

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

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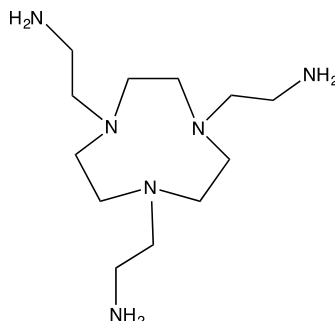
**Abstract.** Three kinds of copper(II) complexes with 1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane (taetacn), [Cu(taetacn)](ClO<sub>4</sub>)<sub>2</sub> (**1**), [Cu(Htaetacn)](ClO<sub>4</sub>)<sub>3</sub> (**2**), and [Cu(Htaetacn)](BF<sub>4</sub>)<sub>3</sub> (**3**) were synthesized and characterized 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) Å<sup>3</sup>, *D<sub>x</sub>* = 1.582 g/cm<sup>3</sup>, and *Z* = 4. The *R*1 [*I* > 2σ(*I*)] and *wR*2 (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 ClO<sub>4</sub><sup>-</sup> 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<sup>+</sup>).

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

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

## Introduction

There have been a considerable interest in coordination chemistry of macrocyclic ligands in the past five decades [1,2]. Small macrocyclic ligand, 1,4,7-triazacyclononane (tacn), is one of the most studied compounds among macrocyclic ligands [3-6] because of the too small size to incorporate metal ion in the triaza-ring, generating mononuclear metal complexes with a sandwich structure [7] and a piano-stool structure [8]. Previously, we reported on metal complexes with cyclam-based octadentate ligand having four 2-aminoethyl groups as pendant arms, 1,4,8,11-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclododecane (taec) [9-16]. The taec ligand forms unique dinuclear metal complexes, where the two metal ions are bound by the four pendant groups outside the cyclam ring. Substitution of the 2-aminoethyl pendant groups by other groups such as salicylideneaminoethyl groups also afforded similar dinuclear metal complexes [17-20]. Concerning these cyclam-based ligands with four pendant groups, the corresponding tacn-based hexadentate ligands with three pendant groups are of interest [21-23]. Especially, 1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane (taetacn), as shown in Figure 1, is interesting for us due to the comparison with the taec ligand. However, there are still only few reports on metal complexes with taetacn [21,22]. Therefore, we have been engaged in synthesis of metal complexes with taetacn and found out that a mononuclear nickel(II) complex with octahedral geometry is formed by reactions of taetacn and nickel(II) salt [24].



**Figure 1.** The hexadentate macrocyclic ligand taetacn.

In this study, we synthesized new metal complexes with taetacn from reactions of copper(II) salts and taetacn and characterized the isolated complexes. Herein we report on the synthesis, variable temperature magnetic moments, and electronic spectra of  $[\text{Cu}(\text{taetacn})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  (**1**) and  $[\text{Cu}(\text{Htaetacn})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$  (**2**), where taetacn denotes 1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane. We also report on the crystal structure and electrochemical properties of  $[\text{Cu}(\text{Htaetacn})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$  (**2**).

## Experimental

**Synthesis.** The ligand taetacn was synthesized by a reaction of tacn with *N*-(*p*-tosylsulfonyl)aziridine according to the method described in the literature [24]. Other reagents and solvents were obtained from commercial sources and were used without further purification.

### $[\text{Cu}(\text{taetacn})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**)

Copper(II) perchlorate hexahydrate (31.5 mg, 0.086 mmol) dissolved in methanol (1 cm<sup>3</sup>) was added to a methanol solution of taetacn (22.4 mg, 0.087 mmol) in methanol (1 cm<sup>3</sup>). The resulting solution was kept at ambient temperature overnight to give blue crystals. The crystals were filtered, washed with small amount of methanol, and dried *in vacuo*. Yield: 19.7 mg (43%). Anal. Found: C, 26.80; H, 6.33; N, 15.78%. Calcd for C<sub>12</sub>H<sub>32</sub>Cl<sub>2</sub>CuN<sub>6</sub>O<sub>9</sub>: C, 26.75; H, 5.99; N, 15.60%. IR (KBr):  $\nu(\text{OH})$  3569;  $\nu(\text{NH})$  3328, 3279;  $\nu(\text{CH})$  2954, 2876;  $\delta(\text{NH})$  1595;  $\nu(\text{ClO})$  1088, 625 cm<sup>-1</sup>. Diffuse reflectance spectrum:  $\lambda_{\text{max}}$  292, 694 nm.

