

SYNTHESIS, CRYSTAL STRUCTURE, AND PROPERTIES OF COPPER(II) COMPLEXES WITH 1,4,7-TRIS(2-AMINOETHYL)-1,4,7-TRIAZACYCLONONANE

Masahiro Mikuriya^{a*}, Mayu Hamagawa^a, Natsuki Tomioka^a, Daisuke Yoshioka^a, Naoko Uehara^a, Rika Fujimori^a, Hiroki Yamamoto^a, Yoshinari Ando^a, Shoichi Hori^a, Taro Kuriyama^a, Ryoji Mitsuhashi^a, Makoto Handa^b

^aDepartment of Applied Chemistry for Environment and Research Center for Coordination Molecule-based Devices, School of Science and Technology, Kwansai Gakuin University, 2-1 Gakuen, Sanda 669-1337, Japan

^bDepartment of Chemistry, Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue 690-8504, Japan

*e-mail: junpei@kwansai.ac.jp; phone: (+81 79) 565 8365; fax: (+81 79) 565 9729

Abstract. Three kinds of copper(II) complexes with 1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane (taetacn), [Cu(taetacn)](ClO₄)₂ (**1**), [Cu(Htaetacn)](ClO₄)₃ (**2**), and [Cu(Htaetacn)](BF₄)₃ (**3**) were synthesized and characterized by elemental analyses, IR and UV-Vis spectroscopies. The spectral features are in harmony with an octahedral geometry for **1** and a square-pyramidal coordination for **2** and **3**. The crystal structure of **2** was determined by the single-crystal X-ray diffraction method at 293 K. It crystallizes in the orthorhombic space group *Pnma* with $a = 20.605(3)$ Å, $b = 12.7944(18)$ Å, $c = 9.8972(14)$ Å, $V = 2609.2(6)$ Å³, $D_x = 1.582$ g/cm³, and $Z = 4$. The $R1$ [$I > 2\sigma(I)$] and $wR2$ (all data) values are 0.0723 and 0.2389, respectively, for all 3253 independent reflections. The compound consists of square-pyramidal copper(II) cation with protonated Htaetacn and tetrahedral ClO₄⁻ anions. The temperature dependence of magnetic susceptibilities obeyed the Curie-Weiss law with $\theta = -2.4$, -5.2 and -7.2 K for **1**, **2**, and **3**, respectively. Cyclic voltammetry of **2** in DMF showed two quasi-reversible reduction waves ($E_{pc} = -0.98$, $E_{pc} = -0.92$; $E_{pc} = -1.30$, $E_{pc} = -1.22$ V versus Fc/Fc⁺).

Keywords: copper(II) complex, magnetic properties, macrocyclic ligand, 1,4,7-triazacyclononane.

Received: October 2015/ Revised final: October 2015/ Accepted: October 2015