ORIGINAL PAPER

Syntheses and Crystal Structures of Two Cu^{II} Coordination Isomers [Cu(pmt)$_2$] · 4H$_2$O (1) and {[Cu(pmt)$_2$] · 2H$_2$O}$_n$ (2)

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Abstract A pair of Cu^{II} coordination isomers [Cu(pmt)$_2$] · 4H$_2$O (**1**) and {[Cu(pmt)$_2$] · 2H$_2$O}$_n$ (**2**) [Hpmt = 2-(2-pyridylmethylamino) ethanesulfonic acid] have been prepared by reaction of the same proportion CuCl$_2$ · 2H$_2$O and Hpmt but with different experimental methods in water–methanol mixed solution, and were characterized by X-ray diffraction, elemental analysis, IR spectrum. X-ray analysis indicates that complex (**1**) is a mononuclear complex in which two deprotonated pmt ligands coordinate in a facial tridentate arrangement about the Cu^{II} atom. While complex (**2**) is a coordination polymer, in which four N atoms of pmt ligands coordinate to one Cu^{II} atom but its sulfonate O atoms bond to adjacent Cu^{II} atom. Thus 12-membered rings (–Cu–N–C–C–S–O–)$_2$ are obtained between two neighbouring Cu^{II} atoms and they connect one another to form this new polymer. Crystal data: [Cu(pmt)$_2$] · 4H$_2$O (**1**), Mr = 566.10, monoclinic, $P2_1/c$, a = 9.1950(8) Å, b = 11.5093(10) Å, c = 11.2304(10) Å, β = 105.5550(10)°, Z = 2, V = 1144.96 (17) Å^3, R_1 = 0.0407, wR_2 = 0.1242 [$I > 2\sigma(I)$]; {[Cu (pmt)$_2$] · 2H$_2$O}$_n$ (**2**), Mr = 530.07, triclinic, P-1, a = 7.6165 (19) Å, b = 8.806(2) Å, c = 9.592(4) Å, α = 104.933(4)°, β = 106.732(4)°, γ = 109.503(3)°, Z = 1, V = 534.2(3) Å^3, R_1 = 0.0470, wR_2 = 0.1082 [$I > 2\sigma(I)$].

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Introduction

Schiff base complexes containing both sulfur and amino acid functionalities have aroused considerable recent interest because of their biological activities [1–3]. 2-Aminoethanesulfonic acid, known as taurine, is indispensable to human life and plays a significant part in physiological functions. Casella and Gullotti [4] have found that zinc and copper complexes of schiff bases ligands, prepared by the condensation of 2-pyridinecarboxaldehyde with non-polar amino acid, are unstable. This has been attributed to the rigidity of the C=N double bond in the free schiff bases and this agreement is later confirmed by Wagner and Walker [5]. In order to explore complexes that are more stable and have much stronger biological activities, we have recently drawn our attention to coordination complexes based on the reduced schiff base ligand 2-(2-pyridylmethylamino) ethanesulfonic acid (Hpmt). The present paper reports the syntheses and crystal structures of two Cu^{II} coordination isomers [Cu(pmt)$_2$] · 4H$_2$O (**1**) and {[Cu(pmt)$_2$] · 2H$_2$O}$_n$ (**2**), whose X-ray analysis reveals that (**1**) is a mononuclear structure and (**2**) is a coordination polymer.

Experimental Section

All chemicals except the Hpmt ligand were of reagent grade obtained from commercial sources and used without further purification. The C, H, N, S elemental analyses were preformed on a Elementar Vario EL elemental analyzer. The IR spectrum was recorded with a Shimadzu IR-408 spectrophotometer using the KBr pellet in the range of 4,000–400 cm^{-1}. The Hpmt ligand was prepared according to the procedure in literature [6].

Synthesis of $[Cu(pmt)_2] \cdot 4H_2O$ (1)

A solution (5 ml) of ligand Hpmt (2 mmol, 0.432 g) was basified with KOH (1 mol/l) to a pH of 7.5–8.0. Then a solution of $CuCl_2 \cdot 2H_2O$ (0.171 g, 1.0 mmol) in methanol (8 ml) was added dropwise to it. The resulting mixture was stirred at 333 K for 6 h, filtrated, and kept at room temperature to obtain blue, block-shaped crystals after 1 week. Yield: 0.26 g (47%). Anal. Calcd for $C_{16}H_{30}CuN_4O_{10}S_2$: C, 33.92; H, 5.30; N, 9.89; S, 11.30%. Found: C, 33.87; H, 5.33; N, 9.92; S, 11.25%. IR data (cm^{-1}): 3482 (s), 3232 (m), 1612 (m), 1573 (m), 1217 (s), 1165 (s), 1041 (s), 771 (s), 747 (m).

