

07-Crystallography of Organometallic and Coordination Compounds

$a=9.358(1)$, $b=13.408(1)$, $c=13.755(5)$ Å, space group: $Pm\bar{c}n$, $R=0.042$ for 1590 reflections. Those of the second compound are: monoclinic, $a=9.688(2)$, $b=14.157(2)$, $c=25.520(3)$, $\beta=94.72(1)^\circ$, space group: $P2_1/n$, $R=0.044$ for 3297 reflections. Those of the third compound are: monoclinic, $a=8.050(1)$, $b=12.490(2)$, $c=20.193(4)$, $\beta=95.97(1)$, space group: $P2_1/c$, $R=0.024$ for 3542 reflections. [Work was supported by National Science Council, Taiwan, China].

PS-07.04.44 THE PREPARATION AND CRYSTAL STRUCTURE OF $(C_{10}H_{21}NH_3)_2SnCl_6$. By Wei Wang*, Yonghua Lin, Laiming Li and Shiquan Xi, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China.

The Bis(*n*-decylammonium) tetrahalometallates(II) are known to crystallize in a perovskite-type bidimensional structure. They are of much current interest from both magnetic and structural points of view (K. J. Schenk, G. Chapuis, *J. Phys. Chem.*, 1988, 92, 7141). But very few studies have been performed on bis(*n*-alkylammonium) hexahalometallates(IV) with general formula $(n-C_nH_{2n+1}NH_3)_2MX_6$. Up to now, no structure of a long-chain bis(*n*-alkylammonium) hexahalometallates(IV) has been reported. We have prepared $(C_{10}H_{21}NH_3)_2SnCl_6$ (abbreviated as $C_{10}Sn$) and determined its crystal structure.

The colorless plate-shaped crystals of $C_{10}Sn$ were grown at room temperature from absolute alcohol solution containing decylammonium chloride and $SnCl_4$. Intensity data were collected using a Nicolet R3M/E diffractometer. The structure was solved by the Patterson method and final $R=0.069$ for 2148 unique reflections [$I > 3\sigma(I)$]. At room temperature the crystal is monoclinic with $a=11.960(4)$ Å, $b=7.288(2)$ Å, $c=35.602(17)$ Å, $\beta=94.05(3)^\circ$, $V=3095.30(2.02)$ Å³ and belongs to the space group $P2_1/m$ with four molecules in the unit cell. The structure of $C_{10}Sn$ is characterized by a layer of almost regular $SnCl_6^{2+}$ octahedra sandwiched between two hydrocarbon layers. The NH_3^+ polar heads of the decylammonium cations are linked to the chloride atoms by three N-H...Cl hydrogen bonds. There are two types of inequivalent hydrocarbon chains which are packed together. One has a perfectly ordered all-trans conformation, and the other has an extended conformation with only a single gauche turn between the second and the third carbon atoms. The general arrangement of the alkyl chain of $C_{10}Sn$ is comparable to the bilayer structure of biological membranes.

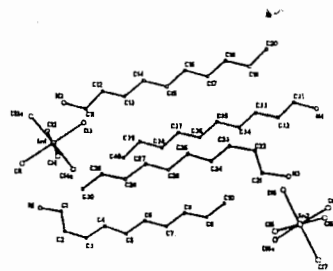


Fig. 1. Perspective view of $C_{10}Sn$.

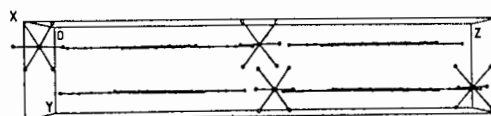


Fig. 2. Arrangement of $C_{10}Sn$ in unit cell.

PS-07.04.45 THE CRYSTAL AND MOLECULAR STRUCTURE OF [1,2-DIMETHYL-1,2-(DI-ISOBUTYL)ETHYL] BISCYCLOPENTADIENYL TITANIUM DICHLORIDE. By Zu-tao Wang, Shou-shan Chen, Ru-ji Wang and Xin-kan Yao, Central Laboratory, Institute of Elemento-organic Chemistry, Nankai University, Tianjin 300071, China.

The study of chiral bridged bis cyclopentadienylmetal complexes has now become a very active field in organometallic chemistry. We report the structure determination of a new compound $C_{22}H_{32}Cl_2Ti$ by X-ray crystallography.