### $[\text{Cu}(\text{Htaetacn})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ (**2**)

Copper(II) perchlorate hexahydrate (27.2 mg, 0.073 mmol) dissolved in methanol (1 cm<sup>3</sup>) was added to a magnetically stirred solution of taetacn (9.5 mg, 0.037 mmol) in methanol (1 cm<sup>3</sup>). The resulting solution was kept at ambient temperature overnight to give purple crystals. The crystals were filtered, washed with small amount of methanol, and dried *in vacuo*. Yield: 7.9 mg (32%). Anal. Found: C, 23.16; H, 5.12; N, 12.84%. Calcd for C<sub>13</sub>H<sub>37</sub>Cl<sub>3</sub>CuN<sub>6</sub>O<sub>14</sub>: C, 23.26; H, 5.55; N, 12.52%. IR (KBr):  $\nu(\text{OH})$  3546;  $\nu(\text{NH})$  3323, 3280;  $\nu(\text{NH}_3^+)$  3178;  $\nu(\text{CH})$  2944, 2884;  $\delta(\text{NH})$  1596;  $\nu(\text{ClO})$  1099, 624 cm<sup>-1</sup>. Diffuse reflectance spectrum:  $\lambda_{\text{max}}$  287, 572, 638sh, 845 nm.

Complex **2** was also prepared by reaction of taetacn and copper(II) perchlorate hexahydrate in the 1:3 mole ratio instead of the 1:2 ratio. Yield: 10.5 mg (15%). Anal. Found: C, 22.60; H, 4.81; N, 12.97%. Calcd for  $[\text{Cu}(\text{Htaetacn})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$  (C<sub>12</sub>H<sub>33</sub>Cl<sub>3</sub>CuN<sub>6</sub>O<sub>13</sub>): C, 22.54; H, 5.20; N, 13.15%. IR (KBr):  $\nu(\text{OH})$  3585;  $\nu(\text{NH})$  3322, 3280;  $\nu(\text{NH}_3^+)$  3180;  $\nu(\text{CH})$  2988, 2943, 2883;  $\delta(\text{NH})$  1596;  $\nu(\text{ClO})$  1102, 625 cm<sup>-1</sup>. Diffuse reflectance spectrum:  $\lambda_{\text{max}}$  290, 574, 640sh, 828 nm.

### $[\text{Cu}(\text{Htaetacn})](\text{BF}_4)_3 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ (**3**)

Copper(II) tetrafluoroborate hexahydrate (31.5 mg, 0.091 mmol) dissolved in methanol (1 cm<sup>3</sup>) was added to a methanol solution of taetacn (22.4 mg, 0.087 mmol) in methanol (1 cm<sup>3</sup>). The resulting solution was kept at ambient temperature overnight to give a deep blue precipitate. The precipitate was filtered, washed with small amount of methanol, and dried *in vacuo*. Yield: 40.0 mg (73%). Anal. Found: C, 24.47; H, 5.61; N, 13.24%. Calcd for C<sub>13</sub>H<sub>37</sub>B<sub>3</sub>CuF<sub>12</sub>N<sub>6</sub>O<sub>2</sub>: C, 24.65; H, 5.89; N, 13.27%. IR (KBr):  $\nu(\text{NH})$  3323, 3279;  $\nu(\text{NH}_3^+)$  3181;  $\nu(\text{CH})$  2955, 2884;  $\delta(\text{NH})$  1604;  $\nu(\text{BF})$  1053, 624. Diffuse reflectance spectrum:  $\lambda_{\text{max}}$  288, 578, 640sh, 840 nm.

