

07-Crystallography of Organometallic and Coordination Compounds

239

structure (Fig.1), which is concentrated on the determination of the positions of hydrogen atoms.

In this compound the layered structure consists of infinite squared networks of $[\text{Co}(\text{HCOO})_2]_4$. Urea molecules are sandwiched between neighboring layers acting as their supporters. No direct covalent bond seems to exist between the layers of $[\text{Co}(\text{HCOO})_2]_4$ except hydrogen bonds. This would prohibit a three-dimensional exchange interaction. Two dimensionality of exchange interactions in a three-dimensional framework is practically actualized in the present crystal. Especially this monoclinic crystal indicates weak-ferromagnetism. In this structure, an asymmetric unit contains two geometrically different molecules, where a Co ion is surrounded by other Co ions of different sites in the a-b plane. Therefore the uncanceled weak-ferromagnetic moment remains even if Co ions are coupled antiferromagnetically.

We determined the positions of 20 hydrogen atoms in this crystal, by difference Fourier synthesis and least squares refinement. And we have found some different types of the hydrogen bonds in it (Fig.2). We will discuss the role of the hydrogen bonds in this crystal based on the accurate positions of hydrogen atoms.

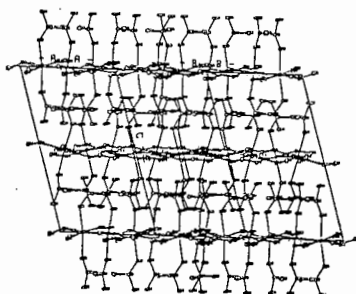


Fig. 1 the monoclinic structure of CoFoUr

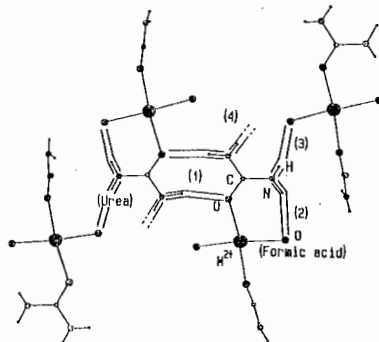


Fig. 2 Hydrogen bonds between the layers structures
TYPE of HYDROGEN BOND
(1) urea pair, (2) reconnect, (3) interlayer, (4) interlayer

PS-07.05.04 THE TRIFLUOROACETATO (AND TRIFLUOROACETATE) GROUP, CF_3COO^- (TFA). By J.T. Gleghorn and R.W.H. Small*, School of Physics and Materials, The University, Lancaster, UK.

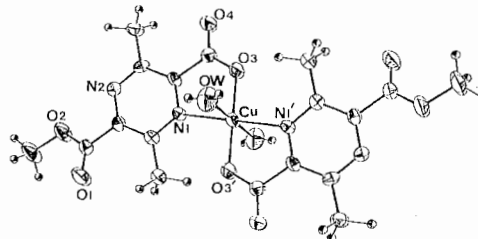
Using data from the Cambridge Structural Database, 414 separate determinations of the structure of the TFA group are reviewed. 194 published crystal structure determinations were involved. A comparison of the resulting molecular parameters is made with those obtained from theoretical calculations for the trifluoroacetate ion and trifluoroacetic acid using a basis set at the 6-

31G+** level. The TFA group was studied because of the wide variations in the reported molecular parameters, in particular the torsion angles of the CF_3 group relative to the carboxyl. Detailed plots will be shown of the distributions of the C-F, C-C and C-O distances and the angles involving the C-F bonds over the 414 structures grouped according to whether the group is mono or bidentate (173, 241 respectively). Mean parameter values and esd from the distributions of the reviewed structures are:-

C-F = 1.292(57) Å (all structures), C-C = 1.530(41) Å (all structures), projected F-C-F angle = 120° (assumed) esd 8.8° (all structures), C-O = 1.242(53) Å (bidentate structures), C-O = 1.213(38) Å (monodentate structures), C-O = 1.250(37) Å (monodentate structures). The torsion angles involving CF_3 for both mono and bidentate groups are spread over all possible values, consistent with rotational CF_3 disorder. Consequently, the uncertainty of position of the F atoms is at least 3 times greater in the azimuthal direction than radially. In the theoretical study the following molecular parameters were obtained:- in the TFA anion, C-F = 1.365 Å, C-C = 1.559 Å, C-O = 1.254 Å, barrier to rotation of CF_3 0.07 kcal/mol. For trifluoroacetic acid C-F = 1.346 Å, C-C = 1.538 Å, C-O = 1.213 Å, C-O = 1.342 Å, barrier to rotation of CF_3 0.61 kcal/mol.

PS-07.05.05 A COMPARISON OF THE CHEMISTRY OF CARBOXYLIC ACIDS OF PYRAZINE AND THEIR ESTERS WITH CuCl_2 . By Yi Wang* and H. Stoeckli-Evans, Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland.

The ligand 2,5-dicarboxylic acid-3,6-dimethyl-pyrazine on reaction with CuCl_2 at room temperature gave a green precipitate which was insoluble in water and organic solvents. Physical and chemical analyses indicate it to be a polymer. The reaction of the dimethyl ester gave a mononuclear complex (1) where one ester group has been hydrolysed to the acid which has then coordinated to the copper atom.



The reaction of the pyrazine-2,3-dicarboxylic acid with CuCl_2 at r.t. also gives a pale green precipitate, the structure of which is thought to be a polymer (Antinelli & Pâris, 1972). The same reaction with the di-ester gave a pale green-blue solid. Physical and chemical analyses lead us to believe that it is a mononuclear complex. We will report on our latest results concerning the reaction of pyrazine and pyridine esters with $\text{Cu}(\text{II})$ and other $3d$ metals. J.-P. Antinelli & M.R. Pâris, C.R. Acad. Sc., Paris, 274,C51(1972).

PS-07.05.06 A DIORGANOZINC COMPOUND WITH AN OXYGEN COORDINATED TRIGONAL PLANAR ZINC ATOM. By G.Bülow, H.-J.Gais*, and G.Raabe*, Institut für Organische Chemie, RWTH Aachen, Prof.-Pirlet-Straße 1, D-5100 Aachen, Germany.

Bis[(dimethylisopropoxysilyl)methyl]zinc ($\text{C}_{12}\text{H}_{30}\text{O}_2\text{Si}_2\text{Zn}$) crystallizes in orthorhombic space group $P2_12_12_1$ with $a=8.071(2)$,