A sample was recrystallized from mixed solvent of dichloromethane and petroleum ether as red transparent crystals. Intensities were collected on a CAD4 diffractometer, ω - 2θ scan mode, Mok_α in the range of $2^\circ < \theta < 25^\circ$. 2008 independent reflections were measured, of which 1344 were observed reflections with $I > 3\sigma(I)$. The intensities were corrected for L_p factors and absorption.

This compound crystallizes in the monoclinic system, space group $C2/c$ with unit cell parameters: $a = 13.217(3)$, $b = 9.496(2)$, $c = 16.449(8)$ Å, $\beta = 94.75(3)^\circ$, $v = 2057.3$ Å³, $M_r = 415.31$, $Z = 4$, $D_x = 1.34$ g/cm³, $\mu = 6.76$ cm⁻¹, $F(000) = 880$.

The structure was solved by direct method (MALTAN-82) and sequent difference Fourier syntheses. Full-matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms led to an R of 0.065 and an R_w of 0.070.

The molecule is shown in Figure 1. Its molecular structure possesses C_2 symmetry which belongs to the type of equivalent homotopic faces of cyclopentadienyl ligands (Ronald L. Halterman, *Chem. Rev.*, 1992, 92, 965-994). There is half molecule in an asymmetric unit. the second half is generated by C_2 symmetry. the dihedral angle between two cyclopentadienyl planes is 53.35° .

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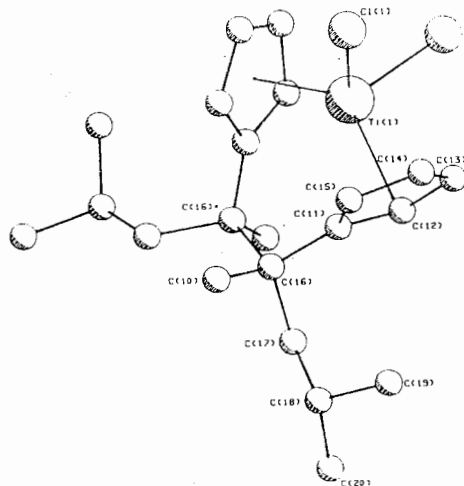
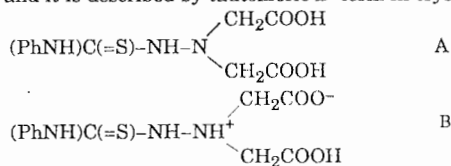


Fig. 1

PS-07.04.46 STRUCTURE OF 4-PHENYLTHIOSEMI CARBAZIDE DIACETIC ACID AND ITS COMPLEXES WITH Co, Ni AND VO by V.Ch.Kravtsov^a, Yu.A.Simonov^{a*}, J.Lipkowski^c, T.J.Malinowski^a, O.A.Bologa^b, N.V.Gerbeleu^b, V.I.Loza^b, ^aInstitute of Applied Physics and ^bInstitute of Chemistry; The Academy of Science of Moldova, Kishinev, 277028 Moldova; ^cInstitute 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-H₂L) and its complexes [Co.L(H₂O)₂]-II, [Ni.L(H₂O)₂]-III, [VO.L.H₂O]-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:



In H₂L 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 ₂ O (=O)
II	2.401	2.190	2.086	2.059
III	2.365	2.099	2.097	2.027
IV	2.423	2.351	1.999	1.962

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

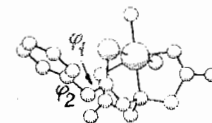
Sp.gr.	Pnam	P1	P1	P2 ₁ /n
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found in II-IV. H₂L proves to be the metal through a set of donor atoms S,N,O,O. In II and III metal coordination is supplemented up to the octahedron by two water molecules, in IV - by water molecule and oxygen atom. The distances (A) in the coordination polyhedron are:

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φ2	90	97.5	78.1	45.2



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 ^aInstitute of Applied Physics and ^bInstitute of Chemistry; The Academy of Sciences of Moldova, Kishinev, 277028 Moldova

Semicarbazide diacetic acid (I)-NH₂C(=O)NH-N(CH₂COOH)₂ is known as a perspective complexone. Its dentation is changed from one to six in the process of the metal coordination. Dihydrazide (II)-NH₂C(=O)NH-N(CH₂C(=O)-NH-NH₂)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:

