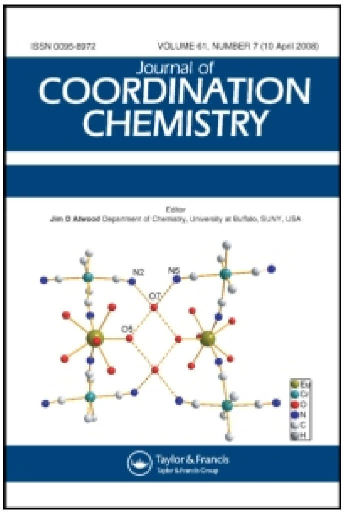

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A 2-D coordination polymer with $Cu_4^IS_4$-core as joints

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To cite this Article Zhu, Hai-Bin , Xu, Gang , Ji, Jun-Feng and Gou, Shao-Hua(2009) 'A 2-D coordination polymer with $Cu_4^IS_4$-core as joints', Journal of Coordination Chemistry, 62: 14, 2276 — 2282
To link to this Article: DOI: 10.1080/00958970902838784
URL: http://dx.doi.org/10.1080/00958970902838784

Journal of Coordination Chemistry
Vol. 62, No. 14, 20 July 2009, 2276–2282

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A 2-D coordination polymer with $Cu^I_4S_4$-core as joints

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(*Received 6 August 2008; in final form 3 December 2008*)

A coordination polymer based on copper(I) and a heterocyclic thione ligand, H**PPT4** (H**PPT4** = 4-pyridin-4-yl-pyrimidine-2-thiol) has been prepared. The compound $C_{21}H_{19}Cu_2N_7OS_2$ (**1**) has a 2-D polymeric structure with Cu^I_4-core as joints linked by μ-thiolate bridges. Crystal data for compound **1**: Monoclinic, space group $C2/c$, $a = 22.346(14)$ Å, $b = 15.649(10)$ Å, $c = 13.588(9)$ Å, $\beta = 97.183(12)^\circ$, $V = 4714(5)$ Å^3, and $Z = 8$. Compound **1** displays multiple emissions with maximum wavelength at 391 and 469 nm under photoexcitation at 340 nm.

Keywords: Copper(I); Multinuclear cluster; NS-donor; Crystal structure

1. Introduction

Multinuclear copper(I) complexes are ubiquitous in synthetic chemistry and biological systems due to their special luminescence and bio-functions in metalloenzymes [1]. For example, nitrous oxide reductase (N_2OR) from *Pseudomonas nautica* (Pn) and *Paracoccus denitrificans* (Pd) contain so-called Cu_A and Cu_Z active sites, of which Cu_Z comprises a μ_4-sulfide bridged $Cu^I_3Cu^{II}$ cluster embedded in seven histidine residues [2]. In our recent study on the assembly of Cu(I) with a multidentate ligand containing O, N, and S donors, a tetranuclear copper(I) cluster, Cu_4(**PPT2**)$_4$, was obtained *via* a C–S bond cleavage [3]; the structure is very close to that of the Cu_Z-core of N_2OR. The Cu_4(**PPT2**)$_4$ cluster could be alternatively generated by direct reaction of CuCl with the heterocyclic-thione ligand of H**PPT2** (H**PPT2** = 4-pyridin-2-yl-pyrimidine-2-thiol). Encouraged by these results, we decided to continue studying the self-assembly of Cu(I) with H**PPT4** (H**PPT4** = 4-pyridin-4-yl-pyrimidine-2-thiol) (the procedure for preparation of H**PPT4** ligand is similar to that for H**PPT2** which has been reported in our previous work, see reference [3]), which is distinct from H**PPT2** only in the position of the substituted group on pyridine (scheme 1). In this article, we report reaction of CuCl with H**PPT4** produces an intriguing 2-D coordination polymer **1** with Cu^I_4-core as joints linked by μ-thiolate bridges instead of the discrete $Cu^I_4S_4$ cluster found for H**PPT2**.