Complex **3** was also prepared by reaction of taetacn and copper(II) tetrafluoroborate hexahydrate in the 1:2 and 1:3 mole ratio instead of the 1:1 ratio. Yield: 19.3 mg (36%); 22.5 mg, (42%). Anal. Found: C, 23.48; H, 5.60; N, 13.30%. Calcd for  $[\text{Cu}(\text{Htaetacn})](\text{BF}_4)_3 \cdot 2\text{H}_2\text{O}$  (C<sub>12</sub>H<sub>35</sub>B<sub>3</sub>CuF<sub>12</sub>N<sub>6</sub>O<sub>2</sub>): C, 23.27; H, 5.70; N, 13.57%. IR (KBr):  $\nu(\text{NH})$  3341, 3285;  $\nu(\text{NH}_3^+)$  3182;  $\nu(\text{CH})$  2954, 2884;  $\delta(\text{NH})$  1603;  $\nu(\text{BF})$  1082, 625 cm<sup>-1</sup>. Diffuse reflectance spectrum:  $\lambda_{\text{max}}$  282, 577, 640sh, 840 nm.

**Measurements.** Elemental analyses for carbon, hydrogen, and nitrogen were done using a Thermo-Finnigan FLASH EA1112 series CHNO-S analyzer. Infrared spectra were measured with a JASCO MFT-2000 FT-IR Spectrometer in the 4000–600 cm<sup>-1</sup> region. Electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer (Model UV-3100). Cyclic voltammetric measurements were performed using a BAS ALS-Model 1200B Electrochemical analyzer. A three-electrode cell consisting of a glassy carbon electrode, a platinum-wire counter electrode and a non-aqueous Ag/Ag<sup>+</sup> electrode was used. Ferrocene (Fc) was used as the internal standard (for Fc/Fc<sup>+</sup>, E<sub>1/2</sub> = 0.054 V vs. Ag/Ag<sup>+</sup>). Magnetic susceptibilities were measured with a Quantum Design MPMS-XL7 SQUID susceptometer operating at a magnetic field of 0.5 T over a range of 4.5–300 K. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants [25]. The effective magnetic moments were calculated from the equation  $\mu_{\text{eff}} = 2.828\sqrt{\chi_{\text{M}} T}$ , where  $\chi_{\text{M}}$  is the molar magnetic susceptibility per mole of copper(II) unit.

**X-Ray crystallography.** X-Ray diffraction data for **2** were collected on a Bruker SMART APEX CCD diffractometer (Mo K $\alpha$  radiation) at 293 K and indexed using the SMART software. Crystal data and details concerning data collection are given in Table 1. The cell parameters were refined by full-matrix least-squares on *F*<sup>2</sup>. Integrated intensity information for each reflections was obtained and corrected using the SAINT+ program package including the reduction program SAINT and the empirical absorption correction program SADABS. The structure was solved using the SHELXTL program. The structure was solved by direct methods, and the residual non-hydrogen atoms were located by D-Fourier synthesis. All of non-hydrogen atoms were refined by full-matrix least-squares on *F*<sup>2</sup>. The hydrogen atoms

except for those of water molecules were inserted at their ideal positions and fixed there. All of the calculations were carried out on a Windows 7 Core i5 computer utilizing the SHELXTL software package [26] and SHELXL-2014/7 [27]. CCDC 1417656 for **2** contains supplementary crystallographic data for this paper. The data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB12 1EZ, UK; fax: (internet.) +44 1223 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

Table 1

## Crystal and experimental data.

Parameter	Value
Chemical formula	C <sub>12</sub> H <sub>31</sub> Cl <sub>3</sub> CuN <sub>6</sub> O <sub>12</sub>
Formula weight	621.32
Temperature, (K)	293
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
<i>Z</i>	4
<i>a</i> , (Å)	20.605(3)
<i>b</i> , (Å)	12.7944(18)
<i>c</i> , (Å)	9.8972(14)
<i>V</i> , (Å <sup>3</sup> )	2609.2(6)
<i>D<sub>x</sub></i> , (g/cm <sup>3</sup> )	1.582
Radiation: Mo Ka, λ, (Å)	0.71073
μ (Mo Ka), (mm <sup>-1</sup> )	1.208
<i>F</i> (000)	1284
Crystal size, (mm <sup>3</sup> )	0.60 x 0.30 x 0.30
No. of reflections collected	15491
No. of independent reflections	3253
θ range for data collection, (°)	1.977 - 28.528
Data/Restraints/Parameters	3253/0/167
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.955
<i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0723, <i>wR</i> 2 = 0.2199
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0990, <i>wR</i> 2 = 0.2389
(Δ/σ) <sub>max</sub>	0.023
(Δρ) <sub>max</sub> , (eÅ <sup>-3</sup> )	0.826
(Δρ) <sub>min</sub> , (eÅ <sup>-3</sup> )	-0.411
Measurement	Bruker Smart APEX CCD diffractometer
Program system	SHELXTL
Structure determination	Direct methods (SHELXS-97)
Refinement	full matrix least-squares (SHELXL-2014/7)
CCDC deposition number	1417656

