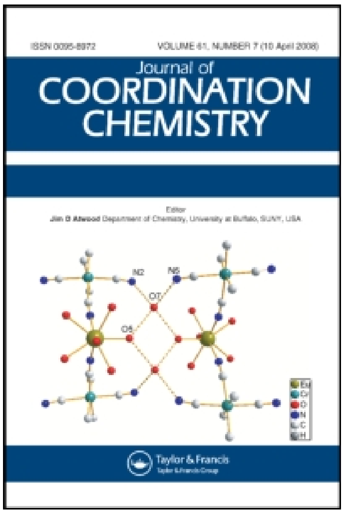

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
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Synthesis, structure, magnetic, and spectroscopic properties of a chloro-bridged trinuclear copper(II) complex: $\{[Cu(bpea)Cl]_2CuCl_4\}$

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To cite this Article Qian, Jing , Xie, Ming-Jin , Feng, Li , Tian, Jin-Lei , Shang, Jing , Zhang, Yuan and Yan, Shi-Ping(2010) 'Synthesis, structure, magnetic, and spectroscopic properties of a chloro-bridged trinuclear copper(II) complex: $\{[Cu(bpea)Cl]_2CuCl_4\}$', Journal of Coordination Chemistry, 63: 13, 2239 — 2246, First published on: 13 July 2010 (iFirst)
To link to this Article: DOI: 10.1080/00958972.2010.501862
URL: http://dx.doi.org/10.1080/00958972.2010.501862

Journal of Coordination Chemistry
Vol. 63, No. 13, 10 July 2010, 2239–2246

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Synthesis, structure, magnetic, and spectroscopic properties of a chloro-bridged trinuclear copper(II) complex: $\{[Cu(bpea)Cl]_2CuCl_4\}$

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(*Received 18 December 2009; in final form 28 April 2010*)

In this work, a chloro-bridged trinuclear copper complex $\{[Cu(bpea)Cl]_2CuCl_4\}$ (**1**) (bpea = *N*,*N*-bis(2-pyridylmethyl)ethylamine) has been synthesized and structurally characterized. In **1**, two mononuclear $[Cu(bpea)Cl]^+$ are linked by one $CuCl_4^{2-}$, generating a sandwich-like trinuclear unit. A crystallographic C_2 axis passes through the Cu of the connecting $CuCl_4^{2-}$. Susceptibility data of **1** indicate weak intratrimer ferromagnetic coupling with $J = 5.16\,cm^{-1}$. Elemental analysis, infrared, UV spectra, and electrochemistry of the complex were also determined.

Keywords: Crystal structure; Magnetic properties; Electrochemistry; Spectroscopic properties

1. Introduction

The ligands bpa-R, first reported by Romary *et al.* [1], are classical tridentate nitrogen donors which can bind to metal both facially and meridionally [2] and are more flexible than triazacyclononane (TACN), which is strictly facially coordinating [3–5]. Like trispyrazolylborates, bpa-R can adopt both k_2 and k_3 coordination, but unlike trispyrazolylborates, bpa-R can coordinate in both facial and meridional k_3 modes [6]. A variety of transition metal complexes with bpa-R have been reported [7–17]. The Cu(II), owing to the well-known "plasticity" of the coordination sphere, forms complexes of coordination number four to six, with a variety of irregular geometries [18, 19]. In this article, we report the synthesis, crystal structure, magnetism, spectroscopic properties, and electrochemistry of a new single chloro-bridged trinuclear copper(II) complex, $\{[Cu(bpea)Cl]_2CuCl_4\}$ (**1**) (bpea = *N*,*N*-bis(2-pyridylmethyl)ethylamine) (scheme 1).

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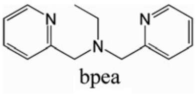
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.501862



Scheme 1. Structure of ligand (bpea).

2. Experimental

2.1. *Materials and instrumentation*

All reagents and chemicals were from commercial sources and used without purification. Solvents were purified by standard procedures. The bpea was synthesized according to the procedure of the literature [20].

Elemental analyses for C, H, and N were obtained on a Perkin-Elmer analyzer model 240. Infrared spectroscopy on KBr pellets was performed on a Bruker Vector 22 FT-IR spectrophotometer from 4000 to 400 cm^{-1}. Electronic spectra were measured on a JASCO V-570 spectrophotometer. Magnetic susceptibilities on crystal samples in a PE cling film were measured with a Quantum Design MPMS SQUID magnetometer from 3 to 300 K. We have determined the diamagnetic data of a film without sample with known weight; then, deducting the value of the corresponding diamagnetic contribution of the sample film, we obtained the magnetic data of the sample. The applied magnetic field was 0.2 T. Diamagnetic correction was made with Pascal's constants for all constituent atoms. The cyclic voltammetry measurement was performed under argon on BAS Epsilon Electrochemical Workstation with a three-electrode system consisting of platinum glassy carbon as the working electrode, platinum wire as the auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode.

2.2. *Synthesis of* $\{[Cu(bpea)Cl]_2CuCl_4\}$ *(1)*

To a 10 mL acetonitrile solution of $CuCl_2$ (0.17 g, 1 mmol) was added dropwise a 5 mL acetonitrile solution of bpea (0.227 g, 1 mmol) with stirring. The resulting blue solution was stirred for 2 h at room temperature and filtered. Blue microcrystalline powder was obtained, washed with diethyl ether and dried in air. The powder was redissolved in a mixture of acetonitrile : ethanol (1 : 3) and blue crystals were obtained by slow evaporation of this solution at room temperature after several days. (Yield: 0.13 g, ~52% based on the copper salt). Anal. Calcd (%) for $C_{28}H_{34}Cl_6Cu_3N_6$: C, 39.19; H, 3.99; N, 9.80; Found (%): C, 38.85; H, 4.12; N, 9.67. FT-IR (KBr phase) (cm^{-1}): 2940s, 1604s, 1571m, 1481s, 1444s, 1414w, 1386m, 1353s, 1314m, 1297m, 1224w, 1186w, 1159s, 1116m, 1104m, 1052w, 1020s, 989w, 894w, 865w, 766s, 730w, 641m, 412m (w, weak; m, medium; s, strong).

2.3. *X-ray crystallographic procedure*

A suitable single crystal with approximate dimensions $0.28 \times 0.22 \times 0.16\ \mathrm{mm}^3$ was used for X-ray diffraction analysis by mounting on the tip of a glass fiber in air. Data were collected on a Bruker Smart-1000 CCD diffractometer with Mo-Kα ($\lambda = 0.71073$ Å) at 273(2) K. The structure was solved by direct methods using

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{28}H_{34}C_{l6}Cu_3N_6$
Formula weight	857.93
Temperature (K)	273(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C_2/c
Unit cell dimensions (Å, °)	
a	23.633(9)
b	10.458(4)
c	14.619(6)
α	90
β	99.304(5)
γ	90
Volume (A^3), Z	3566(2), 4
Calculated density ($g\,cm^{-3}$)	1.598
Absorption coefficient (mm^{-1})	2.251
$F(000)$	1732
Crystal size (mm^3)	0.28 × 0.22 × 0.16
θ range for data collection (°)	2.13 to 25.03
Limiting indices	$-28 \le h \le 23$; $-12 \le k \le 12$; $-17 \le l \le 17$
Reflection collected	9472
Independent reflections (R_{int})	3162 (0.0203)
Max. and min. trans.	1.0000 and 0.7787
Data/restraints/parameters	3162/0/196
Goodness-of-fit on F^2	1.050
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0245$, $wR_2 = 0.0636$
R indices (all data)	$R_1 = 0.0341$, $wR_2 = 0.0673$
Largest difference peak ($e\,A^{-3}$)	0.336 and −0.264

SHELXS-97 and refined with full anisotropy by full-matrix least-squares on F^2 using SHELXL-97 [21]. Hydrogens were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. All non-hydrogen atoms were refined anisotropically. Molecular graphics were drawn with the program package XP. Further crystallographic data and experimental details for the structural analysis of **1** are summarized in table 1 (Supplementary material).

3. Results and discussion

3.1. *Crystal structure*

An ORTEP diagram of **1** with atom numbering scheme is given in figure 1. Bond dimensions about copper are listed in table 2. In **1**, two mononuclear $[Cu(bpea)Cl]^+$ are linked by three atoms (Cl2, Cu2, Cl2A) from one $CuCl_4^{2-}$, generating a sandwich-like trinuclear unit. A crystallographic C_2 axis passes through Cu2 of the connecting $CuCl_4^{2-}$. Such trimer structure of **1** resembles that of a related trinuclear Cu complex $\{[Cu(DAPDH_2)Cl]_2CuCl_4\}$ ($DAPDH_2$ = 2,6-diacetylpyridine dioxime) [22].

In **1**, two different coordination geometries of Cu ions are observed. Terminal Cu's (Cu1 and Cu1A) are five-coordinate with N_3Cl_2 donor sets derived from a bridging Cl^-, a terminal Cl^- and three bpea nitrogens. The coordination geometry is best described as a distorted square pyramid with $\tau = 0.17$ [23]. The equatorial plane is formed by N1, N2, N3 from bpea, and Cl1 (terminal), with average Cu–N bond length of 2.013 Å.

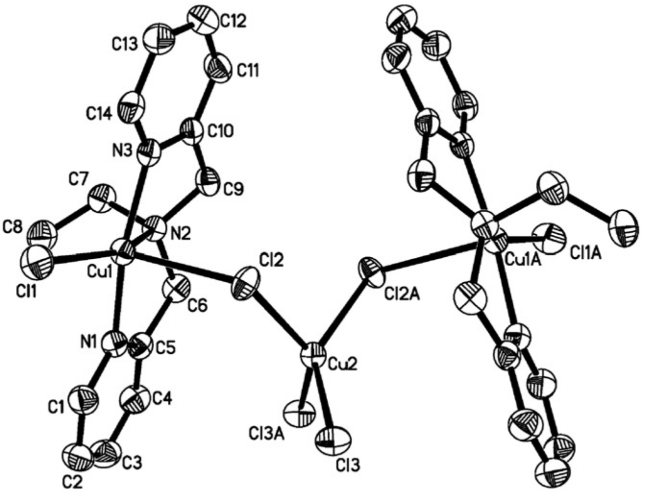


Figure 1. ORTEP drawing of **1** and the atom numbering; hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu(1)–N(1)	1.994(2)	Cu(1)–Cl(2)	2.652(10)
Cu(1)–N(2)	2.040(18)	Cu(2)–Cl(3)	2.223(9)
Cu(1)–N(3)	2.002(2)	Cu(2)–Cl(2)	2.272(9)
Cu(1)–Cl(1)	2.234(10)		
N(1)–Cu(1)–N(3)	164.03(8)	N(1)–Cu(1)–N(2)	83.31(8)
N(3)–Cu(1)–N(2)	81.63(8)	N(1)–Cu(1)–Cl(1)	98.08(6)
N(3)–Cu(1)–Cl(1)	97.78(6)	N(2)–Cu(1)–Cl(1)	153.81(6)
N(1)–Cu(1)–Cl(2)	92.07(6)	N(3)–Cu(1)–Cl(2)	85.39(6)
N(2)–Cu(1)–Cl(2)	100.16(6)	Cl(1)–Cu(1)–Cl(2)	105.91(4)
Cl(3A)–Cu(2)–Cl(3)	101.48(5)	Cl(3A)–Cu(2)–Cl(2)	136.30(3)
Cl(3)–Cu(2)–Cl(2)	97.54(3)	Cl(3A)–Cu(2)–Cl(2A)	97.54(3)
Cl(3)–Cu(2)–Cl(2A)	136.30(3)	Cl(2)–Cu(2)–Cl(2A)	95.11(5)
Cu(2)–Cl(2)–Cu(1)	119.27(3)		

The axial site is occupied by Cl2 from $CuCl_4^{2-}$ with Cu1–Cl2 distance of 2.652 Å, which is the longest Cu–Cl distance in the trimer and is also significantly longer than that of Cu1–Cl1 (2.234 Å). In $\{[Cu(DAPDH_2)Cl]_2CuCl_4\}$, the corresponding Cu1–Cl1 and Cu1–Cl2 bond distances are 2.193 and 2.604 Å, respectively.

The central Cu2 is bound to two bridging chlorides and two terminal chlorides in a distorted tetrahedral geometry. The two $Cu–Cl_{bridge}$ distances of 2.272 Å are longer than the terminal $Cu2–Cl3_{terminal}$ bond length of 2.223 Å. The structure of $[CuCl_4]^{2-}$ is highly distorted, with Cl3A–Cu2–Cl2 of 136.3° and Cl3–Cu2–Cl2 of 97.54°, comparing to the reported example with 133.9° and 99°, respectively [22]. A useful comparison is the bridging angle, between **1** and the example [22], where Cu2–Cl2–Cu1 is 119.3° for **1** and 130.8° for the reference paper.

3.2. *Electronic spectrum*

The electronic absorption spectrum in $H_2O:CH_3CN$ (4 : 1 in volume) solution of **1** is shown in figure 2. Two very strong absorptions appear at 306 nm

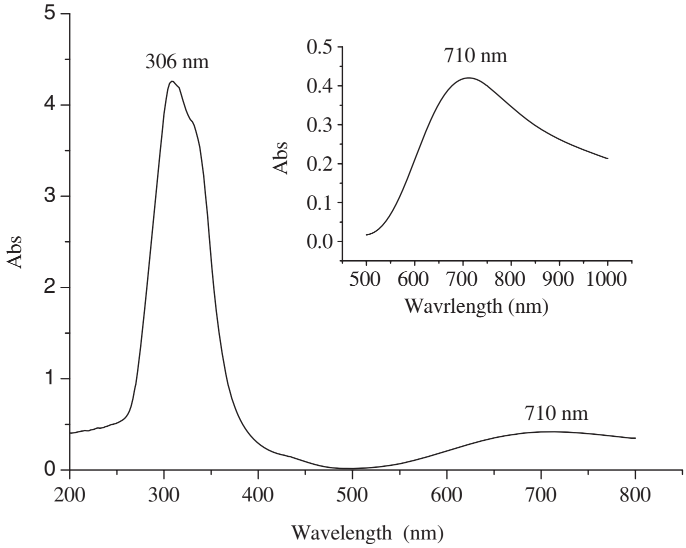


Figure 2. The UV-Vis spectrum of **1** in $H_2O:CH_3CN$.

($\varepsilon = 3.0 \times 10^3\,dm^3\,mol^{-1}\,cm^{-1}$) and 325 nm (shoulder, $\varepsilon = 2.6 \times 10^3\,dm^3\,mol^{-1}\,cm^{-1}$) assigned to the π–π* transition of the organic ligand and/or MLCT. A weak absorption at 425 nm is assigned to chloride to copper charge transfer. In the visible region the maximum absorption appears at 710 nm ($\varepsilon = 230\,dm^3\,mol^{-1}\,cm^{-1}$), consistent with square-pyramidal geometry for copper(II), suggesting that in solution square pyramidal geometry is maintained. The transition may be assigned as the d_{xy}, d_{xz}, d_{yz}, $d_{z^2} \rightarrow d_{x^2-y^2}$ [24].

3.3. *Electrochemistry*

The electrochemical properties of **1** have been studied using cyclic voltammetry in aqueous solution with 0.1 M $NaClO_4$ as supporting electrolyte in aqueous solution. The cyclic voltammogram of **1** is given in figure 3. Complex **1** showed two well-defined cathodic waves for Cu(II) to Cu(I) reduction at *ca* $E^1_{pc} = -0.23\,V$ and $E^2_{pc} = -0.53\,V$, respectively; the reverse scan gave two anodic waves at *ca* $E^2_{pa} = -0.45\,V$ and $E^1_{pa} = -0.07\,V$, respectively. The corresponding $E_{1/2}$ were estimated as $E^1_{1/2} = -0.15\,V$ and $E^2_{1/2} = -0.49\,V$ *versus* SCE. Although the ΔE_p value for the second redox couple was slightly higher than that for Nernstian behavior it may be assumed a reversible process with an i_{pc}/i_{pa} value approximately unity. However, it is important to note that the intensity of the anodic peak for the oxidation of copper(I) to copper(II) in the reverse scan was greatly increased, which is assigned to irreversible oxidation ($\Delta E_p = 160\,mV$) of the metal-bound ligand. Considering the solution behavior of the trinuclear **1** (see solution behavior section), complex **1** may dissociate into binuclear,

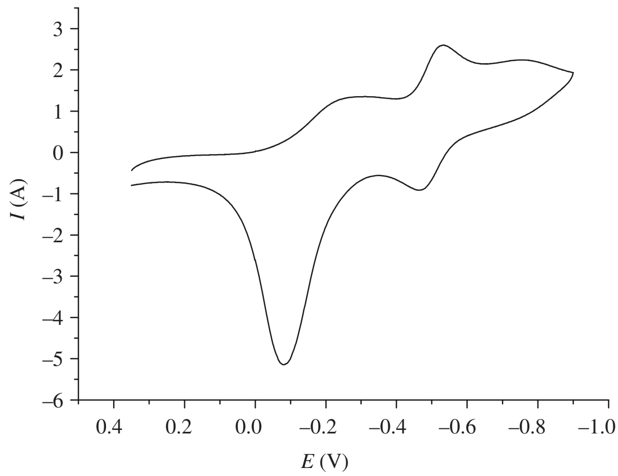


Figure 3. Cyclic voltammogram of **1** in H_2O at $100\,mV\,s^{-1}$ with $NaClO_4$ as an internal standard.

$[Cu_2L_2Cl_3]^+$, and/or mononuclear, $[CuLCl]^+$, species. Therefore it is reasonable to assign the stepwise redox processes as follows:

$$Cu^{II} \leftrightarrow Cu^{I}$$

$$Cu^{II}Cu^{II} \leftrightarrow Cu^{II}Cu^{I} \quad \text{and} \quad Cu^{II}Cu^{I} \leftrightarrow Cu^{I}Cu^{I}$$

3.4. *Magnetism*

Variable-temperature magnetic susceptibility studies were carried out on powdered samples of crystalline **1** from 3 to 300 K. The $\chi_M T$ and molar magnetic susceptibilities (χ_M) *versus* T are plotted in figure 4 (χ_M being the magnetic susceptibility per trimer unit). At room temperature, $\chi_M T$ is $1.303\,cm^3\,mol^{-1}\,K$, a value which is somewhat larger than that expected for a magnetically uncoupled trinuclear Cu(II) compound ($1.23\,cm^3\,mol^{-1}\,K$, $g = 2.1$). Upon cooling of the sample, $\chi_M T$ increases and reaches a value of $1.548\,cm^3\,mol^{-1}\,K$ at approximately 9 K. Such magnetic behavior reveals a weaker intramolecular ferromagnetic coupling of copper ions through chloride bridges. Below 9 K, $\chi_M T$ decreases rapidly to $1.305\,cm^3\,mol^{-1}\,K$, which is most likely due to zero-field splitting (ZFS) within the quartet ground state or intertrimer antiferromagnetic interactions [25].

Assuming the absence of interaction between the two terminal Cu ions for such isolated symmetric trimer, the molar paramagnetic susceptibility data approximately fit the following expression, which is based on the general isotropic exchange Hamiltonian, $\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3)$, with $J =$ intratrimer magnetic exchange coupling constant, $zJ' =$ intertrimer magnetic exchange coupling constant and $S_1 = S_2 = 1/2$:

$$\chi_{tri} = \frac{Ng^2\beta^2[1 + \exp(-2J/kT) + 10\exp(J/kT)]}{4kT[1 + \exp(-2J/kT) + 2\exp(J/kT)]} + N_\alpha$$

$$\chi_M = \frac{\chi_{tri}}{1 - \chi_{tri}(2zj'/Ng^2\beta^2)}$$

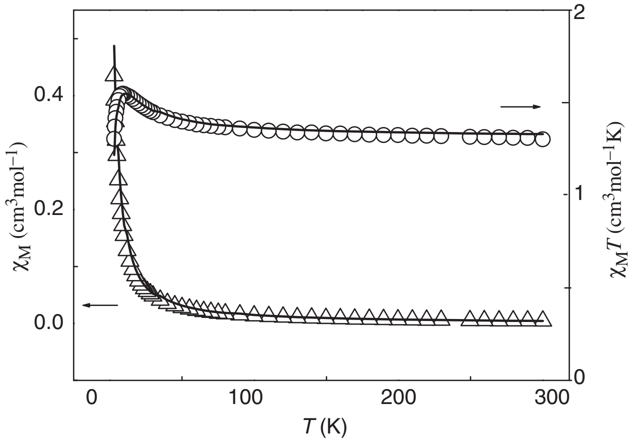


Figure 4. Plots of χ_M (Δ) and $\chi_M T$ ($\circ$) *vs.* T for **1**. The solid lines are theoretical fits.

This model reproduces very satisfactorily the magnetic data of **1** in the whole temperature range with the following set of parameters: $g = 2.16$, $J = 5.16\,\mathrm{cm}^{-1}$, $zj' = -1.08\,\mathrm{cm}^{-1}$ and the agreement factor $R = 3.94 \times 10^{-6}$. As expected, the values of J and zj' demonstrate intratrimer ferromagnetic and intertrimer antiferromagnetic interactions, respectively. Such magnetic behavior of **1** resembles that of the related trinuclear Cu complex of [Cu(DAPDH$_2$)]$_2$CuCl$_4$) [22]. The presence of the weak ferromagnetic coupling is consistent with the structure of the trimer. According to the structural information, the magneto-structural relations could be concluded as follows. In these complexes, two [CuLCl] units are linked by one CuCl_4^{2-} anion. The unpaired electron for each terminal Cu ion, which has square pyramidal configuration, is in a predominantly $d_{x^2-y^2}$ orbital lying in the equatorial plane while for the highly distorted tetrahedral CuCl_4^{2-}, the $d_{x^2-y^2}$ orbital is the HOMO [22]. According to Kahn's formalism [22], the magnetic orbitals on Cu1 and Cu2 are accidently orthogonal, which must lead to ferromagnetic coupling.

4. Conclusion

A new linear trinuclear copper(II) complex containing chloro-bridges has been synthesized and characterized both crystallographically and spectroscopically. Complex **1** is built from two mononuclear [Cu(bpea)Cl]$^+$ and one CuCl_4^{2-}, generating a sandwich-like trinuclear unit. A crystallographic C_2 axis passes through Cu of the connecting CuCl_4^{2-}. The magnetic susceptibility measurements of this trinuclear copper(II) complex reveal an intramolecular weak ferromagnetic coupling between copper(II) ions.

Supplementary material

Crystallographic data for the structure analysis in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC

No. 602630. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email for inquiry: fileserv@ccdc.cam.ac.uk; Email for deposition: deposit@ccdc.cam.ac.uk).

Acknowledgments

Financial support from the National Natural Science Foundation of China (Grant No. 20771063), Tianjin Educational Committee Foundation (Grant No. 20070606) and Tianjin Normal University PhD Foundation (Grant No. 52LX28) are gratefully acknowledged.

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