

07-Crystallography of Organometallic and Coordination Compounds

235

PS-07.04.42 THE INFLUENCE OF TEMPERATURE FACTORS ON THE DETERMINATION OF NEW CRYSTAL STRUCTURES. By Jyh-Liong Lin*, Tian-Huey Lu, Department of Physics; Wei-Jen Lan, Chung-Sun Chung, Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, China.

The importance of temperature factors on the determination of new structures, as revealed by the structure determination of thiocyanato (tetraazacyclododecane) copper(II) diaquatetrakis (isothiocyanato) calcate, has been described after a previous paper about real, symmetric and positive definite Debye-Waller factors was reviewed. In addition to the thermal and the environmental influence on the temperature factors of atomic positions, specific atomic mass influences the value of either isotropic or anisotropic Debye-Waller factors. The method to determine correct heavy atoms in a molecule by evaluating relative temperature factors is described in this report. The refinement of the atomic parameters for a Ca ion to replace a Cu(II) ion provides an example. Originally, it was thought that only Cu(II) ion exist in the crystals. The disparate temperature factors on the isothiocyanato metal ion relative to the thiocyanato copper(II) ion suggested Ca(II) ions may displace metal ions although environmental influence on the temperature factor were considered. Data at 298(3)K; $[\text{Cu}(\text{SCN})(\text{C}_8\text{H}_{20}\text{N}_4)(\text{H}_2\text{O})]_2[\text{Ca}(\text{NCS})_4(\text{H}_2\text{O})_2]$, Mr=932.25, monoclinic, $P2_1/c$, $a=8.050(1)$, $b=12.490(2)$, $c=20.193(4)$ Å, $\beta=95.97(1)^\circ$, $V=2019.3(5)$ Å³, $Z=2$, $D_x=1.533$ Mg m⁻³, $\lambda(\text{MoK}\alpha)=0.7093$ Å, $\mu=1.50\text{mm}^{-1}$, $F(000)=965.74$, $R=0.024$, $wR=0.025$ for 2976 observed reflections. The coordination geometry about Cu(II) is distorted square pyramidal with the tetraamine N atoms equatorial and thiocyanato S atoms axial. All four H atoms of the tetraamine groups are on the same side of the metal-nitrogen plane. The four donor N atoms of the macrocyclic ligand from a buckled plane, the Cu(II) ion lies 0.556 Å out of this plane towards the thiocyanato group. The four five-membered rings are in stable gauche form. Ca(II) ion is situated at a special position and is in symmetry octahedral coordination geometry. Water molecule binds

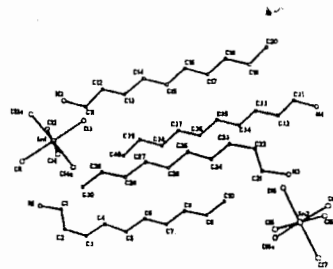
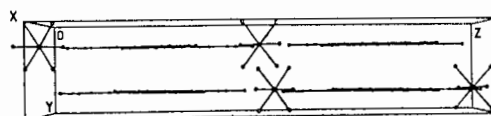
the Cu(II) molecule and the Ca(II) molecule together through hydrogen bonding. [Work was supported by National Science Council, Taiwan, China].

PS-07.04.43 THE INFLUENCE OF LIGAND ON THE STRUCTURE OF COPPER(II) COMPLEXES. By Tahir H. Tahirov, Tian-Huey Lu, Department of Physics; Wei-Jen Lan* and Chung-Sun Chung; Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, China.

Complexes of the thiocyanate ion have been extensively investigated. One aspect of these compounds which has been of interest is the mode of bonding of this ligand; either the nitrogen or the sulfur atom may be bonded to the metal ion. According to Pearson's theory, S in SCN⁻ is soft and prefers to coordinate with soft acid (class b metals), whereas N in SCN⁻ is hard and coordinates with hard acid (class a metals) (Pearson, J. Am. Chem. Soc. 1963, 85, 3533-3539; Ahrlund, Chatt & Davies, Q. Rev. Chem. Soc. 1958, 265-276). Cu(II) is on the borderline between hard and soft (Yingst & McDaniel, Inorg. Chem. 1967, 6, 1067-1068). Thus, the nature of the other ligands attached to it has a very great effect on the coordination behavior of the thiocyanato group (Wu & Chung, Inorg. Chem. 1986, 25, 3584-3587; Bennett, Clark & Goodwin, Inorg. Chem. 1967, 6, 1625-1631). In order to expand the investigation in this area, we determined the X-ray crystal structure of three macrocyclic complexes. The structure of $[\text{Cu}(\text{cyclam})(\text{NSC})]\text{SCN}$ (cyclam=1,4,8,11-tetraazacyclotetradecane) and $[\text{Cu}(\text{isocyclam})(\text{NSC})]\text{SCN}$ (isocyclam=1,4,7,11-tetraazacyclotetradecane) are distorted square pyramid with the macrocycle equatorial and the N atom of the isothiocyanato group axial. For $[\text{Cu}(\text{cyclen})(\text{SCN})(\text{H}_2\text{O})]_2[\text{Ca}(\text{NCS})_4(\text{H}_2\text{O})_2]$ (cyclen = 1,4,7,10-tetraazacyclododecane) complex, the Cu(II) ion is five-coordinated with tetraamine N atoms equatorial and thiocyanato S atoms axial. Complexes in which the four donor nitrogen atoms of the tetraamine ligand form a perfect plane, result in the formation of N-bonded isomers. As the distortion of the plane formed by the four amino nitrogen atoms increases, the S-bonded isomer becomes the more stable one. The crystal data of the first compound are: orthorhombic,

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].

Fig. 1. Perspective view of $C_{10}Sn$.Fig. 2. Arrangement of $C_{10}Sn$ in unit cell.

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.

PS-07.04.45 THE CRYSTAL AND MOLECULAR STRUCTURE OF [1,2-DIMETHYL-1,2-(DI-ISOBUTYL)ETHYL] BISCYCLOPENTADIENYL TITANIUM DICHORIDE. 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° .