Å, $\alpha = 94.28(2)$, $\beta = 91.09(2)$, $\gamma = 120.30(2)^\circ$, and $Z = 4$. The structure was solved by direct methods and refined by blocked-cascade anisotropic least squares to $R_p = 0.060$ for 4803 $\text{MoK}\alpha$ data. In the crystal structure, ordered Et_4N^+ cations are sandwiched between layers of hydrogen-bonded water molecules and acetate anions. All protons in the scheme of hydrogen bonding are uniquely located.

* This corrects the previous assignment of stoichiometry and space group in Y.-S. Lam and T.C.W. Mak, J. Appl. Crystallogr. 11, 193 (1978).