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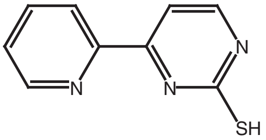
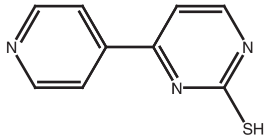
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970902838784

H**PPT2**



H**PPT2** = 4-pyridin-2-yl-pyrimidine-2-thiol

H**PPT4**



H**PPT4** = 4-pyridin-4-yl-pyrimidine-2-thiol

Scheme 1. Heterocyclic thione H**PPT4**.

2. Experimental

2.1. *Synthesis and characterization*

2.1.1. Preparation of 1. A solution of CuCl (0.100 g, 1.00 mmol) in CH_3CN (100 mL) was added to a solution of H**PPT4** (0.189 g, 1.00 mmol) in MeOH (100 mL) with a small amount of Et_3N (0.3 mL, 2.0 mmol). The mixture was stirred at room temperature for 1 min and left for 3 days to generate dark red micro-crystals. Yield: 0.150 g, 52%. IR (KBr, cm^{-1}): $\nu = 3434$ s, 1626 w, 1558 s, 1525 m, 1400 m, 1337 m, 1188 w. Anal. Calcd for $C_{21}H_{19}Cu_2N_7OS_2$(%): C, 43.74; H, 3.32; N, 17.00. Found: C, 43.70; H, 3.39; N, 16.87. TGA-DSC analysis showed the onset temperature for decomposition to be *ca* 320°C.

Elemental analyses (C, H, and N) were performed on a CHN-O-Rapid analyzer. Infrared spectra were conducted on a Bruker Vector 22 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. Thermal analysis data were collected on a PerkinElmer Pyris 1 TGA analyzer in N_2 at a rate of $10°C\,min^{-1}$. Luminescence spectra for solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrophotometer.

2.2. *Single-crystal X-ray diffraction*

Single-crystal data were collected on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The crystal structure was solved by direct methods and refined using a full-matrix least-square technique with SHELXL-97 [4]. All non-hydrogen atoms were refined anisotropically, whereas all hydrogen atoms were placed at idealized positions. Experimental details of the X-ray analysis for **1** are given in table 1. Selected bond lengths (Å) and angles (°) are listed in table 2.

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

Empirical formula	$C_{21}H_{19}Cu_2N_7OS_2$
Molecular weight	576.67
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions (Å, °)	
a	22.346(14)
b	15.649(10)
c	13.588(9)
β	97.183(12)
V (Å^3)	4714(5)
Z, ρ_{Calcd} (Mg m^{-3})	8, 1.625
μ (Mo-Kα) (mm^{-1})	2.010
$F(000)$	2336
Goodness of fit	0.922
R_1 $[I > 2\sigma(I)]$	0.0694
wR_2 $[I > 2\sigma(I)]$	0.1599

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

Cu1–S1	2.220(2)	Cu1–S2	2.238(2)
Cu1–N6a	2.049(5)	Cu2–S2	2.300(2)
Cu2–N1	2.082(5)	Cu2–S1a	2.350(3)
Cu2–N4b	2.139(5)		
S1–Cu1–S2	133.61(7)	S1–Cu1–N6a	105.23(14)
S2–Cu1–N6a	119.97(14)	S2–Cu2–N1	122.22(15)
S1a–Cu2–S2	118.16(7)	S2–Cu2–N4b	107.08(14)
S1a–Cu2–N1	106.91(15)	N1–Cu2–N4b	97.80(19)
S1a–Cu2–N4b	100.32(19)		

Note: Symmetry codes (a): $1-x$, y, $1/2-z$; (b): $1/2-x$, $1/2-y$, $1/2-z$.

