ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 10, pp. 776–779. © Pleiades Publishing, Ltd., 2009.

Synthesis and Crystal Structure of a Cu(II) Complex $Cu_2(Endc)_2(Bipy)_2$ and its Photoluminescence Properties[1]

E. J. Gao*, S. Ma, Y. Huang, H. Y. Liu, F. C. Liu, and Q. Z. Shi

Laboratory of Coordination Chemistry, Shenyang Institute of Chemical Technology, Shenyang, 110142, P.R. China

**e-mail: ejgao@yahoo.com.cn*

Received January 14, 2009

Abstract–A novel Cu(II) complex $Cu_2(Endc)_2(Bipy)_2$ has been synthesized by the reaction of $Cu(NO_3)_2 \cdot 3H_2O$, Endc (*endo*-norbornene-*cis*-5,6-dicarboxylic acid), and Bipy (2,2-bipyridine) at room temperature. Elemental analysis, IR spectra, and X-ray single-crystal diffraction were carried out to determine the composition and crystal structure. Crystal data for this complex: triclinic, $P\bar{1}$ with $a = 9.0373(10)$, $b = 10.1637(11)$, $c = 10.5574(12)$ Å, $\alpha = 65.78(1)°$, $\beta = 72.32(2)°$, $\gamma = 73.23(2)°$, $Z = 1$, $V = 827.46(16)$ Å^3, $\rho_c = 2.160$ g/cm^3, $F(000) = 410.0$, $R = 0.0483$ and $wR = 0.0958$ independent reflections for 4468 observed ones ($I > 2\sigma(I)$).The Cu^{2+} ion is coordinated by two nitrogen atoms from the Bipy molecule and three oxygen atoms from two Endc, giving a distorted square-pyramidal coordination geometry. Two neighboring Cu^{2+} ions are bridged by a pair of bimonodentate carboxyl groups of different Endc acids, giving a centrosymmetrical binuclear structure which a Cu···Cu distance of 3.2946 Å. The photoluminescence properties of the complex were studied at room temperature. The complex displays an obvious photoluminescent emission upon excitation at 390 nm in the solid state.

DOI: 10.1134/S107032840910011X

INTRODUCTION

The design and synthesis of novel metal-organic coordination frameworks based on transition metals possessing special properties of ligand are currently attracting significant attention [1]. Owing to their fascinating topological structure, they find potential applications in many fields, such as catalysis, material science, optoelectronics, and magnetic chemistry [2–5]. Aromatic dicarboxylic acids or heterocyclic nitrogen dicarboxylic acids are good candidates for inorganic–organic hybrid crystal engineering, i.e., they could exhibit one-, two-, and three-dimensional compounds with metal ions via coordinated covalent bonds or weak interactions [6–9]. The 2.2-bipyridine (**Bipy**) and *endo*-norbornene-*cis*–5.6-dicarboxylic acid (**Endc**) are interesting ligands. Carboxylate anions of the Endc may coordinate to metal cations in versatile binding modes, such as monodentate, chelating bidentate, and bridging bidentate, generating varied and sometimes surprising molecular architectures. To our best knowledge, Endc or its metal complexes have biological activity [10]. However, the luminescence properties of Endc or its transition metal complexes have not been reported [10]. Furthermore, we designed and synthesized Endc to design and synthesize new surpramolecular compounds.

In this paper, a novel complex $Cu_2(Endc)_2(Bipy)_2$ (**I**) was synthesized and characterized by elemental analysis, IR, and crystal structure determination. Moreover, the complex exhibits an intense luminescence with an emission maximum at 418 nm upon excitation at 390 nm in solid state.

EXPERIMENTAL

Materials and Measurements

The ligand Endc was synthesized by ourselves. All reagents and solvents (beside Endc) were purchased commercially and used without further purification. Elemental analyses (C, H, and N) were performed on a model Finnigan EA 1112. IR spectra were recorded in the 4000–400 cm^{-1} region using KBr pellets on a Nicolet IR–470 instrument. The crystal determination was recorded on a Siemens Smart CCD diffractometer. Structure analysis was performed on a computer with the SHELX-97 program package.