## Results and discussion

The taetaen ligand was reacted with copper(II) perchlorate in a molar ratio of 1:1, 1:2, and 1:3 in methanol. Only the 1:1 ratio case afforded a 1:1 complex, [Cu(taetaen)](ClO<sub>4</sub>)<sub>2</sub> (**1**), whereas a protonated complex, [Cu(Htaetaen)](ClO<sub>4</sub>)<sub>3</sub> (**2**), was isolated for the 1:2 and 1:3 cases. Single crystals suitable for the X-ray structure analysis were obtained from the methanol solution of **2**, and the crystal structure was determined by the X-ray diffraction method. The formulation of mononuclear species of **1** and **2** was confirmed by the elemental analysis, infrared and electronic absorption spectroscopies, and magnetic susceptibility measurements (4.5–300 K).

In the infrared spectra of the perchlorate complexes, **1** and **2**, two N-H stretching vibration bands of the 2-aminoethyl pendant groups were observed at 3328–2323 cm<sup>-1</sup> and 3280–3279 cm<sup>-1</sup>. These two bands can be assigned to the antisymmetric ν<sub>as</sub>(NH<sub>2</sub>) and symmetric ν<sub>s</sub>(NH<sub>2</sub>) vibrations, respectively. In the case of **2**, another N-H stretching band due to NH<sub>3</sub><sup>+</sup> was observed at 3178–3180 cm<sup>-1</sup>, in accordance with the presence of the protonated 2-aminoethyl pendant group. Stretching band of the perchlorate ion appeared as a strong broad band at around 1088–1102 cm<sup>-1</sup>. Small splitting of the band suggests no coordination of the perchlorate ions to the copper center [28]. The infrared spectrum of the tetrafluoroborate complex **3** shows a similar spectral feature to that of the perchlorate **2** with ν<sub>as</sub>(NH<sub>2</sub>) at 3323–3341 cm<sup>-1</sup>, ν<sub>s</sub>(NH<sub>2</sub>) at 3279–3285 cm<sup>-1</sup>, ν(NH<sub>3</sub><sup>+</sup>) at 3181–3182 cm<sup>-1</sup> and ν(BF<sub>4</sub><sup>-</sup>) at 1053–1082 cm<sup>-1</sup>.

The diffuse reflectance spectra of **1** and **2** are shown in Figure 2. In the spectra of **1**, one absorption band appeared at around 694 nm in the visible region. This band may be attributed to d-d transition (<sup>2</sup>E<sub>g</sub> → <sup>2</sup>T<sub>2g</sub>) of an octahedral

copper(II) ion. On the other hand, three bands appeared in the visible region of the spectra of **2**. The band at 572 nm may be assigned to spin-allowed  ${}^2B_1 \rightarrow {}^2E$  transition, a shoulder at 638 nm to a spin-allowed  ${}^2B_1 \rightarrow {}^2B_2$  transition, and a band at around 845 nm to spin-allowed  ${}^2B_1 \rightarrow {}^2A_1$  transition [29]. The spectral feature is in harmony with a square-pyramidal copper(II) ion. The electronic spectra of **1** and **2** in  $H_2O$  become a little similar to each other, although keeping the difference between **1** and **2** in the solid state to some extent in the visible region [**1**: 275 nm ( $\epsilon = 4600 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ), 606 nm ( $\epsilon = 130 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ); **2**: 275 nm ( $\epsilon = 4300 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ), 578 nm ( $\epsilon = 160 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ), and 802 nm ( $78 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ )]. The diffuse reflectance spectrum of **3** is similar to that of **2**, suggesting the similar square-pyramidal geometry of the copper(II) ion in **3**.