3. Results and discussion

3.1. *Structure description*

Compound **1** crystallizes in the *C2/c* space group with a simple asymmetric unit consisting of two H**PPT4** ligands, two cuprous ions, and two solvent molecules (CH_3CN and CH_3OH). Similar to the reported Cu_4(**PPT2**)$_4$, compound **1** also has a Cu^I_4-core supported by six individual H**TTP4** ligands, wherein four Cu^I ions are joined together by four S atoms in μ_2 coordination to form a saddle-shaped, eight-membered Cu_4S_4 ring (figure 1). The Cu–S bond distances vary in the range 2.220(2)–2.350(3) Å, comparable to those of Cu_Z [2]. The inter-metallic distances of Cu1–Cu1a (2.517(2) Å), Cu1–Cu2a (2.982(2) Å), Cu1–Cu2 (2.708(2) Å), Cu2–Cu1a (2.982(2) Å), and Cu1a–Cu2a (2.708(2) Å) are close to the sum of the van der Waals radii of Cu^I centers (2.80 Å) [5], which imply the existence of Cu^I–Cu^I interactions [6]. The relatively longer Cu2–Cu2a separation of 3.945(3) Å suggests that the inter-metallic interaction is rather weak. Cu^I–Cu^I interactions have been widely invoked to be a driving force for assembly of Cu^I aggregates [7]. In our case, Cu^I–Cu^I interactions may also play an important role in the formation of the $Cu^I_4S_4$ core in addition to the inherent propensity of sulfur to bridge. Notably, the Cu^I_4-core consists of a tetrahedron of copper(I) atoms, which resembles those found in $[Cu_4(tpdt)_3]^{2-}$ (tpdt = 3,4-thiophenedithiolate) and

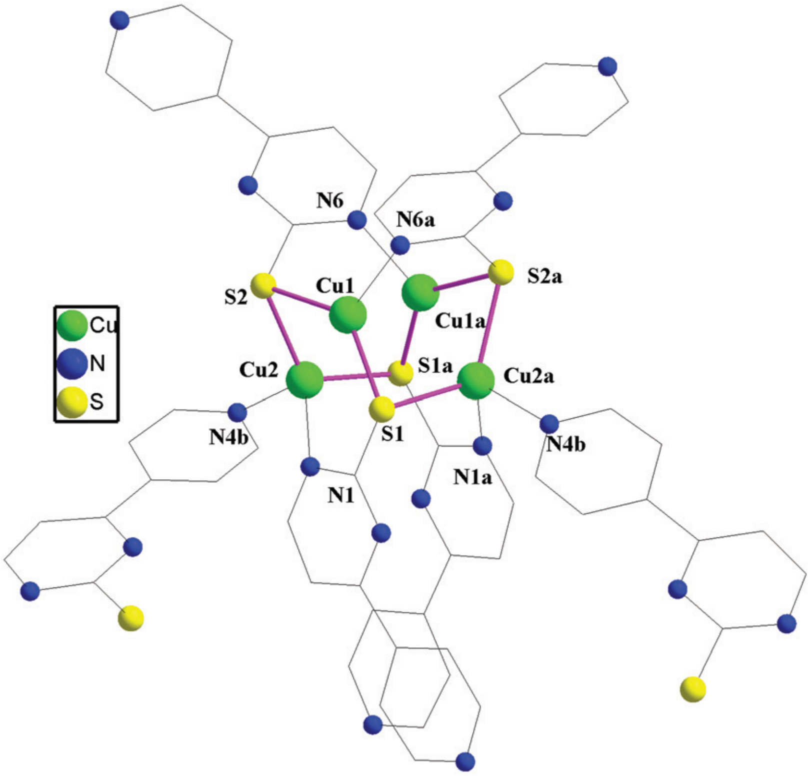


Figure 1. Structure of $Cu^{I}_{4}S_4$ cluster in **1** (hydrogen atoms and solvent molecules omitted for clarity) and Cu_4S_4 eight-membered ring indicated with thick ball-and-stick model [selected interatomic distances (Å): Cu1–Cu1a, 2.571(2); Cu1–Cu2a, 2.982(2); Cu1–Cu2, 2.708(2); Cu1a–Cu2a, 2.708(2); Cu1a–Cu2, 2.982(2); Cu2-Cu2a, 3.945(3)].