Synthesis of endo-norbornene-cis–5,6-dicarboxylic acid

Carbic anhydride was synthesized by the reaction of maleic anhydride with cyclopentadiene in a tri-flask at 160 to 190°C until no back heat flow. The reaction was a cycloaddition to abide by the Diels-Alder rule, along with the performing of the reaction there was a transient

---

[1] The article is published in the original.

state intermediate product first, then transforming into carbic anhydride instead. It was going to a get a white precipitation after putting the mixture into diethyl ether for dissolving at room temperature. The powder without diethyl ether was volatilized and hydrolyzed into Endc in the boiling water for continuous heating [11].

*Synthesis of the Complex **I***

Water (10 ml) containing 0.1 mmol of Endc and 10 ml of ethanol involving 0.1 mmol of Bipy was mixed, and then 0.1 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ in 10 ml of water was added into the above mixture. The resultant solution was stirred, and the pH value was adjusted to 6.247 with 0.5 M KOH. The solution was continuously stirred for 5 h until the pH value was constant at 5.845. The mixture was condensed with rotatory evaporation, and 25 ml of a blue clear concentrated solution obtained was kept at room temperature. Slightly blue transparent crystals were provided after 30 days. IR spectrum (KBr; ν, cm^{-1}): 3378 s, 1631 s, 1515 m, 1424 m, 1402 m, 1376 s, 1336 s, 854 s, 818 m, 727 s.

For $C_{38}H_{32}N_4O_8Cu_2$

anal. calcd, %:	C, 57.0;	H, 4.0;	N, 16.0.
Found, %:	C, 56.8;	H, 3.8;	N, 15.5.

X-ray Structure Determination

0.18 × 0.14 × 0.10 mm was mounted on a glass fiber. X-ray diffraction intensity data were collected on a Siemens SMART CCD diffractometer equipped with a graphite-monochromatized MoK_α (λ = 0.71073 Å) radiation using an ω-2θ scan mode ($2.16 \le \theta \le 25.69$) at 293(2) K. The intensity data were corrected by Lorentz-polarization factors and empirical absorption. The structure was solved by direct methods and expanded using difference Fourier techniques. The non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were added theoretically. The structure was refined on F^2 by full-matrix least-squares techniques. All calculations were performed on a Pentium VI computer with the SHELXTL-97 [12] program package.

The crystal data and structure refinements and the selected bond lengths and bond angles are given in Tables 1 and 2, respectively.

RESULTS AND DISCUSSION

In IR spectrum of I, peaks at 1516 and 1486 cm^{-1} could be attributed to the stretching vibration of –N=C– in Bipy ligand. Two characteristic adsorption peaks of COO^- are $\gamma_{as}(COO^-)$ 1563 and $\gamma_s(COO^-)$ 1350 cm^{-1}. Generally, coordination modes of carboxylic acid could be extracted from the perk value difference between γ_{as} and γ_s [13]. Being larger than 200 cm^{-1}, the difference indicates the monodentate coordination mode of the COO^- group. On the contrary, being less than 200 cm^{-1}, it suggests a bidentate coordination mode. In the present work, a difference of 213 cm^{-1} indicates that the Endc adopts the monodentate coordination mode, which is consistent with the crystal structural analysis.

Table 1. Crystallographic data and details of the experiment and refinement of structure **I**

Parameter	Value
Formula weight	799.78
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal size, mm	0.18 × 0.14 × 0.10
a, Å	9.0373(10)
b, Å	10.1637(11)
c, Å	10.5574(12)
α, deg	65.78(1)
β, deg	72.32(2)
γ, deg	73.23(2)
V, Å^3	827.46(65)
Z	1
μ, mm^{-1}	1.348
F(000)	410.0
Reflections collected/unique ($I > 2\sigma(I)$); R_{int}	4468/3067; 0.0174
GOOF on F^2 (Δ/σ_{max})	1.078 (0.001)
Variable parameters	388
Final *R* indices ($I > 2\sigma(I)$)*	$R_1 = 0.0403$, $wR_2 = 0.0916$
R indices (all data)	$R_1 = 0.0483$, $wR_2 = 0.0958$
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	0.545/–0.292

* $w = 1/[\sigma^2(F_o^2) + (0.0664P)^2 + 0.9800P]$, $P = (F_o^2 + 2F_c^2)/3)$.

