07-Crystallography of Organometallic and Coordination Compounds

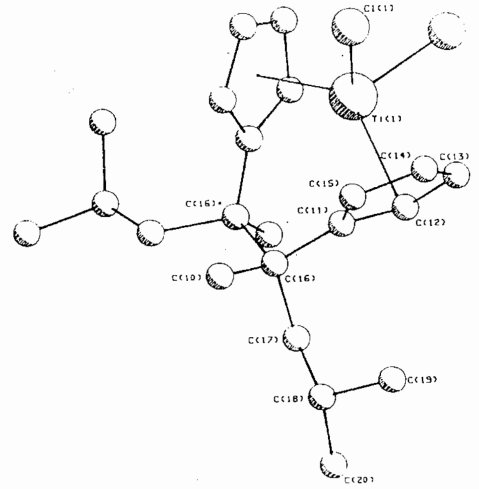
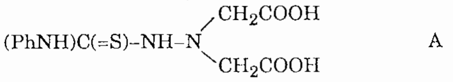


Fig. 1

PS-07.04.46 STRUCTURE OF 4-PHENYLTHIOSEMICARBAZIDE DIACETIC ACID AND ITS COMPLEXES WITH Co, Ni AND VO

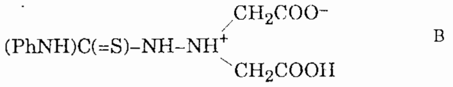
by V.Ch.Kravtsov[a], Yu.A.Simonova[a]*, J.Lipkowski[c], T.J.Malinowski[a], O.A.Bologa[b], N.V.Gerbeleu[b], V.I.Lozan[b], [a]Institute of Applied Physics and [b]Institute of Chemistry; The Academy of Science of Moldova, Kishinev, 277028 Moldova; [c]Institute of Physical Chemistry, The Academy of Sciences of Poland, Warsaw, 01224 Poland

Thio- and semicarbazide diacetic acids and their derivatives are perspective reagents as the complexones, e.g., the analogs of nitrilotriacetate. The structures of 4-phenylthiosemicarbazide diacetic acid (I-H_2L) and its complexes [Co.L(H_2O_2)]-II, [Ni.L($H_2O)_2$]-III, [VO.L.H_2O]-IV were investigated. In I the molecule framework conformation differs from that one found for dimethyl ether of semicarbazide diacetic acid (Burstein I.F., Sotman S.S., Gerbelu N.V. et al. Kristallografiya. 1990, V.35, No1, P68) and it is described by tautomeric B-form in crystal:



$$(PhNH)C(=S)\text{-}NH\text{-}N\begin{cases}CH_2COOH\\CH_2COOH\end{cases}$$

A



$$(PhNH)C(=S)\text{-}NH\text{-}NH^+\begin{cases}CH_2COO^-\\CH_2COOH\end{cases}$$

B

In H_2L the arrangement of acetate branches is defined by two NH...O intramolecular hydrogen bonds and familiar to that one revealed for nitriloacetic acid. Such a mutual arrangement of the ligand branches ensures the most favourable conditions was found in II-IV. H2L proves to be the metal through a set of donor atoms S,N,O,O. In II and III metal coordination is supplemented up to the octahedron by two water molecules, in IV - by water molecule and oxygen atom. The distances (A) in the coordination polyhedron are:

	M-S	M-N	M - O		M-H_2O	(=O)
II	2.401	2.190	2.086	2.059	2.021	2.211
III	2.365	2.099	2.097	2.027	2.021	2.129
IV	2.423	2.351	1.999	1.962	2.035	1.600

The main changes in the ligand during complexation are connected with 4-phenylgroup rotation around C-N and N-C bonds:

	I	II	III	IV
φ1	0	1.1	3.0	14.0
φ2	90	97.5	78.1	45.2

Crystal data

Sp.gr.	Pnam	P1	P1	$P2_1/n$

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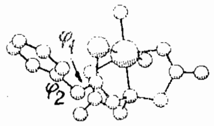