$[Cu_4L_3]^+$ [8], but is different from the square-planar arrangement of Cu^{I}_{4} cores found both in the synthetic product $Cu^{I}_{4}(SR)_4$ and in the embedded Cu_4S_4 cofactor of a synthetic miniature metalloprotein [9]. It should be noted that the number of coordinated nitrogens around Cu^{I}_{4}-core in **1** is one less than in Cu_Z and Cu_4(**PPT2**)$_4$. Among four Cu^{I} ions in the Cu^{I}_{4}-core, two are three-coordinate by one N_{pym} and two sulfurs belonging to three different ligands; the other two are four-coordinate by one N_{pym}, one N_{py}, and two sulfurs from four different ligands (pym = pyrimidine, py = pyridine). The mean Cu–N bond length of **1** is quite close to that in Cu_Z (Cu_Z, 2.06 Å; **2**, 2.09 Å). Complex **1** is remarkably dissimilar to the reported Cu_4(**PPT2**)$_4$ which is made up of three four-coordinate Cu^{I} ions and one three-coordinate Cu^{I} [3].

Each Cu^{I}_{4}-core is coordinated by six H**PPT4** ligands which behave differently. Among them, four ligands share four adjacent Cu^{I}_{4}-cores with N_{pym} and S-donors bridging three Cu^{I} ions in one Cu^{I}_{4}-core unit and one N_{py} bound to one Cu^{I} ion from another Cu^{I}_{4}-core, while the remaining two are connected to copper only through N_{pym} and S-donors with the N_{py} uncoordinated, forming π–π offset stacking with a separation of ~3.4 Å and an intercrossing angle ~62°. By repeating the unit in the *ab* plane, an infinite rhombus 2-D network is formed with the Cu^{I}_{4}-core as joints and

