

07-Crystallography of Organometallic and Coordination Compounds

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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; Ahrland, 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,