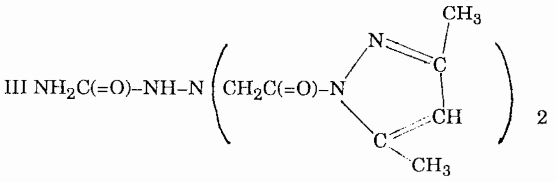
Crystal data

Sp.gr.	Pnam	P1	P1	$P2_1/n$
a(A)	13.568	15.665	15.570	6.70
b(A)	10.601	7.411	7.333	12.47
c(A)	9.647	6.673	6.668	16.95
α(deg)	90	103.12	104.49	90
β(deg)	90	95.29	94.28	90
γ(deg)	90	98.18	97.90	95.1
Z	4	2	2	4
No refl.	968	1127	3049	2014
R(hkl)	0.067	0.053	0.043	0.067

PS-07.04.47 STRUCTURE OF THE BIS-2,5-DIMETHYL-1-PYRAZOLAMIDE SEMICARBAZIDE DIACETIC ACID AND OF THE PRODUCT OF ITS INTERACTION WITH COPPER ACETATE

by T.J.Malinowski[a]*, V.Ch.Kravtsov[a], Yu.A.Simonov[a], O.A.Bologa[b], N.V.Gerbeleu [a]Institute od Applied Physics and [b]Institute of Chemistry; The Academy of Sciences of Moldova, Kishinev, 277028 Moldova

Semicarbazide diacetic acid (I)-$NH_2C(=O)NH\text{-}N(CH_2COOH)_2$ is known as a perspective complexone. Its dentation is changed from one to six in the process of the metal coordination. Dihydrazide (II)-$NH_2C(=O)NH\text{-}N(CH_2C(=O)\text{-}NH\text{-}NH_2)_2$ was obtained from (I) in order to create the new coordination centers in the ligand. III was synthesized by interaction of II with acetyl acetone:



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–H_2).Pz.H_2O] 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 H_2O and Pz. The distances in the coordination polyhedron are:

Cu–N(I)	2.047A	Cu–O(I)	1.993A
Cu–O(I)	2.339A	Cu–N(Pz)	1.967A
Cu–O(I)	1.967A	Cu–O(H_2O)	2.438A

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.	P$\bar{1}$	Pnab
a(A)	7.579	14.388
b(A)	9.665	9.204
c(A)	12.757	21.949
a(deg)	85.29	90
b(deg)	77.19	90
c(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) bisoxalatodiphenylstannate. 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(SiX_3)Cl(CO)(PPh_3)$_2$]. 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(SiX_3)Cl(CO)(PPh_3)$_2$], 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 chronium-Fischercarbene complexes, $(CO)_5Cr\text{-}C(NH_2)Ph(1)$, $(CO)_5Cr\text{-}C[N(CH_3)_2]Ph(2)$, and $(CO)_5Cr\text{-}C(NH_2)CH_3(3)$ 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(NH_2)CO By K.Nakayama*, H.Takakura, M.Fujino, N.Achiwa, N.Koyano[a], and K.Yamagata[b] Department of Physics, Faculty of Science Kyushu University, Higashi-ku, Fukuoka 812, Japan. [a]Research Reactor Institute, Kyoto University, Kumatori, Osaka-fu 590-04, Japan. [b]College of Science and Engineering, Iwaki Meisei university, Chuodai, Iwaki, Fukushima-ken 970, Japan.

Title compounds (abbreviated as CoFoUr) are polymorphic. Their crystal structurtes belong to two kinds of space group, either tetragonal $P4_12_12$ or monoclinic $C2/c$ (Yamagata, K., Koyano, N., Ridwan, Achiwa, N., Fujino, M., Iwata, Y. & ShibuyaI. (1992). J. Magn. Magn. Mater. 104/108, 2557A.) . Here we report the result of crystal structure analysis about CoFoUr of the monoclinic