



A novel ligand *N,N'*-di(2-pyridyl)-2,4-diamino-6-phenyl-1,3,5-triazine (dpdapt) and its complexes: [Cu(dpapt)Cl₂] and [Cu(dpapt)(NO₃)(H₂O)] · NO₃ · H₂O

Cui-Juan Wang^a, Yao-Yu Wang^{a,*}, Hai-Rui Ma^a, Hui Wang^a,
Qi-Zhen Shi^a, Shie-Ming Peng^b

^a Department of Chemistry, Shaanxi Key Laboratory of Physico-inorganic Chemistry, Northwest University, Xi'an 710069, PR China

^b Department of Chemistry, National Taiwan University, Taipei, Taiwan

Received 30 March 2005; accepted 23 June 2005

Available online 22 August 2005

Abstract

The novel ligand *N,N'*-di(2-pyridyl)-2,4-diamino-6-phenyl-1,3,5-triazine (dpdapt) has been synthesized and the reactions of CuCl₂ · 2H₂O and Cu(NO₃)₂ · 8H₂O with the new ligand afforded two crystalline forms [Cu(dpapt)Cl₂] (**1**) and [Cu(dpapt)(NO₃)(H₂O)] · NO₃ · H₂O (**2**), respectively. The molecular structures of **1** and **2** were established by single-crystal X-ray diffraction studies. The copper(II) atoms in complexes **1** and **2** are both five-coordinated in trigonal bipyramidal environments. In **1**, antiparallel dimers construct a two-dimensional supramolecular architecture by π - π stacking and hydrogen bonding, whereas **2** is connected by the same interactions to form a three-dimensional supramolecular framework. Quantum chemical calculations have been performed using Density Functional Theory (DFT) in order to gain some insight about the coordination behavior of dpdapt and complex **1**.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Novel ligand; Copper(II) complexes; Crystal structure; Supramolecular compounds; DFT studies

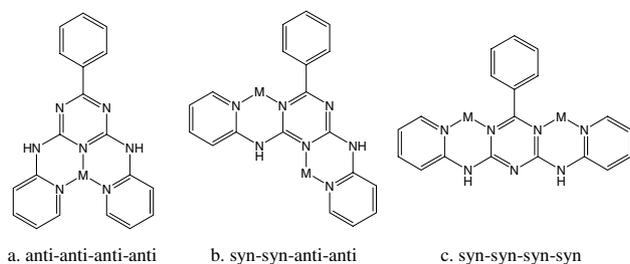
1. Introduction

The crystal engineering of coordination polymers and supramolecular compounds has attracted considerable current attention, not only because of their fascinating structural diversities [1], but also for their potential applications in optical, electrical, magnetic and biological materials [2]. The design of suitable organic ligands is one of the important roles in the synthetic strategies for these polymers and supramolecular compounds [3]. The

modified 1,3,5-triazine ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt) [4] and several transition-metal complexes using the ligand tpt have been reported [5,6]. We have synthesized a novel modified 1,3,5-triazine ligand, *N,N'*-di(2-pyridyl)-2,4-diamino-6-phenyl-1,3,5-triazine (dpdapt). The ligand dpdapt is a versatile ligand like tpt, but with more diversity than 2,2',6',2''-terpyridine (tpy). Dpdapt, which functions as a tridentate or a bis-bidentate ligand, has gained our interest because of its use as a spacer for designing supramolecular complexes. Thus, dpdapt has its own coordination feature and functions primarily as a tridentate ligand (Scheme 1(a); *anti-anti-anti-anti*) forming complexes of the general type ([Cu(dpapt)]²⁺), as we described in this paper.

* Corresponding author. Tel.: +86 29 88303097; fax: +86 29 88373398.

E-mail address: wyaoyu@nwu.edu.cn (Y.-Y. Wang).



Scheme 1. Coordination modes of the ligand dpdapt.

The second coordination mode as a bis-bidentate ligand, including *syn-syn-anti-anti* (b) and *syn-syn-syn-syn* (c), is shown in Scheme 1. DFT studies have been applied to dpdapt. Theoretical calculations illuminate the coordination modes of the ligand.

Herein, we report the copper(II) complexes with dpdapt as a tridentate ligand. The crystal structures of the copper(II) complexes with the all-*anti* conformation of the chelating ligand are presented. Complex **1** consists of dimeric units, doubly bridged by π - π stacking and hydrogen bonding, thus forming an unusual 1-D ladder structure. Complex **2** self-assembles into a 1-D chain by hydrogen bonding and π - π stacking, and a 3-D layer structure which is sustained via hydrogen bonds. We also employed DFT studies to **1** and explained its coordination behavior.

2. Experimental

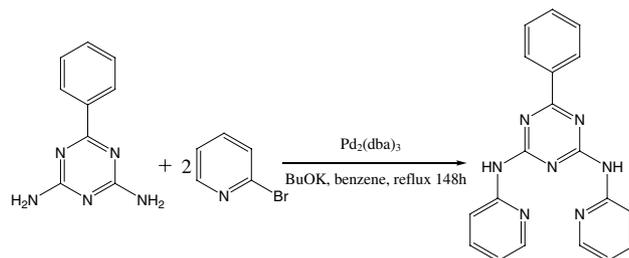
2.1. Materials and physical measurements

Commercially available chemicals were reagent grade and were used without further purification. Infrared spectra on KBr pellets were recorded on a Nicolet 170SX FT-IR spectrophotometer in the range 4000–400 cm^{-1} . Elemental analyses were determined with a Perkin-Elmer model 240C instrument. Electronic spectra were recorded on a Cary 300 Bio UV-Vis spectrophotometer. FAB-MS mass spectra were obtained with a JEOL HX-110 HF double focusing spectrometer operating in the positive ion detection mode. Fluorescence experiments used a HITACHI F-4500 Fluorescence Spectrophotometer and were measured in methanol.