Table 2. Selected bond lengths and angles for **I**

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O(1)	1.941(2)	Cu(1)–N(1)	1.993(2)
Cu(1)–O(2)	1.983(2)	Cu(1)–N(2)	2.014(2)
Cu(1)–O(2*A*)	2.224(2)	O(2)–Cu(1*A*)	2.224(2)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)Cu(1)O(2)	89.75(9)	O(2)Cu(1)N(1)	168.59(9)
O(1)Cu(1)O(2*A*)	93.00(8)	O(1)Cu(1)N(2)	165.25(10)
O(1)Cu(1)N(1)	92.46(10)	O(2)Cu(1)N(2)	94.24(9)
N(1)Cu(1)N(2)	80.95(10)	N(2)Cu(1)O(2*A*)	101.73(9)
O(2)Cu(1)O(2*A*)	77.08(8)	N(1)Cu(1)O(2*A*)	113.95(9)

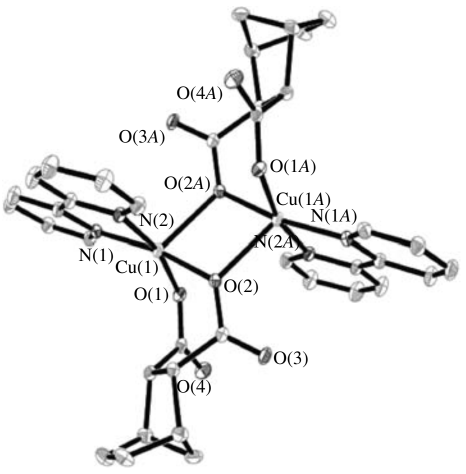

Fig. 1. Coordination environment of Cu(II) in the complex **I**.

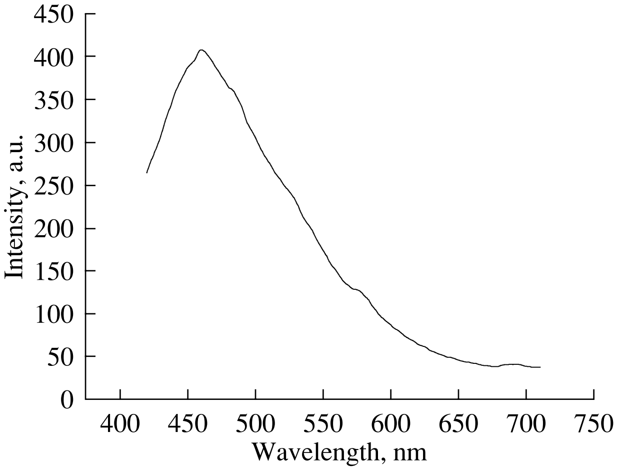

Fig. 4. Solid state photoinduced emission spectrum of the complex **I** at room temperature.

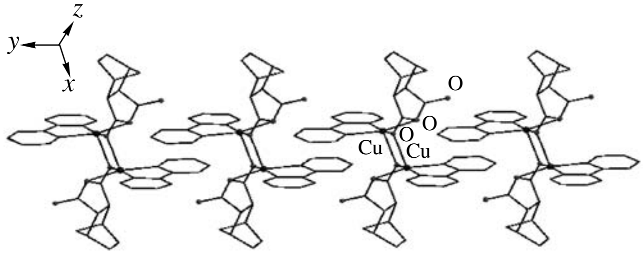

Fig. 2. One-dimensional net structure of the complex **I**.

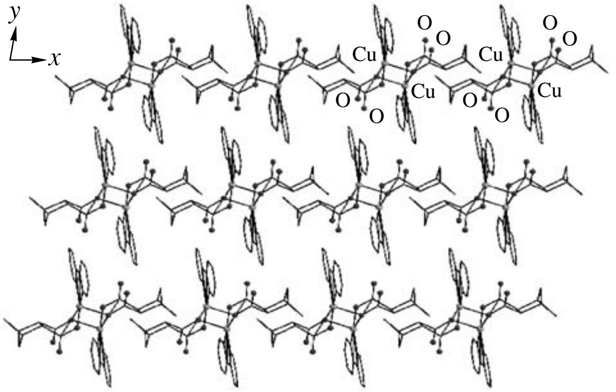

Fig. 3. Complex constructed 2D framework via π–π stacking interaction (some carbon atoms and nitrogen atoms are omitted for clarity).