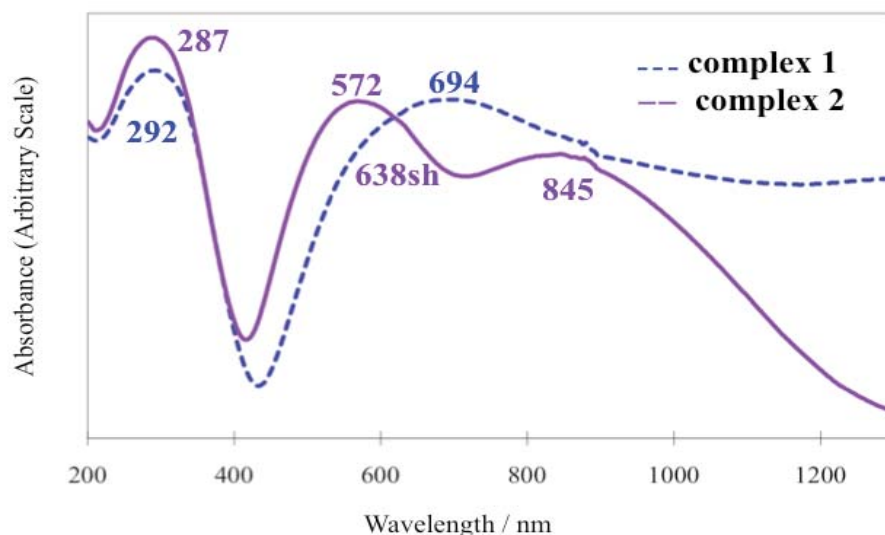


Figure 2. Diffuse reflectance spectra of **1** and **2**.

In the crystal, the asymmetric unit consists of one half of  $[Cu(Htaetacn)]^{3+}$  cation, and one and a half of  $ClO_4^-$  ions. The complex cation structure drawn by ORTEP program is shown in Figure 3. The molecule has a crystallographic mirror plane intersecting the Cu1, N1, C4, C5, and N4 atoms. In the cation, the copper(II) atom is coordinated by three amino nitrogen atoms of tacn moiety and two amino nitrogen atoms of the pendant groups in a distorted square pyramid.

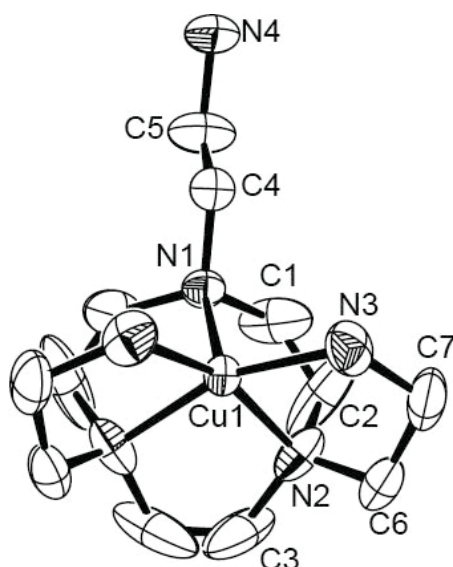


Figure 3. ORTEP drawing of the structure of the copper complex showing the 50% probability level thermal ellipsoids.

Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): Cu1-N1 2.242(5), Cu1-N2 2.015(4), Cu1-N3 2.012(4); N1-Cu1-N2 83.52(17), N1-Cu1-N3 112.73(17), N2-Cu1-N3 85.4(2), N2-Cu1-N2 $^i$  84.9(3), N2-Cu1-N3 $^i$  160.0(2), N3-Cu1-N3 $^i$  98.1(3). Symmetry code: (i)  $x, 1/2 - y, z$ .

It is to be noted that one pendant arm is protonated and does not take part in coordination to the metal atom. This is in contrast with the case for  $[\text{Ni}(\text{taetacn})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ , where the metal atom takes an octahedral geometry with three pendant amino groups [24]. The axial Cu1-N1 distance (2.242(5) Å) is considerably longer than those with the basal Cu-N distances (2.012(4) and 2.015(4) Å). The  $\tau$  value is 0.0, showing the square-pyramidal geometry around the copper atom [30]. In the crystal, the protonated amino nitrogen atom N4 is surrounded by four perchlorate-oxygen atoms by hydrogen bonds  $[\text{N4} \cdots \text{O3} (x, y, 1+z) 2.965 \text{ \AA}, \text{N4} \cdots \text{O7} (x, y, 1+z) 3.065 \text{ \AA}]$  (Figure 4).