2.2. Synthesis of *N,N'*-di(2-pyridyl)-2,4-diamino-6-phenyl-1,3,5-triazine (dpdapt)

2,4-Diamino-6-phenyl-1,3,5-triazine (5.0 g, 26.7 mmol), BuOK (14.3 g, 127.7 mmol) and tris(dibenzylideneacetone)dipalladium ($\text{Pd}_2(\text{dba})_3$) (2.0 g, 2.2 mmol) were added to a 200 ml flask under nitrogen. Then 100 ml dry benzene and 2-bromopyridine (14 g, 13.5 ml, 88.6 mmol) were injected into the former solid sequentially also under nitrogen. The resulting solution was

stirred for 148 h under reflux. The product was filtered and washed three times each with methanol and water.



Dpdapt was obtained as a white powder in 64% yield (5.8 g). *Anal. Calc.* for $\text{C}_{19}\text{H}_{15}\text{N}_7$: C, 66.86; H, 4.399; N, 28.74. Found: C, 66.87; H, 4.328; N, 28.56%. IR (KBr, cm^{-1}): $\nu = 3025(\text{w}), 2952(\text{w}), 1604(\text{m}), 1563(\text{w}), 1496(\text{s}), 1425(\text{s}), 1364(\text{m}), 1307(\text{m}), 1244(\text{w}), 1194(\text{w}), 1047(\text{w}), 989(\text{m}), 934(\text{w}), 770(\text{s}), 729(\text{m}), 693(\text{w})$. MS (FAB) m/z (%) 342.1 (dpdapt).

2.3. Synthesis of $[\text{Cu}(\text{dpdapt})\text{Cl}_2]$ (**1**)

A green solution was obtained by adding a methanol solution (10 ml) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (34.1 mg, 0.20 mmol) to a methanol suspension (15 ml) of dpdapt (75.0 mg, 0.22 mmol) and stirring for 4 h. Diffused in Et_2O , after filtering green needle-shaped crystals of **1** were produced. Yield: 56%. *Anal. Calc.* for $[\text{Cu}(\text{C}_{19}\text{H}_{15}\text{N}_7)\text{Cl}_2]$: C, 47.92; H, 3.152; N, 20.60. Found: C, 47.86; H, 3.185; N, 20.52%.

2.4. Synthesis of $[\text{Cu}(\text{dpdapt})(\text{NO}_3)(\text{H}_2\text{O})] \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$ (**2**)

A suspension of $\text{Cu}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$ (53.9 mg, 0.2 mmol) in 10 ml water was allowed to react with dpdapt (75.0 mg, 0.22 mmol) dissolved in 20 ml methanol. The resulting mixture was stirred for 3 h and the product was removed by filtration. After a few days, dark green crystals were obtained by diffusion in Et_2O . Yield: 48%. *Anal. Calc.* for $[\text{Cu}(\text{dpdapt})(\text{NO}_3)(\text{H}_2\text{O})] \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$: C, 40.36; H, 3.363; N, 22.30. Found: C, 40.46; H, 3.385; N, 22.52%.

2.5. Crystal structures determination

X-ray diffraction data were collected on a BRUKER SMART APEX-II diffractometer using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) for complexes **1** and **2**. The structures were solved by direct methods [7]. Then the structures were refined by the least-squares method using SHELXL-97 [8] with anisotropic temperature factors for all non-H atoms. Crystal data and structure refinement details are summarized in

Table 1
Data collection and processing parameters for [Cu(dpapt)Cl₂] (1) and [Cu(dpapt)(NO₃)(H₂O)] · NO₃ · H₂O (2)

Complex	1	2
Empirical formula	C ₁₉ H ₁₅ Cl ₂ CuN ₇	C ₁₉ H ₁₉ CuN ₉ O ₈
Formula weight	475.82	564.97
<i>T</i> (K)	273(2)	273(2)
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	8.374(2)	12.156(5)
<i>b</i> (Å)	17.789(5)	8.708(3)
<i>c</i> (Å)	12.647(4)	21.327(8)
β (°)	95.226(4)	92.847(6)
<i>V</i> (Å ³)	1876.3(9)	2255(1)
<i>Z</i>	4	4
<i>D</i> _{calc} (g/cm ³)	1.684	1.664
Absorption coefficient (nm ⁻¹)	1.471	1.037
<i>F</i> (000)	964	1156
Crystal size (mm ³)	0.37 × 0.11 × 0.07	0.29 × 0.13 × 0.08
θ Range for data collection (°)	1.98–29.22	1.91–29.17
Limiting indices	–11 ≤ <i>h</i> ≤ 10, –23 ≤ <i>k</i> ≤ 17, –17 ≤ <i>l</i> ≤ 13	–16 ≤ <i>h</i> ≤ 13, –11 ≤ <i>k</i> ≤ 11, –27 ≤ <i>l</i> ≤ 27
Reflections collected	11 889	13 865
Independent reflections	4671	5559
Absorption correction	semi-empirical	semi-empirical
Maximum and minimum transmission	0.9040 and 0.6121	0.9244 and 0.7557
Refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4671/0/262	5559/0/364
Goodness-of-fit on <i>F</i> ²	1.114	1.005
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0321, 0.0859	0.0378, 0.1007
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0483, 0.0898	0.0605, 0.1082
Largest difference in peak and hole (e Å ⁻³)	0.334 and –0.505	0.400 and –0.614

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [(F_o^2)^2]]^{1/2}$.