Synthesis of $\{[Cu(pmt)_2] \cdot 2H_2O\}_n$ (2)

A solution (5 ml) of ligand Hpmt (2 mmol, 0.432 g) was added dropwise to a solution of $CuCl_2 \cdot 2H_2O$ (0.171 g, 1.0 mmol) in methanol (8 ml), the obtained mixture was stirred at 333 K for 3 h. After that, the mixture was basified with KOH (1 mol/l) to a pH of 7.5–8.0 and continued stirring for another 6 h, filtrated. One month later, dark-blue block crystals were grown from the filtrate by slow evaporation. Yield: 0.18 g (34%). Anal. Calcd for $C_{16}H_{26}CuN_4O_8S_2$: C, 36.26; H, 4.91; N, 10.57; S, 12.08%. Found: C, 36.22; H, 4.96; N, 10.61; S, 12.01%. IR data (cm^{-1}): 3426 (s), 3233 (m), 1614 (m), 1570 (m), 1213 (s), 1185 (s), 1037 (s), 781 (s), 726 (m).

X-ray Diffraction Determination

The diffraction data for (1) and (2) were collected on a Bruker APEX-II CCDC areadetector diffractometer using graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å). Cell constants and orientation matrix for data collection were obtained from least-squares refinement by using the setting angles in the range of 2.58–27.50 for (1) and 2.41–25.50 for (2). Absorption corrections were applied using the SADABS program [7]. The structure was solved by direct methods [8] and refined by full-matrix least squares on F^2 using the SHELXL97 software [9]. All the non-hydrogen atoms were anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. The crystallographic data for complexes 1–2 are listed in Table 1.

Results and Discussion

The thermal ellipsoid plots for (1) and (2) with the percent probability of 30% are depicted in Figs. 1 and 2,

Table 1 Crystallographic data for Compounds **1** and **2**

|	(1)	(2)
Empirical formula	$C_{16}H_{30}CuN_4O_{10}S_2$	$C_{16}H_{26}CuN_4O_8S_2$
Formula weight	566.10	530.07
Temperature (K)	273(2)	291(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
a (Å)	9.1950(8)	7.6165(19)
b (Å)	11.5093(10)	8.806(2)
c (Å)	11.2304(10)	9.592(4)
α (°)	90	104.933(4)
β (°)	105.5550(10)	106.732(4)
γ (°)	90	109.503(3)
V (Å^3)	1144.96(17)	534.2(3)
Z	2	1
D_{calc} (g/cm^3)	1.642	1.648
μ (mm^{-1})	1.197	1.270
$F(000)$	590	275
Crystal size (mm)	$0.36 \times 0.27 \times 0.18$	$0.30 \times 0.18 \times 0.16$
θ Range (°)	2.58–27.50	2.41–25.50
Limiting indices $h/k/l$ (max, min)	−11, 11/−12, 14/−9,14	−9, 9/−10, 10/−11, 11
Reflections collected	6994	3333
Independent reflections (R_{int})	2613(0.0122)	1920(0.0271)
Absorption correction	SADABS	SADABS
Completeness to θ (%)	99.6	96.2
Max. and Min. transmission	0.8108 and 0.6712	0.8207 and 0.7019
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/ parameters	2613/7/155	1920/3/154
Goodness-of-fit on F^2	1.125	1.012
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0407$, $^a wR_2 = 0.1242$	$R_1 = 0.0470$, $^b wR_2 = 0.1082$
R indices (all data)	$R_1 = 0.0424$, $^a wR_2 = 0.1254$	$R_1 = 0.0596$, $^b wR_2 = 0.1157$
Largest diff. peak and hole (e/Å^3)	0.427 and −0.942	0.840 and −0.511

^{a} $w = 1/[\sigma^2(Fo)^2 + (0.0652P)^2 + 1.4794P]$, P = (Fo^2 + 2Fc^2)/3 for (1)

^{b} $w = 1/[\sigma^2(Fo)^2 + (0.0552P)^2 + 0.5815P]$, P = (Fo^2 + 2Fc^2)/3 for (2)

respectively. The selected bond lengths (Å) and angles (°) are shown in Table 2.

