

07-Crystallography of Organometallic and Coordination Compounds

Its composition and structure were defined by X-ray methods. Crystal structure of (III) is characterized by NH...O hydrogen bonds joining the molecules into the centrosymmetric dimer. NH₂-group of semicarbazide fragment and its oxygen atom take part in hydrogen bonds. In general the conformation of (III) is similar to that one found for free (I) (Burstein I.F., Sotman S.S., Gerbeleu N.V. et al. Kristallografiya 1990, V.35, No1, p68). Compound (IV) [Cu(I-H₂).Pz.H₂O] was obtained by interaction of (III) with copper acetate. The hydrolysis of C-N bonds in two branches of (III) transforms it into (I). Ligand (I) in the complex (IV) is coordinated to the metal through the set of donor atoms O,O,O,N in accordance to the tripode type. Copper coordination is supplemented up to the octahedron by H₂O and Pz. The distances in the coordination polyhedron are:

Cu-N(I)	2.047Å	Cu-O(I)	1.993Å
Cu-O(I)	2.339Å	Cu-N(Pz)	1.967Å
Cu-O(I)	1.967Å	Cu-O(H ₂ O)	2.438Å

In Pz radical in (III) bond distances are changed in comparison with the coordinated Pz in Pz-H radical, because of its n-conjugation with carbonyl fragment.

	Crystal data	
	(III)	(IV)
Sp.g.	Pf	Pnab
a(Å)	7.579	14.388
b(Å)	9.665	9.204
c(Å)	12.757	21.949
α(deg)	85.29	90
β(deg)	77.19	90
γ(deg)	73.71	90
Z	2	8
No of refl.	2256	2143
R(hkl)	0.048	0.051

PS-07.04.48 CRYSTAL STRUCTURES OF DICYCLOHEXYLAMMONIUM OXALATOORGANOSTANNATES. Ng Seik Weng* and V.G. Kumar Das, Institute of Advanced Studies & Department of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia.

Bis(dicyclohexylammonium) trisoxalatotetrakis(tributylstannate)·2ethanol crystallizes as a centrosymmetric chain in which four tributyltin cations are linked by three oxalato dianions; the chains are hydrogen bonded to the cation and ethanol molecules into a three-dimensional structure. The ethanol-coordinated terminal tin atom is six-coordinate in a skew-trapezoidal geometry owing to a long (2.890(3) Å) tin-oxygen coordinative bond. The oxalato group chelates to tin in bis(dicyclohexylammonium) bisoxalatodibutylstannate and in bis(dicyclohexylammonium) bisoxalato-diphenylstannate. The geometry at tin is a skew-trapezoidal bipyramid in the former and a cis-octahedron in the latter. In bis(dicyclohexylammonium) benzoatobisoxalatobenzylstannate the octahedral geometry is defined by two chelating oxalato units, the benzylic carbon atom and the esteryl oxygen atom of the monodentate benzoate ion. The ammonium cations are also hydrogen bonded to the stannate dianion to give rise to a network structure.

07.05 – Correlation with Theory, Spectra, Electron Magnetic and Other Properties

PS-07.05.01 VARIATION OF THE M-Si BOND LENGTH WITH SILICON SUBSTITUENT IN THE COMPLEXES [M(SiX₃)Cl(CO)(PPh₃)₂]. By G.R. Clark, S. Maddock, C.E.F. Rickard*, W.R. Roper, D.M. Salter and L.J. Wright. Department of Chemistry, University of Auckland, New Zealand.

The metal-silicon distance in the series of five-coordinate complexes, [M(SiX₃)Cl(CO)(PPh₃)₂], is found to be dependent on the electronegativity of the group X. Structural data is presented for: M = Os, X = Me, Cl, OH and F; and M = Ru, X = Et and OEt. There is a correlation between the M-Si bond length and the infra-red stretching frequency of the CO ligand. This correlation is presented, along with infra-red data for other complexes for which structural data is not available.