Table 1. Selected bond lengths and bond angles are given in Table 2.

2.6. Computational details

The calculations were carried out using the GAUSSIAN-03 program suite [9], including optimized geometries, and calculation of vibrational frequencies were carried out at the B3LYP [10,11] level of theory. Mulliken population analysis was also performed under this method. We employed the 6-31G(d) basis set for H, C, N and Cl, and the LANL2DZ effective core potential (ECP) set of Hay and Wadt [12] for Cu. All of the results (structures and energies) from the DFT calculations are available as electronic supplementary information.

3. Results and discussion

3.1. Description of structures

The crystal structure of complex 1 reveals that the coordination geometry around the copper(II) atom is a distorted trigonal bipyramid with the dpapt ligand

existing in an all-*anti* configuration. The Cu(1) atom is coordinated by three nitrogen atoms (N(3) of triazine and N(5), N(1) of different pyridyls) with two additional chloride atoms resulting in five-coordinated geometry (Fig. 1). The Cu(1)–N(3) distance is 2.024(2) Å and the distance to the pyridyl donors N(5) and N(1) are 2.079(2) and 2.066(2) Å, respectively. The distance of Cu(1)–Cl(2) is 2.288(1) Å whereas Cu(1)–Cl(1) forms a long bond with a distance of 2.424(1) Å. The average Cu–N bond length is observed to be 2.056 Å while the average Cu–Cl bond length is 2.356 Å. The bond angles N(1)–Cu(1)–N(5) (124.53(7)°), N(5)–Cu(1)–Cl(1) (113.66(5)°) and N(1)–Cu(1)–Cl(1) (120.32(5)°) sum up approximately to 360° and the angle N(3)–Cu(1)–Cl(2) (177.41(5)°) is approximately 180°, so the coordinated geometry of Cu(II) may be described as distorted trigonal bipyramidal with Cu(1), N(1), N(5) and Cl(1) forming the equatorial plane and Cl(2), N(3) occupying the axial positions. The dihedral angle between the plane (Cu(1), N(1), N(5), Cl(1)) and the triazine plane is 86.7°.

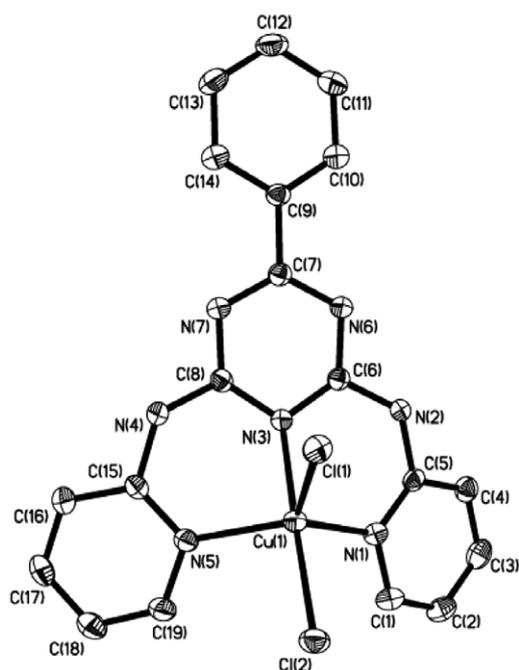
Two molecules of 1 form an antiparallel dimer structure as a result of two N–H···Cl hydrogen bonds (Cl(1A)···N(4B) 3.258 Å, N(4A)···Cl(1B) 3.258 Å) which are symmetry related, then each dimer is linked

Table 2

Selected bond lengths (Å) and bond angles (°) of Cu(dpdpapt)Cl₂ (**1**) and [Cu(dpdpapt)(NO₃)(H₂O)] · NO₃ · H₂O (**2**)