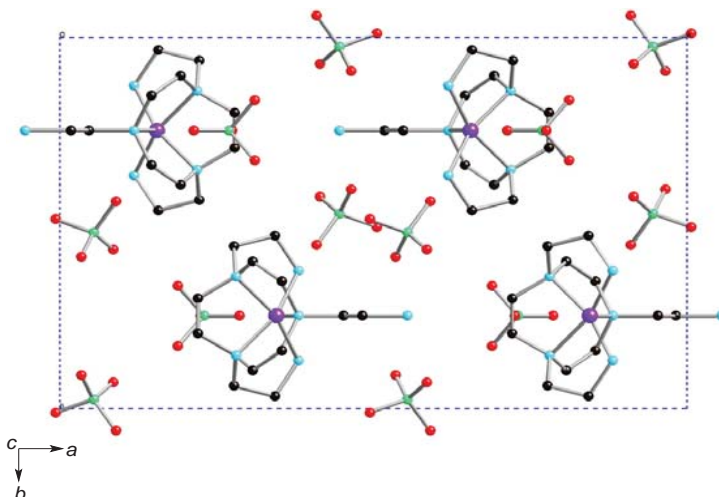


Figure 4. Packing diagram of **2** viewed along the *c* axis. Hydrogen atoms are omitted for clarity.

The magnetic moment of **1** is  $1.96 \mu_B$  at 300 K. This value is larger than the spin-only value of copper(II) ( $1.73 \mu_B$ ,  $S = 1/2$ ), being typical for the octahedral copper(II) complexes due to spin-orbital coupling with the excited *T* state [18]. The moment decreases slightly with the lowering of temperature, reaching a value of  $1.86 \mu_B$  at 4.5 K. In Figure 5, magnetic susceptibilities and inverses of magnetic susceptibilities of **1** were plotted versus temperature. As can be seen in Figure 5, the magnetic data obey the Curie-Weiss law,  $\chi = C/(T - \theta)$ , with a small Weiss constant ( $\theta = -2.4 \text{ K}$ ,  $C = 0.481 \text{ cm}^3\text{Kmol}^{-1}$ ). This result shows that magnetic interaction between copper(II) ions is weak. The magnetic moments of **2** and **3** are  $2.02$  and  $2.04 \mu_B$ , respectively, at 300 K and decrease to  $1.78$  and  $1.81 \mu_B$ , respectively, at 4.5 K, with the lowering of temperature. The magnetic data obey the Curie-Weiss law (**2**:  $\theta = -5.2 \text{ K}$ ,  $C = 0.527 \text{ cm}^3\text{Kmol}^{-1}$ ; **3**:  $\theta = -7.2 \text{ K}$ ,  $C = 0.515 \text{ cm}^3\text{Kmol}^{-1}$ ), similarly to **1**.