PS-07.05.02 Structural and Theoretical Calculation Studies of Cr-carbene Complexes. By Gene-Hsiang Lee*, Liang-Kuei Chou, Chih-Chieh Wang, Kin-Shing Chan and Yu Wang, Department of Chemistry, National Taiwan University, Taipei, Taiwan

Three chromium-Fischer carbene complexes, (CO)₅Cr-C(NH₂)Ph(1), (CO)₅Cr-C[N(CH₃)₂]Ph(2), and (CO)₅Cr-C(NH₂)CH₃(3) were studied by X-ray diffraction at room temperature. Compound (1): monoclinic, C 2/c, a=29.163(7), b=7.740(5), c=11.502(4) Å, β=94.71°, Z=8, R=0.048 for 2051 reflections; compound (2): triclinic, P1, a=6.714(7), b=14.814(7), c=16.022(9) Å, α=107.39(4), β=94.32(6), γ=90.11(6)°, Z=4, R=0.049 for 3955 reflections; compound (3): monoclinic, P 2/c, a=23.449(5), b=8.796(2), c=12.058(3) Å, β=90.95(1)°, Z=10, R=0.039 for 4382 reflections. The three complexes differ only by the substituents on the hetero atom N attached to carbene C atom. The Cr-C and C-N bond lengths of these three compounds do not show significant differences among them. The substituent effect on the N-atom or carbene C atom does not have a significant influence on carbene bonding. The bonding character of the three complexes is roughly the same. A related ab initio calculation is going to be discussed with the structures.

PS-07.05.03 HYDROGEN BONDS IN Co (HCOO)₂ 2(NH₂)CO By K.Nakayama*, H.Takakura, M.Fujino, N.Achiwa, N.Koyano*, and K.Yamagata^b Department of Physics, Faculty of Science Kyushu University, Higashi-ku, Fukuoka 812, Japan. *Research Reactor Institute, Kyoto University, Kumatori, Osaka-fu 590-04, Japan. ^bCollege of Science and Engineering, Iwaki Meisei university, Chuodai, Iwaki, Fukushima-ken 970, Japan.

Title compounds (abbreviated as CoFoUr) are polymorphic. Their crystal structures belong to two kinds of space group, either tetragonal P₄/2₁2 or monoclinic C2/c (Yamagata, K., Koyano, N., Ridwan, Achiwa, N., Fujino, M., Iwata, Y. & Shibuya. (1992). J. Magn. Magn. Mater. 104/108, 2557A.). Here we report the result of crystal structure analysis about CoFoUr of the monoclinic

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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.

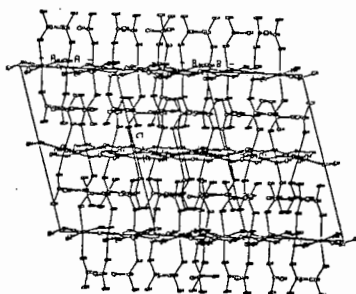


Fig. 1 the monoclinic structure of CoFoUr

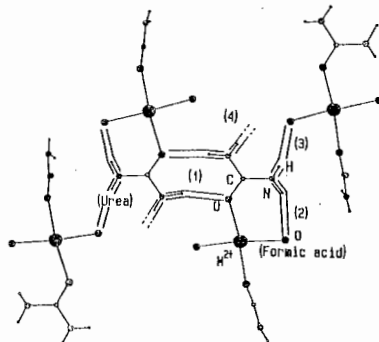


Fig. 2 Hydrogen bonds between the layers structures
TYPE of HYDROGEN BOND
(1) urea pair, (2) reconnect, (3) interlayer, (4) interlayer

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.

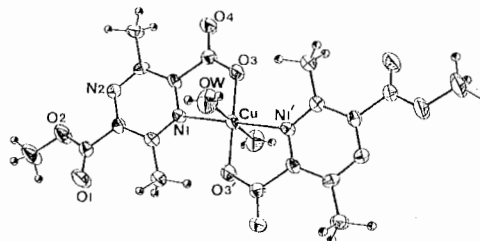
Using data from the Cambridge Structural Database, 414 separate determinations of the structure of the TFA group are reviewed. 194 published crystal structure determinations were involved. A comparison of the resulting molecular parameters is made with those obtained from theoretical calculations for 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 $a=8.071(2)$,