Cu(dpdpapt)Cl ₂ (1)			[Cu(dpdpapt)(NO ₃)(H ₂ O)] · NO ₃ · H ₂ O (2)	
	Experimental	Optimized		Experimental
<i>Bond lengths</i>				
Cu(1)–N(3)	2.024(2)	2.095	Cu(1)–N(3)	2.018(2)
Cu(1)–N(1)	2.066(2)	2.175	Cu(1)–N(1)	1.974(2)
Cu(1)–N(5)	2.079(2)	2.246	Cu(1)–N(5)	1.980(2)
Cu(1)–Cl(1)	2.4243(8)	2.363	Cu(1)–O(5)	2.114(3)
Cu(1)–Cl(2)	2.2878(7)	2.333	Cu(1)–O(7)	2.225(2)
N(1)–C(1)	1.351(3)	1.360	N(9)–O(5)	1.197(4)
N(1)–C(5)	1.335(3)	1.351	N(8)–O(1)	1.250(3)
N(3)–C(8)	1.364(2)	1.362	N(1)–C(1)	1.358(3)
N(3)–C(6)	1.346(2)	1.358	N(1)–C(5)	1.337(3)
N(5)–C(15)	1.331(2)	1.348	N(3)–C(6)	1.359(3)
N(5)–C(19)	1.351(3)	1.359	N(3)–C(8)	1.364(3)
N(6)–C(7)	1.346(2)	1.355	N(5)–C(9)	1.341(3)
N(7)–C(8)	1.326(2)	1.352	N(5)–C(13)	1.365(3)
<i>Bond angles</i>				
N(3)–Cu(1)–N(1)	86.93(7)	84.74	N(1)–Cu(1)–N(5)	170.03(7)
N(3)–Cu(1)–N(5)	87.79(7)	84.33	N(1)–Cu(1)–N(3)	92.90(7)
N(1)–Cu(1)–N(5)	124.53(7)	122.56	N(5)–Cu(1)–N(3)	93.63(7)
N(1)–Cu(1)–Cl(1)	120.32(5)	123.77	N(1)–Cu(1)–O(5)	88.40(9)
N(5)–Cu(1)–Cl(1)	113.66(5)	111.44	N(5)–Cu(1)–O(5)	89.65(9)
N(5)–Cu(1)–Cl(2)	94.13(5)	94.28	N(3)–Cu(1)–O(5)	150.3(1)
N(1)–Cu(1)–Cl(2)	93.39(5)	92.41	N(1)–Cu(1)–O(7)	83.58(8)
N(3)–Cu(1)–Cl(2)	177.41(5)	180.0	N(3)–Cu(1)–O(7)	116.54(7)
N(3)–Cu(1)–Cl(1)	82.94(5)	86.16	N(5)–Cu(1)–O(7)	86.76(8)
Cl(2)–Cu(1)–Cl(1)	94.69(3)	98.05	O(5)–Cu(1)–O(7)	93.10(1)
<i>Hydrogen bonds</i>				
N(2)–H(2A)···Cl(2)#1	3.588		N(2)–H(2)···O(4)#4	3.051
N(4)–H(4A)···Cl(1)#2	3.258		O(7)–H(7A)···O(1)	2.815
C(4)–H(4)···Cl(1)#3	3.405		C(12)–H(12)···O(2)#4	3.205

Symmetry codes: #1: 1/2 + x, 1/2 – y, –1/2 + z; #2: –x, 1 – y, –z; #3: 1 + x, y, z; #4: x, –1 + y, z.

Fig. 1. The ORTEP drawing of Cu(dpdpapt)Cl₂ (**2**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

by face to face π – π stacking (3.461 Å) (between the triazine rings of two neighboring dimers) and two weak hydrogen bonds interactions (Cl···H–C 3.405 Å) forming a 1-D supramolecular ladder structure along the *c*-axis (Fig. 2). The structural characterization of such hydrogen-bonded dimeric structures linked by self-complementary donor/acceptor groups is scarce for metal organic framework [13]. On the other hand, the 1-D supramolecular stacking in the *ab*-plane using N(2)–H···Cl(2) hydrogen bonds, thereby gives rise to a 2-D layer structure (Fig. 3).

Complex **2** has the same coordination configuration as **1**. The Cu(1) atom sits in a five-coordinated environment composed of three nitrogen donors (N(3) of triazine and N(5), N(1) of different pyridyls) with two different oxygen atoms, one (O(7)) from a water molecule, the other (O(5)) from a nitrate anion (Fig. 4). The bond distance to the terminal triazine N(3), (Cu(1)–N(3)) is 2.018(2) Å and the distance to the pyridyl donors N(5) (Cu(1)–N(5)) and N(1) (Cu(1)–N(1)) are 1.980(2) and 1.974(2) Å, respectively. The average Cu–N bond length is observed to be 1.990 Å, which is shorter than that of **1**. Both Cu–N bond lengths are typical of those found for the five-coordinate Cu(II)- μ -

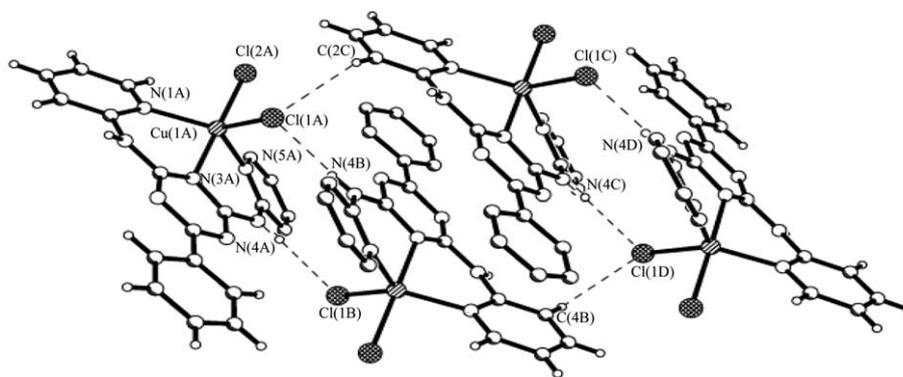


Fig. 2. The one-dimensional ladder structure of $[\text{Cu}(\text{dpapt})\text{Cl}_2]$ (**1**) formed by hydrogen-bonding interactions (dashed lines) and π - π stacking along the c -axis. Some hydrogen atoms are omitted for clarity.

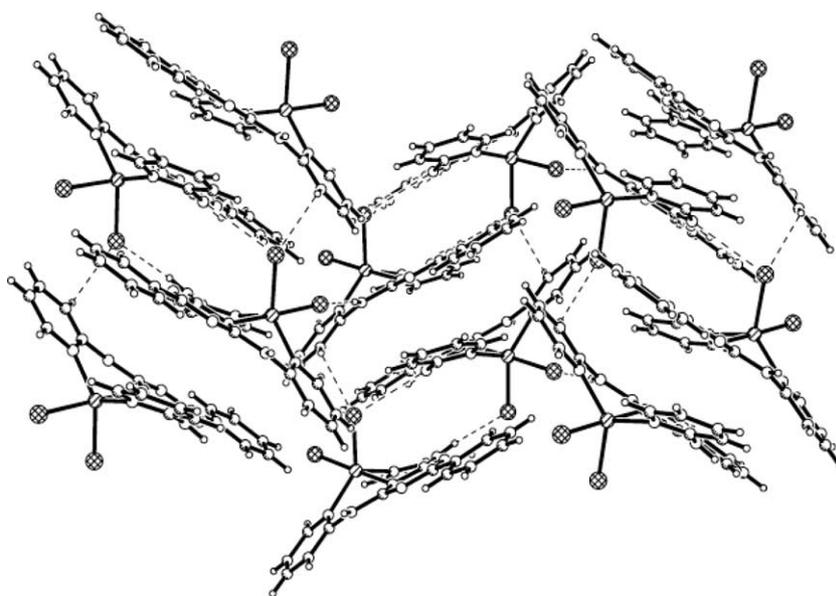


Fig. 3. The layer structure of $[\text{Cu}(\text{dpapt})\text{Cl}_2]$ (**1**).

pmea analogues [14]. The $\text{Cu}(1)\text{--O}(7)$ distance is 2.225(2) Å and $\text{Cu}(1)\text{--O}(5)$ is 2.114(3) Å. The coordination geometry of $\text{Cu}(1)$ is also distorted trigonal bipyramidal with $\text{O}(7)$, $\text{N}(3)$, $\text{Cu}(1)$ and $\text{O}(5)$ in the equatorial plane and the apical sites are occupied by the $\text{N}(1)$ and $\text{N}(5)$ atoms of the pyridyl rings. The dihedral angle between the plane ($\text{Cu}(1)$, $\text{O}(5)$, $\text{O}(7)$, $\text{N}(3)$) and the triazine ring plane is 85.8° .

The crystal framework testifies a one-dimensional chain along the b -axis with hydrogen bonds and π - π stacking interactions. As depicted in Fig. 5, the one-dimensional chains along the b -axis are formed by three different types of hydrogen bonds involving the coordinated molecular water, the coordinated nitrate anion and the non-coordinated nitrate anion ($\text{N}(2\text{A})\text{--H}\cdots\text{O}(4\text{B})$, 3.051 Å; $\text{O}(7\text{A})\text{--H}\cdots\text{O}(1\text{A})$, 2.815 Å; $\text{C}(12\text{B})\text{--H}\cdots\text{O}(2\text{A})$, 3.201 Å) as well as π - π stacking (3.345 Å) between the phenyl and pyridyl rings of two neighboring molecules. Moreover, the crystal structure

consists of alternate layers with an antiparallel alignment of the molecules, and each layer is built up via solvent molecular interactions and hydrogen bonds in the ac -plane as shown in Fig. 6. The adjacent layers are interconnected by solvent molecules, resulting in a 3-D structure.

Although the structures of **1** and **2** exhibit the coordination character of dpapt in part, the framework structures of **1** and **2** are scarce for inorganic triazine compounds. To the best of our knowledge, only one dimeric unit of a transition-metal complex based on tpt has been reported [6a], but no π - π interactions were discussed. Additionally, the ladder and layer frameworks of **1** and **2** are exclusive and structures of this type containing tpt have not been reported to date. The coordination of one metal ion, especially $\text{Cu}(\text{II})$, to tpt induces the hydrolysis of tpt [5,6]. Dinuclear metal complexes of tpt have also been described [6]. Although tpt has a more versatile coordination ability [6b] than

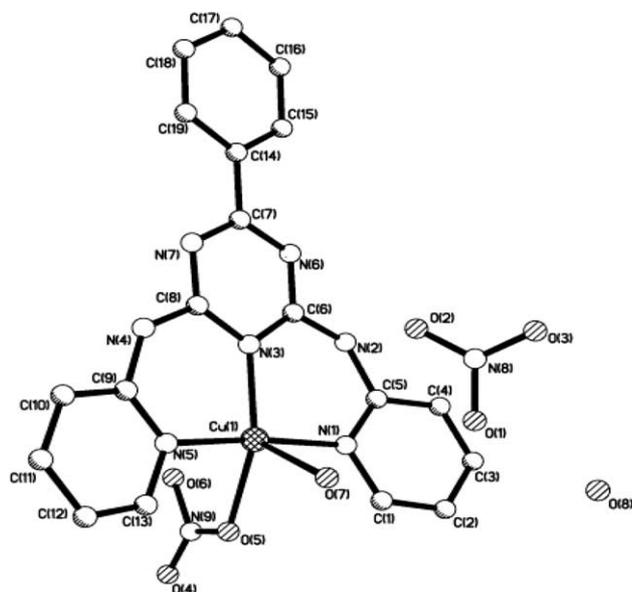


Fig. 4. Molecular structure of $[\text{Cu}(\text{dpdpdapt})(\text{NO}_3)(\text{H}_2\text{O})] \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$ (**2**). Thermal ellipsoids represent the 50% probability surfaces. Hydrogen atoms are omitted for clarity.

dpdpdapt, in theory, the dpdpdapt ligand has its intriguing character revealed in this article.

3.2. Spectroscopic properties

The IR spectra of the complexes exhibit several characteristic strong bands. In complex **1**, the bands around 1425 and 1496 cm^{-1} in the ligand dpdpdapt, attributed to the $\text{C}=\text{N}$ groups, are shifted to 1464 and 1570 cm^{-1} , respectively, confirming the involvement of dpdpdapt in the copper complexation. In complex **2**, the corresponding bands are shifted to 1580 and 1640 cm^{-1} . The bands corresponding to NO_3^- are at 1421 , 1382 , 1022 and 775 cm^{-1} and the broad band at $3290\text{--}3421 \text{ cm}^{-1}$ represents the existence of $\nu(\text{H}_2\text{O})$ in complex **2**.

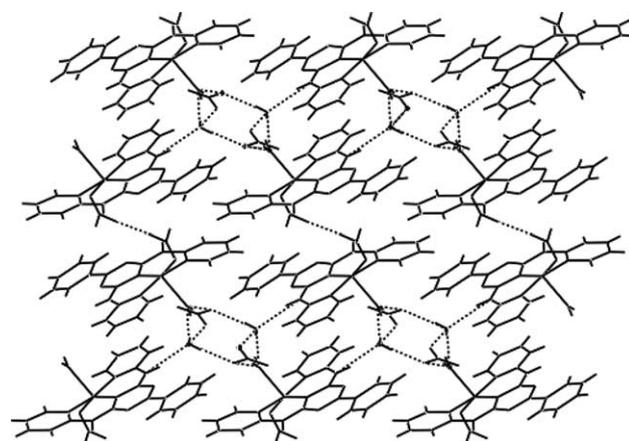


Fig. 6. Layer framework of $[\text{Cu}(\text{dpdpdapt})(\text{NO}_3)(\text{H}_2\text{O})] \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$ (**2**) in the ac -plane.

The UV–Vis spectra of the complexes are recorded in methanol and are characterised by several spectral regions. The absorption bands in the region of 260 and 285 nm for the ligand dpdpdapt are ligand-centered (LC) due to $\pi\text{--}\pi^*$ transitions [15,16]. The shoulder at 300 nm for complexes **1** and **2** is due to a d–d transition and the low-energy bands at 341 , 384 and 389 nm are assigned to metal-to-ligand charge transfer (MLCT) transitions [17,18].

The luminescence data were recorded in methanol at room temperature. The excitation–emission spectrum of dpdpdapt shows the strongest emission peak at 375.4 nm with the excitation peak at 330.0 nm . The emission band of dpdpdapt is attributed to the $\pi^*\text{--n}$ transitions. The strongest excitation peak for complex **1** is at 310.0 nm and for complex **2** at 300.0 nm , and their emission spectra show a main strong peak at 413.6 and 438.0 nm , respectively. These shoulder peaks of the emission spectra are probably due to the ligand-to-metal charge-transfer (LMCT) bands [19]. The strong fluorescent emissions of the dpdpdapt supramolecular complexes **1**

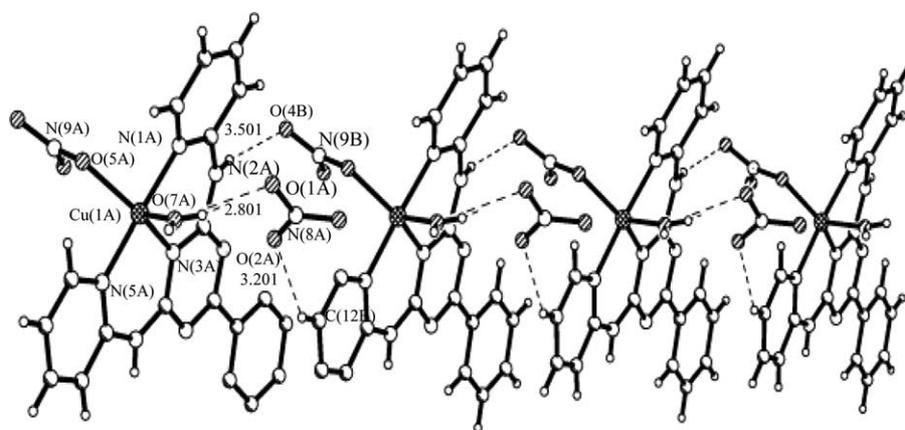


Fig. 5. The one-dimensional chain structure of $[\text{Cu}(\text{dpdpdapt})(\text{NO}_3)(\text{H}_2\text{O})] \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$ (**2**) formed by hydrogen-bonding interactions (dashed lines) and $\pi\text{--}\pi$ stacking along the b -axis. Some hydrogen atoms are omitted for clarity.

and **2** make them potentially useful photoactive materials.

3.3. Computational results and discussion

DFT calculations (B3LYP/6-31G(d)) have been carried out for the coordination conformations of dpdapt, and the optimized structures (verified by calculating the vibrational frequencies that result in the absence of imaginary eigenvalues) are shown in Fig. 7. The relative energies of each conformation given in this article include zero-point corrections (ZPE). $E_{anti-anti-anti-anti}$, $E_{syn-syn-anti-anti}$ and $E_{syn-syn-syn-syn}$ equal -1115.698749 , -1115.700689 and -1115.699802 hartree, respectively. It is found that the energies of the conformers are similar, while the *syn-syn-anti-anti* conformer is the most stable by 5.09 – 2.33 kJ mol $^{-1}$. Complexes **1** and **2** exist with the ligand in the all-*anti* conformation. Clearly the free ligand, with its preferred *syn-syn-anti-anti* conformation, does not effect the conformation change in **1** and **2** because of its minimal energy difference.

Optimized geometries for **1** were verified by performing a frequency calculation. The optimized bond lengths and angles are presented in Table 2. In general, the calculated bond lengths and angles are in agreement with experimental crystal data and the large differences (~ 0.2 Å, $\sim 3^\circ$) may be noticed for deviations around the central copper atoms. The deviations come mainly from two factors: one is that the theoretical calculations do not consider the effects of chemical environment (the complex is treated as a free molecule), and basis sets are still approximate to a certain extent. However, the coordination geometry of Cu(II) is also a distorted trigonal bipyramid. The bond angles N(1)–Cu(1)–N(5) (121.56°), N(5)–Cu(1)–Cl(1) (111.44°) and N(1)–Cu(1)–Cl(1) (124.77°) sum up approximately to 360° and the angle N(3)–Cu(1)–Cl(2) is 180° . So the results should be significant in computations of this large system.

The overlap populations (Table 3) between Cu(1) and Cl(1) (0.2663) is stronger than that of Cu(1)–Cl(2) (0.2275), which is consistent with the experimental result that the bond length of Cu(1)–Cl(2) is clearly longer

Table 3
Population analysis of **1**

Bond	
Cu(1)–Cl(1)	0.2663
Cu(1)–Cl(2)	0.2275
Cu(1)–N(3)	0.1236
Cu(1)–N(1)	0.1123
Cu(1)–N(5)	0.1065
N(3)–C(6)	0.2716
N(3)–C(8)	0.2790
N(6)–C(7)	0.3589
N(7)–C(8)	0.4484

than that of Cu(1)–Cl(1). The bond intensity order is Cu(1)–N(3) > Cu(1)–N(1) > Cu(1)–N(5) in accord with that in the experimental results (Cu(1)–N(5) > Cu(1)–N(1) > Cu(1)–N(3)). Because N(3) is coordinated to the center Cu atom, the populations of N(3)–C(6) and N(3)–C(8) are less than that of N(6)–C(7) and N(7)–C(8).

The Mulliken charge of the central Cu metal (Table 4) changes from +2 to 0.275. Obviously, Cu has been coordinated by the ligand and its charge transfers to the ligand. The net atomic charge of the coordinated Cl(1), Cl(2), N(1), N(3) and N(5) atoms are negative. Compared to the dpdapt ligand (N(1), -0.259 ; N(3) and N(5), -0.438 ; N(6) and N(7), -0.353), the change in the charge distribution value of the donor nitrogen atoms (N(1), N(3), N(5)) are more than that of the non-coordinated nitrogen atoms (N(6), N(7)) in triazine.

Table 4
Mulliken atomic charges (e) for **1**

Atom	Charge
Cu(1)	0.275
Cl(1)	-0.397
Cl(2)	-0.383
N(3)	-0.498
N(5)	-0.518
N(1)	-0.545
N(6)	-0.432
N(7)	-0.437

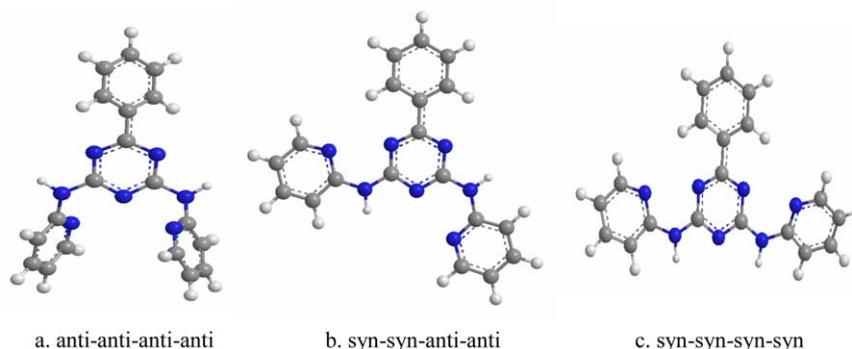


Fig. 7. Optimized structures of dpdapt's coordination conformations.

Table 5

The energy (eV) and character of the selected molecular orbitals with α spins for **1**

Orbital	Energy	Character
HOMO – 3	–6.126	$\pi(\text{Cu}-\text{Cl}), \pi(\text{Cl})$
HOMO – 2	–5.711	$d_{xz}(\text{Cu}), \pi(\text{Cl})$
HOMO – 1	–5.472	$d_{yz}(\text{Cu}), \pi(\text{Cl})$
HOMO	–5.364	$d_{xy}(\text{Cu}), \pi(\text{Cl})$
LUMO	–3.096	$\pi^*(\text{dpdapt}), d_{xy}(\text{Cu})$
LUMO + 1	–1.989	$\pi^*(\text{dpdapt})$
LUMO + 2	–1.686	$\pi^*(\text{dpdapt}), d_{xy}(\text{Cu})$
LUMO + 3	–1.600	$d_z(\text{Cu})-\sigma(\text{Cl})$

All this data show strong complexation between Cu and its coordinated atoms.

The energies and characters of the selected MOs for **1** are presented in Table 5. According to molecular orbital theory, the frontier orbital and nearby molecular orbitals are the most important factors to the activity. The highest occupied molecular orbital (HOMO) and the nearby occupied molecular orbitals are prone to donate electrons, but the lowest unoccupied molecular orbital (LUMO) and the nearby unoccupied orbitals are prone to accept electrons. The more different the frontier orbitals are, the more stable the molecular structure is [20]. The copper d_π atomic orbitals (d_{xz}, d_{yz} and d_{xy}) and π orbitals of the chlorine atoms make the main contributions into the HOMO – 2, HOMO – 1 and HOMO. The LUMO orbital has predominantly $\pi^*(\text{dpdapt})$ character. The results approved its coordination behavior and the value of ΔE ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) is 2.268 eV, which shows that the complex **1** can exist stably.

Appendix A. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 260645 for compound **1** and 260646 for compound **2**. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.poly.2005.06.061.

References

- [1] (a) Y.-Q. Sun, J. Zhang, G.-Y. Yang, *J. Chem. Soc., Dalton Trans.* (2003) 3634; (b) B. Moulton, M.J. Zaworotko, *Chem. Rev.* 101 (2001) 1629; (c) Y.B. Dong, P. Wang, R.Q. Huang, *Inorg. Chem.* 43 (2004) 4727;
- (d) D.N. Dybtsev, H. Chun, K. Kim, *Chem. Commun.* (2004) 1594.
- [2] (a) S. Koner, S. Saha, K.L. Okamoto, J.P. Tuchagues, *Inorg. Chem.* 42 (2003) 4668; (b) Y.Q. Zheng, J.L. Lin, Z.P. Kong, *Inorg. Chem.* 43 (2004) 2590; (c) C.D. Wu, H.L. Ngo, W. Lin, *Chem. Commun.* (2004) 1588; (d) I.G. Filippova, V.K. Kravtsov, M.R.J. Gdaneč, *Coord. Chem.* 39 (2000) 1363.
- [3] (a) Z. Huang, H.B. Song, M. Du, S.T. Chen, X.H. Bu, *Inorg. Chem.* 43 (2004) 932; (b) C. Janiak, *J. Chem. Soc., Dalton Trans.* (2003) 2781.
- [4] F.H. Case, E.J. Koft, *J. Am. Chem. Soc.* 81 (1959) 905.
- [5] (a) A. Cantarero, J.M. Amigo, J. Faus, M. Julve, T. Debaerdemaeker, *J. Chem. Soc., Dalton Trans.* (1988) 2033; (b) E.I. Lerner, S.J. Lippard, *Inorg. Chem.* 16 (1977) 1546; (c) J. Faus, M. Julve, J.M. Amigo, T. Debaerdemaeker, *J. Chem. Soc., Dalton Trans.* (1989) 1681; (d) N.C. Thomas, B.L. Foley, A.L. Rheingold, *Inorg. Chem.* 27 (1977) 1546; (e) X.Y. Chen, F.J. Femia, J.W. Babich, J.A. Zubieta, *Inorg. Chem.* 40 (2001) 2769.
- [6] (a) G. Thorsten, L. Thomas, F. Roland, *Eur. J. Inorg. Chem.* (2004) 394; (b) N.C. Thomas, B.L. Foley, A.L. Rheingold, *Inorg. Chem.* 27 (1988) 3427.
- [7] G.M. Sheldrick, *SHELXL-97: Program for Crystal Structure Determination*, University of Göttingen, Göttingen, Germany, 1997.
- [8] G.M. Sheldrick, *SHELXL-97: Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.
- [9] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Frakas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, K.A. Allaham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *GAUSSIAN-03. Revision B.03*, Gaussian, Inc., Pittsburgh, PA, 2003.
- [10] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [11] C.L.W. Yang, R.G. Parr, *Phys. Rev.* 37 (1988) 785.
- [12] A.K. Vrkic, T. Taverner, *J. Chem. Soc., Dalton Trans.* (2004) 197.
- [13] H.-R. Ma, Y.-Y. Wang, P. Liu, D.-S. Li, G.-H. Lee, S.-M. Peng, *Polyhedron* 24 (2005) 215.
- [14] K.-Y. Choi, Y.-M. Jeon, H. Ryu, J.-J. Oh, H.-H. Lim, M.-W. Kim, *Polyhedron* 23 (2004) 903.
- [15] D.B. MacQueen, J.D. Petersen, *Inorg. Chem.* 29 (1990) 2313.
- [16] R.M. Berger, J.R. Holcombe, *Inorg. Chim. Acta* (1995) 232.
- [17] A. Juris, V. Balzani, F. Barigelli, S. Campagna, P. Belser, A.V. Zelewsky, *Coord. Chem. Rev.* (1998) 8485.
- [18] R.M. Berger, D.D. Ellis, *Inorg. Chim. Acta* (1996) 241.
- [19] Q.R. Fang, G.S. Zhu, M. Xue, *J. Chem. Soc., Dalton Trans.* (2004) 2205.
- [20] K.C. Zheng, Z.N. Chen, *Acta Phys. Chim. Sinica (Chinese)* 15 (1999) 204.