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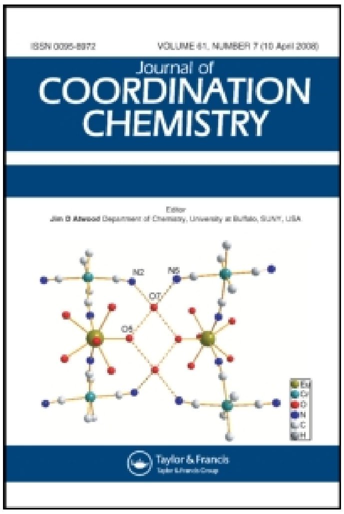

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
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Synthesis and crystal structures of two mixed-ligand Cu(II) complexes of tripyridyldiamine

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To cite this Article Zhang, Min , Ni, Jia and Xie, Yongshu(2007) 'Synthesis and crystal structures of two mixed-ligand Cu(II) complexes of tripyridyldiamine', Journal of Coordination Chemistry, 60: 11, 1173 — 1182
To link to this Article: DOI: 10.1080/00958970601009851
URL: http://dx.doi.org/10.1080/00958970601009851

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Journal of Coordination Chemistry
Vol. 60, No. 11, 20 July 2007, 1173–1182

Synthesis and crystal structures of two mixed-ligand Cu(II) complexes of tripyridyldiamine

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(*Received 5 January 2006; revised 14 May 2006; in final form 15 May 2006*)

Two novel Cu(II) complexes, $[Cu(H_2tpda)(acac)](ClO_4)_{0.5}Cl_{0.5} \cdot H_2O$, $[Cu(H_2tpda)(NO_3)]ClO_4$ (**2**) (H_2tpda = tripyridyldiamine) have been synthesized, and characterized by X-ray analyses, elemental analyses, IR, UV and ESR spectra. Single crystal X-ray diffraction revealed that the Cu atom in complex **1** is coordinated to three N atoms from H_2tpda and two oxygen atoms from acac with an approximately trigonal bipyramidal geometry. The molecules are assembled through intermolecular hydrogen bonds and π–π stacking, affording a two dimensional network. In complex **2**, the Cu atom is coordinated with three N atoms from H_2tpda and two oxygen atoms from NO_3^- in addition to a weak coordination with one oxygen from ClO_4^-, resulting in an irregular octahedral environment, and the molecules are also connected by intermolecular hydrogen bonding and π–π stacking, affording a one dimensional structure.

Keywords: Cu(II) complexes; Crystal structures; Tripyridyldiamine; Supramolecular assembly

1. Introduction

Intensive interest exists to design and synthesize metal complexes with one-, two-, and three-dimensional supramolecular structures via non-covalent weak interactions, such as hydrogen bonding and π–π stacking [1–7], due to their relevance to molecular recognition, materials science, catalysis and biochemistry. Taking advantage of the versatility of the tripyridyldiamine ligand which can coordinate in two ways with the possibility to give pentanuclear or mononuclear species (scheme 1), a series of complexes containing tripyridyldiamine have been reported [8–15]. In complexes containing tripyridyldiamine (H_2tpda) as a tridentate ligand [15], H_2tpda acts as double NH hydrogen bond donors. In addition, the pyridyl rings of H_2tpda can participate in intermolecular π–π interactions, affording various supramolecular structures. However, this aspect still remains relatively unexplored [15]. Herein, we report the preparation and structural characterization of two novel Cu(II) complexes, $[Cu(H_2tpda)(acac)](ClO_4)_{0.5}Cl_{0.5} \cdot H_2O$ (**1**), $[Cu(H_2tpda)(NO_3)]ClO_4$ (**2**). In these two

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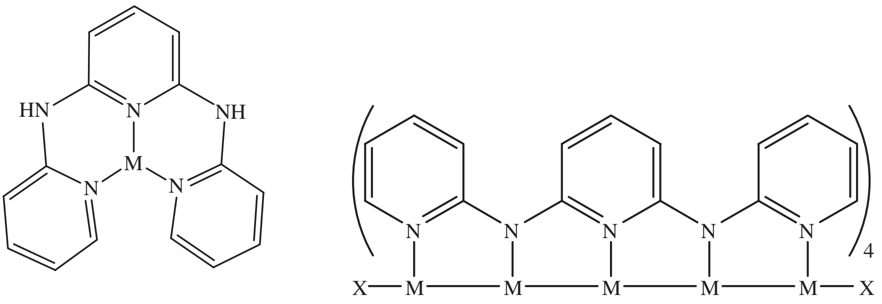
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970601009851



Tridentate form

Pentadentate form

Scheme 1. Various coordination modes of tripyridyldiamine.

complexes, different anionic ligands and counteranions were used, resulting in supramolecular assemblies with 1D and 2D structures for **1** and **2**, respectively.

2. Experimental

2.1. *Materials and measurements*

H_2tpda was synthesized by the reported method [11]. All other reagents were used as commercially received without further purification. IR spectra were recorded on a Bruker Vector-22 spectrometer (KBr Disc). Microanalyses of C, H and N were carried out with a GmbH VarioEL elemental analyzer.

2.2. *Synthesis*

2.2.1. Preparation of [Cu(H_2tpda)(acac)]$(ClO_4)_{0.5}Cl_{0.5}\cdot H_2O$ (1). To a methanol solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.074 g, 0.20 mmol) and $CuCl_2 \cdot 2H_2O$ (0.034 g, 0.20 mmol), was added H_2tpda (0.105 g, 0.40 mmol), followed by the addition of acetylacetone (0.040 g, 0.40 mmol) and aqueous NaOH (4.0 N, 0.40 mL). The reaction mixture was refluxed for 3 h, and then concentrated to ca 5 mL *in vacuo*, and filtered. The filtrate was left in the dark at room temperature for slow evaporation of the solvent. Green crystals were obtained after a few days. Yield: 47%. Anal. Calcd for $C_{20}H_{22}ClCuN_5O_5$: C, 46.97; H, 4.34; N, 13.69%. Found: C, 46.89; H, 4.20; N, 13.74%. IR (KBr pellet, cm^{-1}): 3435s, 3334m, 3215w, 1644m, 1582s, 1519m, 1492w, 1453vs, 1370m, 1271w, 1216w, 1121s, 1056m, 929w, 869w, 798w, 769m, 621w, 571w.

2.2.2. Preparation of [Cu(H_2tpda)(NO_3)]ClO_4 (2). To a suspension of H_2tpda (0.1052 g, 0.40 mmol) in methanol was added $Cu(NO_3)_2 \cdot 3H_2O$ (0.0966 g, 0.40 mmol), and the mixture was heated to reflux for 1 h. The resulting green solution was cooled and treated with a solution of $NaClO_4$ (0.0496 g, 0.4 mmol) in water (5 mL). The resulting solution was concentrated *in vacuo* and left undisturbed at room temperature;

Table 1. Crystal data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Molecular formula	$C_{20}H_{22}ClCuN_5O_5$	$C_{15}H_{13}ClCuN_6O$
Formula weight	511.42	488.30
Crystal color and habit	Green, prism	Green, prism
Crystal dimension (mm^3)	$0.26 \times 0.22 \times 0.12$	$0.28 \times 0.27 \times 0.20$
System, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
T (K)	291(2)	291(2)
a (Å)	8.929(8)	9.1071(13)
b (Å)	11.568(10)	10.6763(16)
c (Å)	10.9730(16)	10.9730(16)
α (°)	111.901(13)	112.433(2)
β (°)	93.036(14)	96.790(2)
γ (°)	97.564(14)	100.839(2)
V ($Å^3$)	1133.1(17)	947.1(2)
Z	2	2
D_c ($kg\,m^{-3}$)	1.499	1.712
μ (Mo-Kα) (mm^{-1})	1.123	1.348
$F(000)$	526	494
θ range (°)	1.92–25.00	2.05–25.00
hkl range	−10/10, −9/13, −14/11	−10/10, −12/12, −13/13
Measured refl. number	5833	6886
Independent refl. number	3983	3315
Observed refl. ($I \geq 2\sigma(I)$)	2815	2990
No. of parameters	351	271
R^a	0.0658	0.0451
$R_w{}^b$	0.1678	0.1208
R_{int}	0.0546	0.0000
GOF for all data[c]	1.098	1.046
Residual electron density ($e\,Å^{-3}$)	0.856/−1.110	0.636/−0.488

[a] $R(F) = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; [b] $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2))^2]^{1/2}$; [c] $\mathrm{GOF} = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{\mathrm{diffrs}} - N_{\mathrm{params}})]^{1/2}$.

green crystals were obtained after a few days. Yield: 72%. Anal. Calcd for $C_{15}H_{13}ClCuN_6O_7$: C, 36.90; H, 2.68; N, 17.21%. Found: C, 36.90; H, 2.65; N, 17.20%. IR (KBr pellet, cm^{-1}): 3436m, 3332m, 3283w, 3083w, 1666m, 1642m, 1592s, 1554m, 1527m, 1501m, 1489m, 1281s, 1451vs, 1382s, 1282w, 1251w, 1209m, 1179m, 1160m, 1107s, 1072s, 933w, 790m, 771m, 679m, 623w, 524w, 425w.

2.3. *Crystal structure determination*

A single crystal was mounted on a glass-fiber. All measurements were made on a Rigaku RAXIS-IV image plate area detector with graphite monochromated Mo-Kα radiation. The data were collected at $18 \pm 1°C$ and corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections ($I > 2.00\sigma(I)$) and variable parameters. All calculations were performed using the SHELXTL-97 software package [16, 17]. Crystal data are summarized in table 1.

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

1			
Cu(1)–O(1)	1.905(4)	Cu(1)–O(2)	1.963(4)
Cu(1)–N(3)	1.971(4)	Cu(1)–N(1)	2.006(5)
Cu(1)–N(5)	2.107(5)		
O(1)–Cu(1)–O(2)	91.82(17)	O(1)–Cu(1)–N(3)	177.49(17)
O(2)–Cu(1)–N(3)	89.14(17)	O(1)–Cu(1)–N(1)	88.74(18)
O(2)–Cu(1)–N(1)	140.99(18)	N(3)–Cu(1)–N(1)	89.06(17)
O(1)–Cu(1)–N(5)	93.11(18)	O(2)–Cu(1)–N(5)	105.12(18)
N(3)–Cu(1)–N(5)	88.87(18)	N(1)–Cu(1)–N(5)	113.80(18)
2			
Cu(1)–N(5)	1.964(3)	Cu(1)–N(1)	1.967(3)
Cu(1)–N(3)	1.997(3)	Cu(1)–O(1)	1.999(2)
Cu(1)–O(2)	2.504(2)		
N(5)–Cu(1)–N(1)	153.68(12)	N(5)–Cu(1)–N(3)	95.01(11)
N(1)–Cu(1)–N(3)	95.18(11)	N(5)–Cu(1)–O(1)	89.92(11)
N(1)–Cu(1)–O(1)	91.63(11)	N(3)–Cu(1)–O(1)	153.62(11)

3. Results and discussion

Selected bond lengths and angles are listed in table 2. The crystal structure of complex **1** contains a $[Cu(H_2tpda)(acac)]^+$ cation (figure 1). The noncoordinated ClO_4^- and the chloride are both disordered with the site occupancies of 0.5. Thus, they as a whole can be considered as one negative charge. There is also a lattice water in the asymmetric unit. In the $[Cu(H_2tpda)(acac)]^+$, the coordination geometry around copper(II) is distorted trigonal bipyramidal with the H_2tpda ligand in an all-*anti* configuration and tridentate. The equatorial sites of Cu(II) consist of N(3), which comes from the pyridyl ring of the H_2tpda, and two oxygen atoms from acac. The apical sites are occupied by N(1) and N(5) of the pyridyl rings. The Addison index τ [18] value of 0.61 for complex **1** indicates a severe distortion of the trigonal bipyramidal configuration ($\tau = 0$ for an ideal square pyramid, $\tau = 1$ for an ideal trigonal bipyramid). The average Cu–N bond length is 2.028 Å, and the mean Cu–O bond length is 1.934 Å, which is longer than those in $[Cu(acac)_2]$ [19] and $[Cu(acac)(phen)(NO_3)] \cdot H_2O$ [20]. Due to steric hindrance, the tridentate H_2tpda ligand is not coplanar, with dihedral angles of 20.2 and 28.4° between the central pyridyl ring and the terminal ones. The crystal structure of complex **2** (figure 2) consists of a distorted trigonal bipyramidal copper(II) center with two pyridyl nitrogen atoms N(1), N(5) and one oxygen atom O(2) of nitrate occupying the equatorial plane. The other oxygen atom O(1) of the nitrate and N(3) coordinate at the apical positions. The Addison index τ of 0.87 indicates a medium distortion of the trigonal bipyramidal configuration for complex **2**. In addition, ClO_4^- also participates in a very weak coordination with copper, affording an irregular octahedral environment and the Cu–O(7) distance is 3.148(5) Å. The H_2tpda ligand is not coplanar, either, with dihedral angles of 13.4 and 4.9° between the central pyridyl ring and the terminal ones.

Figure 3 shows the crystal packing of complex **1**. The water of crystallization, chloride atom and the NH hydrogen are involved in multiple hydrogen bonds. The oxygen atom [O(7)] of the water participates in an $O \cdots H–N$ type of bonding with the hydrogen atom of the amine from H_2tpda, with the $H \cdots O$ distance of 1.982 Å and $\angle O \cdots H–N$ angle of 171.7°. It is interesting that the chloride atom forms four hydrogen bonds with two water and two NH, with the $H \cdots Cl$ distances of 2.33

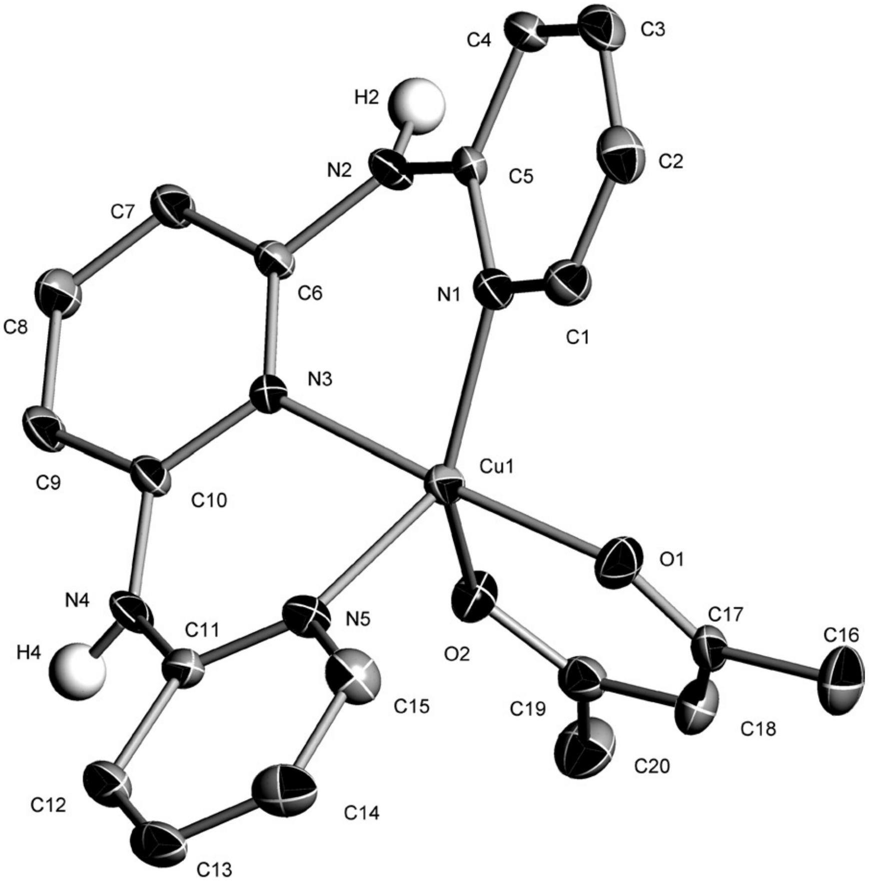


Figure 1. X-ray crystal structure of the $[Cu(H_2tpda)(acac)]^+$ cation in complex **1** at the 30% probability level with H atoms omitted for clarity.

and 2.48 Å, and ∠O–H ··· Cl and ∠N–H ··· Cl angles of 176.5 and 140.4°. In addition to the multiple intermolecular hydrogen bonds, the pyridyl rings are involved in intermolecular offset π–π interactions with the centroid–centroid distance of 4.16(2) Å between the parallel pyridyl rings, and plane–plane distances of 3.63(1) Å. The nearest N ··· C distance of 3.668 Å occurs between N5 and C11 ($-x$, $-y$, $-z$). Thus, a 2D supramolecular structure is formed approximately along the *ab* plane.

For complex **2**, two centrosymmetrically related mononuclear moieties are connected via two N–H ··· O hydrogen bonds between NH and the nitrates, with H ··· O distances of 2.121 Å, and the ∠O ··· H–N angles of 159.15°, affording a dimer. In addition, there are two intradimeric π–π interactions with the centroid–centroid distance of 3.74 Å and the plane–plane angle of 4.93°. The nearest C ··· C distance of 3.463 Å occurs between C3 and C8 ($2-x$, $2-y$, $2-z$). The dimers are further linked by two hydrogen bonds (O ··· H distances of 2.19 Å and O ··· H–N angles of 170.81°) and two weak Cu–O coordination bonds involving two ClO_4^-, affording a one-dimensional supramolecular chain along the 110 direction (figure 4).

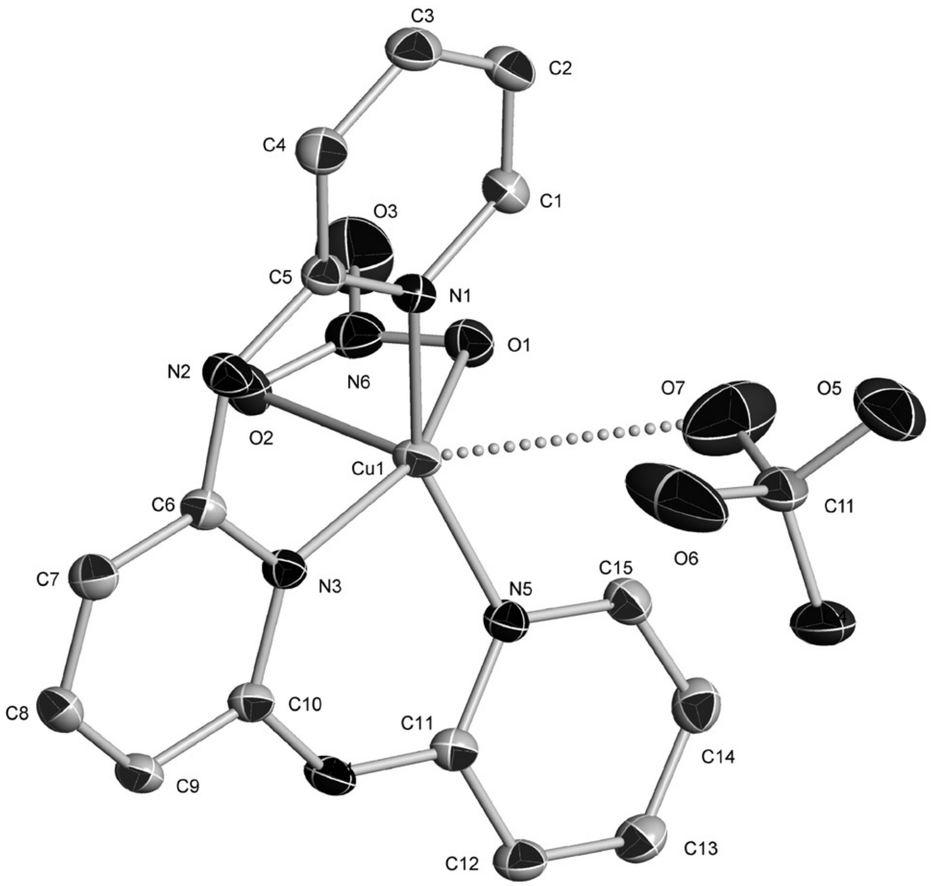


Figure 2. View of complex **2** showing the numbering scheme at the 25% probability level with H atoms omitted for clarity.

3.1. *IR, UV–Vis and ESR data*

The IR spectra of the complexes exhibit several characteristic strong bands. In complex **1**, the C=N and C=C stretching bands are shifted from 1607 and 1589 cm^{-1} for the free H_2tpda ligand to 1644 and 1605 cm^{-1}, respectively. In complex **2**, the corresponding bands are shifted to 1642 and 1592 cm^{-1}.

The perchlorate absorptions were observed at 1121 and 621 cm^{-1} for complex **1**, indicating the presence of ionic perchlorate anions. Whereas, for complex **2**, the bands appear at 1116, 1107 and 623 cm^{-1}, indicating the existence of the weak Cu–O (ClO_4^-) bond [21]. Two strong bands at 1582 and 1519 cm^{-1} are also observed in the spectrum of complex **1**, which can be assigned to (C=O) and (C=C) [20]. The positions are similar to those of the corresponding peaks in related acac complexes [20, 22]. The band observed at 1382 cm^{-1} for complex **2**, suggests coordination of the nitrate group [23].

The UV–Vis spectra of the complexes show similar patterns and the data are listed in table 3. In the UV range, two strong peaks (275 nm, 338 nm) for **1** and (269 nm, 339 nm) for **2** were observed, which can be assigned to the intraligand transition for H_2tpda.

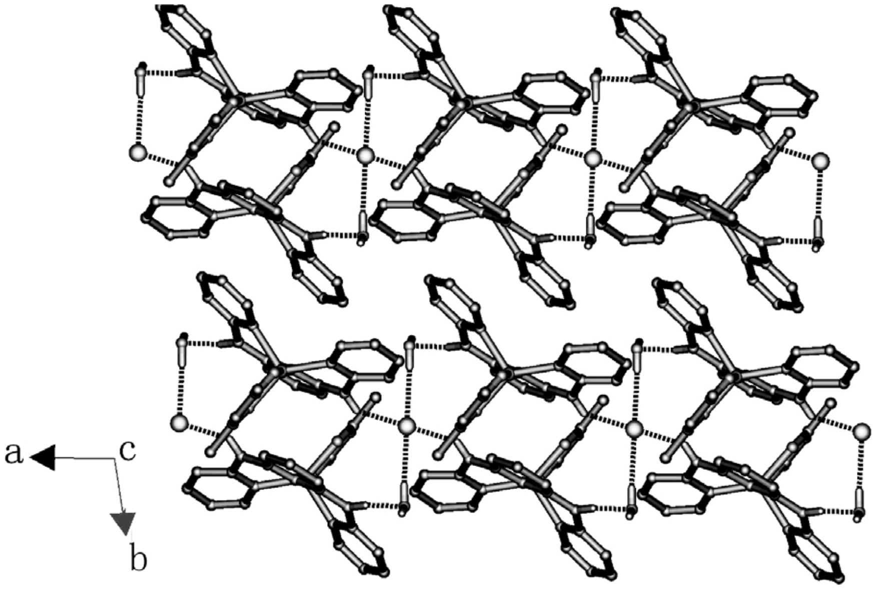


Figure 3. Hydrogen-bonded 2D layer of complex **1** along the *ab* plane.

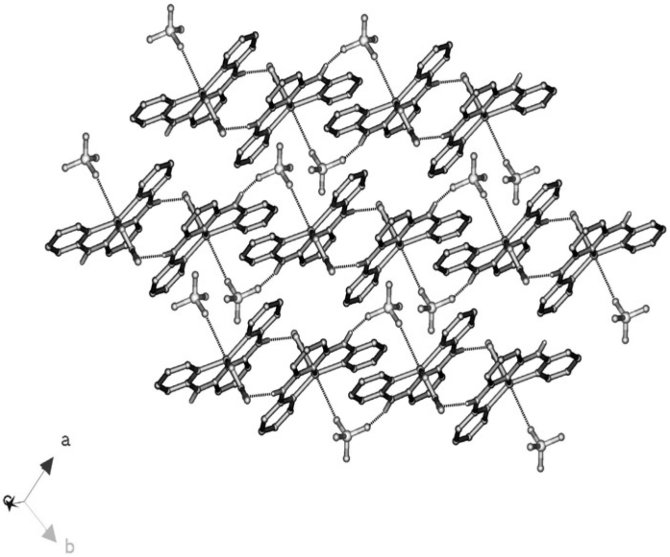


Figure 4. One-dimensional structure through intermolecular π–π stacking along the 110 direction of complex **2**.

In addition, complex **2** exhibits one strong ligand-to-metal charge transfer (MLCT) at 428 nm. In the visible range, one weak band at 690 nm for complex **1** and one weak band at 645 nm for complex **2** can be observed, assigned to the d–d transition bands of Cu(II).

Table 3. Summary of physical data for **1** and **2**.

	$g_{//}$	$g_{\perp}$	g_{av}	$A_{//}/G$	λ_{max} (nm^{-1}) (ε/M^{-1} cm^{-1})
1	2.211	2.021	2.084	155	690 (1.39×10^2) 338 (1.78×10^4) 275 (2.33×10^4)
2	2.221	2.011	2.081	167.5	645 (0.785×10^2) 428 (1.61×10^3) 339 (1.94×10^4) 269 (2.50×10^4)

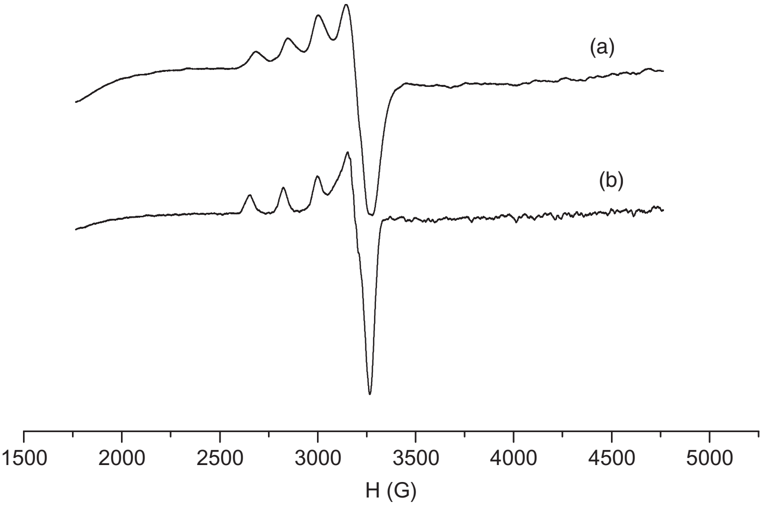


Figure 5. ESR of complex **1** (a) and complex **2** (b) at 77 K.

Both **1** and **2** show axial ESR spectra in DMF at 77K (figure 5). The EPR results were treated by the method reported earlier [24], giving the parameters $g_{//} = 2.211$ and $g_{\perp} = 2.021$ for **1** and $g_{//} = 2.221$ and $g_{\perp} = 2.011$ for **2**. The pattern of $g_{//} > g_{\perp} > 2.0$ for these complexes is indicative of a $(d_{x^2-y^2})^1$ ground state for copper(II), which is in agreement with elongated octahedral stereochemistry [24–26] around the copper centers. These results are different from the distorted trigonal bipyramidal geometry for complex **1** in the solid state, indicating that DMF probably participates in coordination with the copper atom in solution, affording a distorted octahedral structure.

4. Conclusion

In this work, two mononuclear complexes with formulas $[Cu(H_2tpda)(acac)](ClO_4)_{0.5}Cl_{0.5} \cdot H_2O$ (**1**), and $[Cu(H_2tpda)(NO_3)ClO_4]$ (**2**) have been synthesized and characterized by spectroscopic methods and X-ray diffraction analyses. For complex **1**, the coordination environment of Cu(II) can be described as distorted trigonal bipyramidal. Approximately along the *ab* plane, the molecules are assembled by hydrogen bonds and π–π interactions, affording a 2D supramolecular structure. In complex **2**, the Cu atom has an irregular octahedral configuration, and the molecules are assembled by intermolecular hydrogen bonding and π–π stacking, affording a one-dimensional structure. The results in this work indicate that the tripyridyldiamine ligand is promising for the construction of various supramolecular coordination assemblies through hydrogen-bonds involving NH and π–π interactions involving the pyridyl rings. The structures of the assemblies can be tailored by the variation of the coordinated anions and the free counteranions as hydrogen bond acceptors.

Supplementary data

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Center. CCDC 290503 (for complex **1**) and CCDC 290504 (for complex **2**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (30270321).

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