Description for $[Cu(pmt)_2] \cdot 4H_2O$ (1)

The crystal structure reveals that compound (1) is a mononuclear complex which is comprised of one Cu^{II}
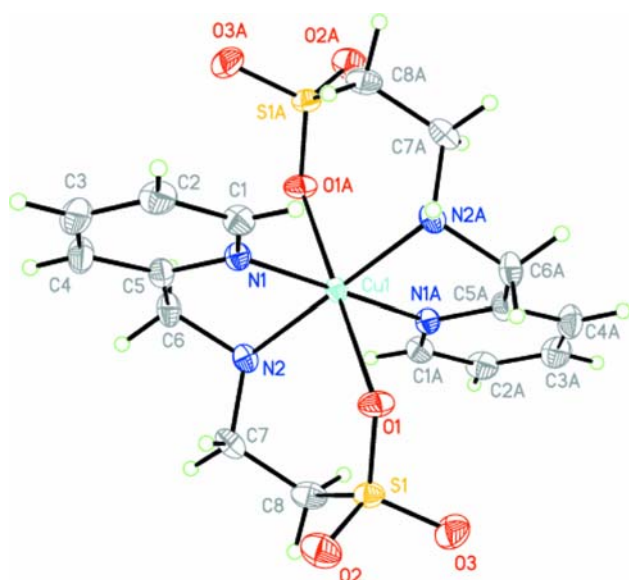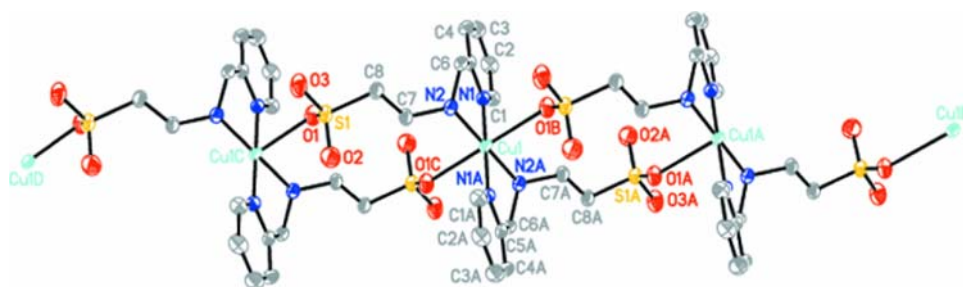
Fig. 1 A view of the structure of **1** with thermal ellipsoids drawn at 30% probability. The solvent water molecules have been omitted

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

Compound (**1**)		Compound (**2**)	
Bond	Distance	Bond	Distance
Cu(1)–N(1)	2.042(2)	Cu(1)–N(1)	2.011(3)
Cu(1)–N(2)	2.039(2)	Cu(1)–N(2)	2.039(3)
Cu(1)–O(1)	2.398(2)	Cu(1)–O(1)	2.572(2)
Angle	(°)	Angle	(°)
N(2)–Cu(1)–O(1)	92.44(9)	N(2)–Cu(1)–O(1)	84.11(9)
N(1)–Cu(1)–O(1)	88.42(8)	N(1)–Cu(1)–O(1)	85.52(10)
N(2)–Cu(1)–N(1)	81.03(9)	N(1)–Cu(1)–N(2)	82.15(13)
N(2)[a]–Cu(1)–O(1)	87.56(9)	N(2)[b]–Cu(1)–O(1)	95.89(11)
N(1)[a]-Cu(1)–O(1)	91.58(8)	N(1)[b]–Cu(1)–O(1)	91.58(8)
N(2)–Cu(1)–N(1)[a]	98.97(9)	N(1)[b]–Cu(1)–N(2)	98.97(9)

[a] $-x, -y + 1, -z + 1$

[b] $-x, -y, -z + 2$

atom, two deprotonated pmt anion ligands and four water molecules. As displayed in Fig. 1, the Cu[II] atom lies on an inversion center with the two pmt ligands coordinated in a tridentate trans arrangement with pyridyl N, amino N and sulfonate O atoms as donors (Fig. 1). The coordination environment at the Cu is distorted octahedral. This complex is isostructural with $[Co(C_8H_{11}N_2O_3S)_2]$ whose structure has been determined earlier [6]. The bond length of Cu–O [2.398(2) Å] is much longer than that of Cu–N [(2.039(2) Å, 2.042(2) Å], while in Co complex they are almost equal [Co–O, 2.1004(11) Å; Co–N, 2.1604(12) Å, 2.1737(13) Å]. This difference shows that there is Jahn-Teller effect for Cu and lack of Jahn-Teller for Co.