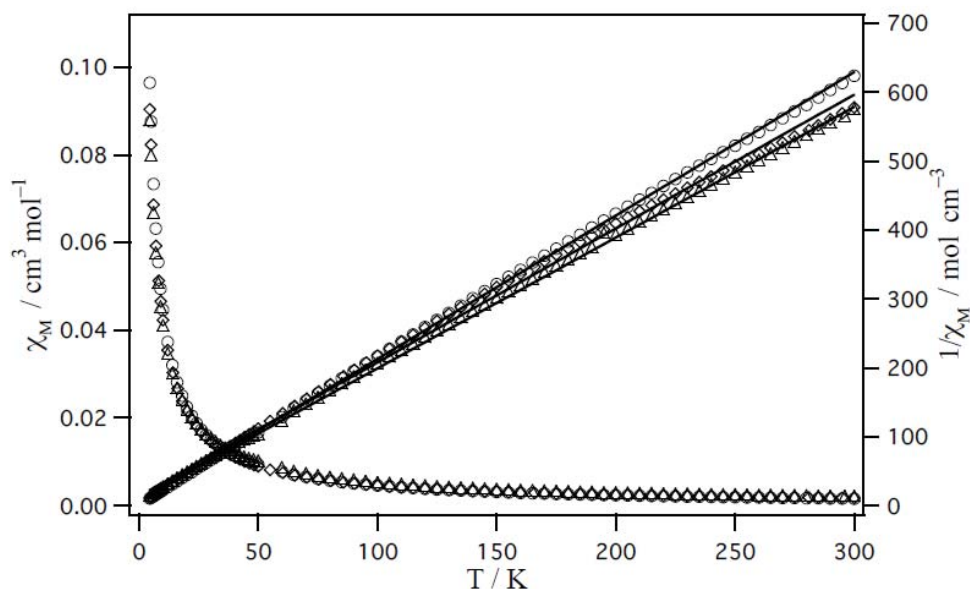
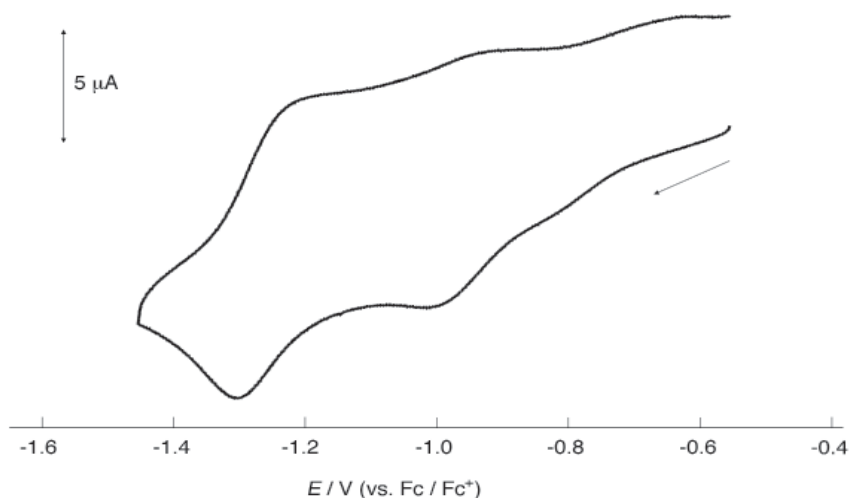


Figure 5. Temperature dependence of magnetic susceptibilities and inverse magnetic susceptibilities for **1** (circles), **2** (triangles) and **3** (diamonds).

The cyclic voltammogram of **2** was measured in DMF containing tetrabutylammonium perchlorate (0.1 M), (Figure 6). In the  $-0.6$  to  $-1.5$  V versus Fc/Fc<sup>+</sup> region, two reduction waves are observed. Both the reduction waves have the characteristic of an electrochemically quasi-reversible couples ( $E_{pc} = -0.98$ ,  $E_{pa} = -0.92$ ,  $E_{1/2} = 0.95$  V versus Fc/Fc<sup>+</sup>;  $E_{pc} = -1.30$ ,  $E_{pa} = -1.22$ ,  $E_{1/2} = -1.26$  V versus Fc/Fc<sup>+</sup>). The former may be assigned to the Cu(II)/Cu(I) couple for the square-pyramidal copper(II) and the latter may be due to the Cu(II)/Cu(I) couple for the octahedral copper(II) center, suggesting the existence of the two species in solution as found in solution spectra. This is in contrast with the case for the nickel(II) complex with taetacn, which shows only one species in solution [24].



**Figure 6.** Cyclic voltammogram of **2** in DMF: [complex] = 0.001 M, [TBAP] = 0.2 M (TBAP = tetrabutylammonium perchlorate), scan rate = 100 mV S<sup>-1</sup>.

## Conclusions

By using taetacn ligand, synthesis of mononuclear copper(II) complexes, [Cu(taetacn)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, [Cu(Htaetacn)](ClO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O, and [Cu(Htaetacn)](BF<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O, was accomplished in this study. The analytical data, infrared spectra, UV-vis-NIR spectra, and temperature dependence of magnetic susceptibilities are consistent with mononuclear structures with octahedral and square-pyramidal geometries for these systems.

## Acknowledgements

The present work was partially supported by Grant-in-Aid for Scientific Research No. 26410080 from the Ministry of Education, Culture, Sports, Science and Technology (MEXT, Japan) and the MEXT-Supported Program for the Strategic Research Foundation at Private Universities, 2010—2014.

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