As shown in Fig. 1, each Cu^{2+} center adopts an elongated square-pyramidal geometry surrounded by two N atoms from the chelating Bipy ligands (Cu(1)–N(1) 1.993(2), Cu(1)–N(2) 2.014(2) Å), and three oxygen atoms, of which one carboxyl oxygen at apical position (Cu(1)–O(2*A*) 2.224(2) Å) coordinated from one Endc and the two carboxyl oxygens (Cu(1)–O(1) 1.941(2), Cu(1)–O(2) 1.983(2) Å) coordinated from the other one. In the complex, the coordination abilities of two nitrogen atoms from Bipy are different, and the bond distances shaped by Cu(II) and nitrogen atoms (Cu(1)–N(1) and Cu(1)–N(2)) are 1.993(2) and 2.014(2) Å, respectively. The former is shorter than the latter, which is probably caused by steric hindrance and π–π stacking interactions in the molecule. A pair of Cu(II) atoms are simultaneously bridged by two O atoms from the carboxyl of two different Endc ligands, generating a binuclear structure with the distance between Cu(1) and Cu(1*A*) being 3.2946 Å.

A weak space environment exists to form hydrogen bonding in two ligands, so hydrogen bonding interactions cannot be found and the π–π stacking interactions represent the accumulation energy factor in the title complex molecules. As shown in Fig. 2, under π–π stacking interactions, a one-dimensional net structure is formed. All aromatic rings are approximately parallel to each other within Bipy ligands, the dihedral angle between two Bipy is 5.97°, and the distance of two neighboring planes is 3.528 Å on the average. As shown in Fig. 3, a 2D supramolecular network is formed through π–π stacking interactions.

The photoluminescence properties of compound **I** were studied and a strong fluorescent emission band with the maximum intensity at 418 nm upon excitation at 390 nm was observed (Fig. 4). This strong emission may be assigned to the intraligand fluorescent emission, since very similar emissions are also observed for Endc. Compared with Endc, the emission intensity of complex **I** is much stronger. This observation indicates that title complex may be an excellent candidate for potential photoactive materials.

In summary, we have synthesized and structurally characterized a novel Cu(II) complex **I**, in which the Cu···Cu distance is 3.2946 Å. This work proves that π–π stacking interactions play an important role in stability of the complex. Complex **I** may be an excellent candidate as one of advanced materials for the light-emitter applications owing to its strong fluorescence emission.

ACKNOWLEDGMENTS

We gratefully acknowledge the Natural Science Foundation of China (no. 20671064), the Natural Science Foundation of Liaoning Province (no. 20052014), the Foundation of Educational Department of Liaoning Province (no. 20060679), the Foundation of Liaoning Bai Qian Wan Talents Program (no. 2008921054) and the Phenom Foundation of Liaoning Colleges and Universities (no. 2007R30).

REFERENCES

1. Natarajan, S. and Vaidhyanathan, R., *Angew. Chem. Int. Ed.*, 2004, vol. 43, p. 1466.
2. Costes, J.-P., Dahan, F., and Wernsdorfer, W., *Inorg. Chem.*, 2006, vol. 45, p. 5.
3. Papaefstathiou, G.S., Friscic, T., and MacGillivray, L.R., *J. Am. Chem. Soc.*, 2005, vol. 127, p. 14160.
4. Kahn, O., *Molecular Magnetism*, New York: VCH, 1993.
5. Colacio, E., Ghazi, M., Kivekas, R., and Moreno, J.M., *Inorg. Chem.*, 2000, vol. 39, p. 2882.
6. Zhao, Y.J., Hong, M.C., Liang, Y.C., et al., *Polyhedron*, 2001, vol. 20, p. 2619.
7. Wang, X.L., Cao, Q., Wang, E.B., et al., *Inorg. Chem.*, 2004, vol. 43, p. 1850.
8. Wang, R.H., Xu, L.J., Li, X. S., et al., *Eur. J. Inorg. Chem.*, 2004, p. 1595.
9. Xu, Y.Q., Yuan, D.Q., Wu, B.L., et al., *Cryst. Growth Des.*, 2006, vol. 6, p. 1169.
10. Geraghtya, M., Sheridana, V., McCanna, M., et al., *Polyhedron*, 1999, vol. 18, p. 2931.
11. Gao, E.J., Sun, Y.Z., Shi, Z.L, and Zhang, J.H., *J. Shenyang Institute Chem. Technol.*, 1997, vol. 11. p. 1.
12. Sheldrick, G.M., *SHELXTLNT, Version 5.1, Program for Solution and Refinement of Crystal Structures*, Göttingen (Germany): Univ. of Göttingen, 1997.
13. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compound*, New York: John Wiley & Sons, 1986.