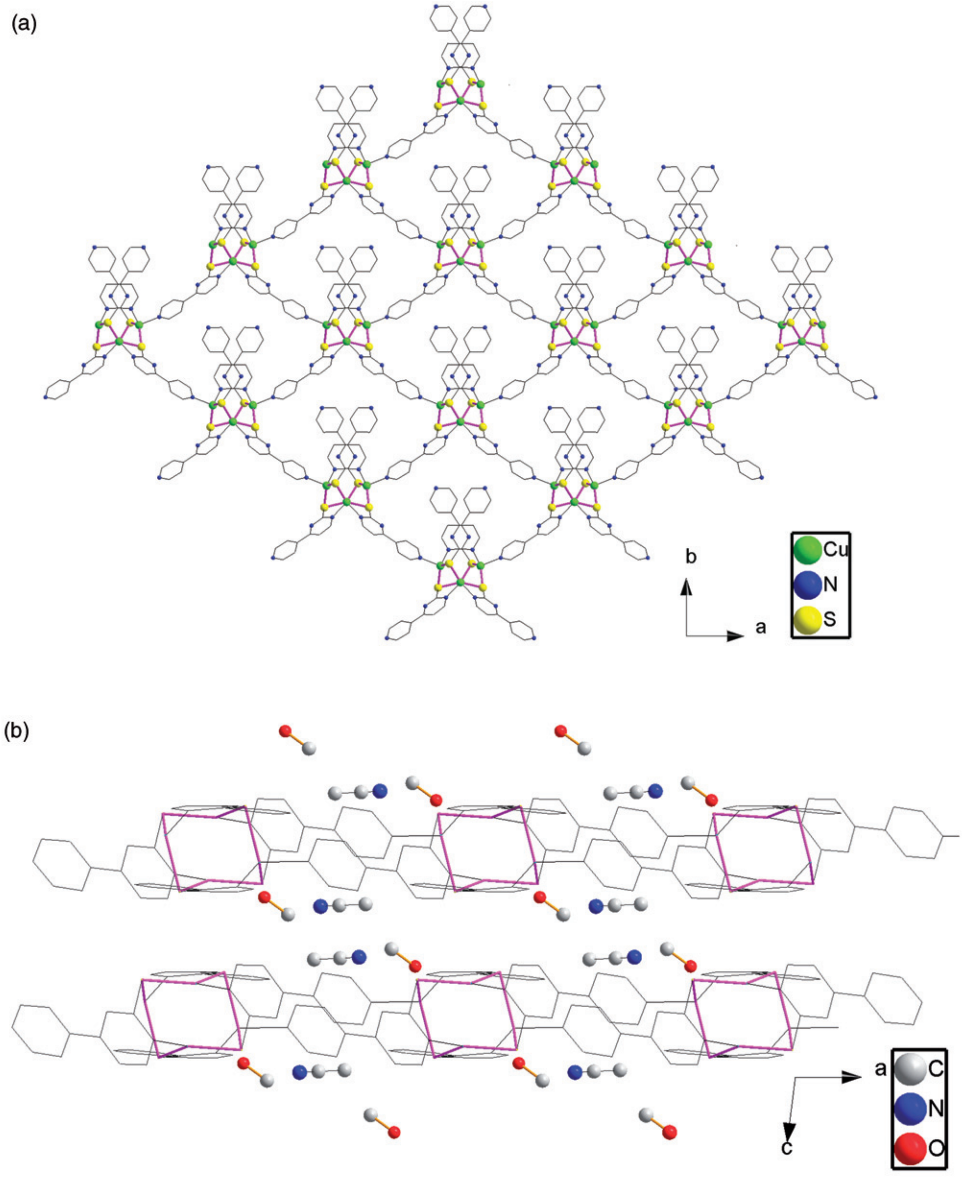


Figure 2. (a) 2-D rhombus network of **1** viewed along the *c*-axis; (b) side view of packing structure of **1** [solvent molecules indicated with ball-and-stick model and Cu_4S_4 core highlighted with thick sticks].

PPT4$^-$ as linkers; the Cu_4S_4 unit lies on a crystallographic two-fold axis parallel to *b* (figure 2a). Along the *c*-axis, layers are stacked in a reversed fashion and the solvent molecules (CH_3OH and CH_3CN) occupy the interlayer space (figure 2b). Thus, the extended structure of **1** could be described as a 2-D coordination polymer with $Cu^I_4S_4$-core as network joints.

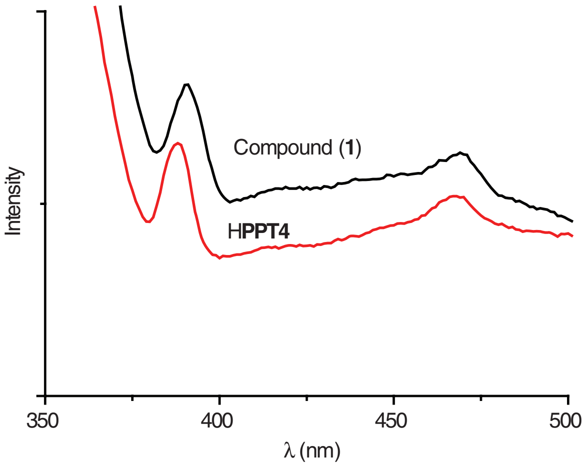


Figure 3. The luminescence emission spectra for **1** and H**PPT4**.

3.2. *Luminescent properties of 1*

Metal-organic polymers have the ability to affect the emission wavelength and intensity of the organic material through metal coordination [10]. Han *et al.* [11] have previously reported on a copper(I) organosulfide $[Cu^I_3(pymt)_3]$ (pymt = pyrimidine-2-thiolate) with strong red photoluminescence. Thus, the solid emission spectra of **1** together with the free ligand H**PPT4** are measured at room temperature (figure 3). Upon excitation at 340 nm, **1** exhibits emission peaks at 391 and 469 nm whereas H**PPT4** gives emission peaks centered at 388 and 468 nm. Obviously, the luminescence of **1** originates from H**PPT4**. The slight shifts are probably resulted from coordination.

4. Conclusion

We have studied the self-assembly of heterocyclic thione ligand of H**PPT4** with CuCl, which results in a 2-D coordination polymer with $Cu^I{}_4$-core as joints, in striking contrast with the discrete $Cu^I_4S_4$ cluster for H**PPT2**.

Supplementary material

Crystallographic data for **1** has been deposited at the Cambridge Crystallographic Data Centre as supplementary publications (CCDC-643415). This data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif

Acknowledgments

We acknowledge financial support from National Natural Science Foundation of China (No. 20801011) and China Postdoctoral Research Fund (No. 20070411010).

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