The water molecules in the lattice and the S=O groups of the pmt ligand are involved in the hydrogen bonding and form three-dimensional network (Fig. 3) These intermolecular hydrogen bonds are of medium strength as the D···A distances are in the range of 2.773(7)–2.923(4) Å, tabulated in Table 3.

Moreover, there exists weak π–π stacking interactions between the parallel pyridine rings of the adjacent units

Fig. 3 Three-dimensional network formed via hydrogen bonds in **1**. H atoms bonded to C atoms have been omitted

(Fig. 4). The interplanar perpendicular distance and ring-centroid separation distance are 3.528(5) and 4.046(1) Å, respectively. π–π stacking help to stabilize three-dimensional network.

Fig. 2 A segment of the one-dimensional linear chain structure of **2** along *a* axis. Water molecules and H atoms have been omitted
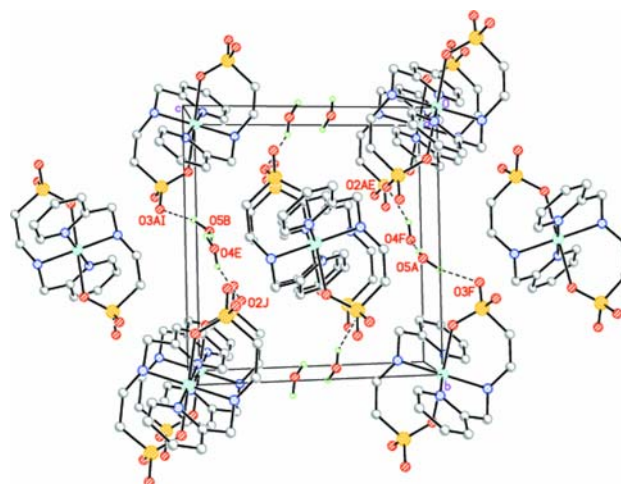
Description for $\{[Cu(pmt)_2] \cdot 2H_2O\}_n$

The crystal structure indicates that compound (2) is a coordination polymer which is build up from one Cu^{II} atom,

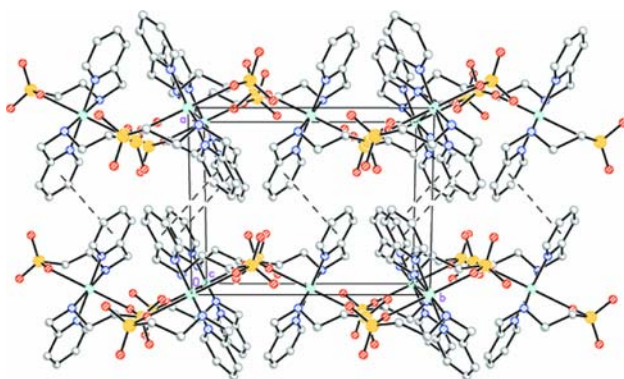**Table 3** Hydrogen bonds geometries (Å, °) for complexes **1** and **2**

| D–H⋯A	d(D–H)	d(H⋯A)	d(D⋯A)	∠(DHA)
Compound (**1**)				
O(4)–H(1W)⋯O(5)[a]	0.87(3)	2.12(4)	2.773(7)	131.2(2)
O(4)–H(2W)⋯O(2)	0.87(4)	2.10(7)	2.923(4)	157.3(5)
O(5)–H(3W)⋯O(3)[b]	0.89(7)	1.96(3)	2.757(6)	147.7(7)
O(5)–H(4W)⋯O(4)[a]	0.90(6)	1.87(6)	2.773(7)	178.9(4)
Compound (**2**)				
O(4)–H(2W)⋯O(3)[c]	0.850(10)	1.921(15)	2.753(4)	166(5)
O(4)–H(1W)⋯O(2)[a]	0.848(10)	2.01(2)	2.829(5)	162(5)
N(2)–H(1N)⋯O(4)[d]	0.70(4)	2.33(4)	3.019(5)	167(4)

[a] $-x + 1, -y, -z + 1$

[b] $x + 1, y, z$

[c] $x, y + 1, z$

[d] $x - 1, y - 1, z$

Fig. 4 Packing diagram for **1**, with π–π stacking shown as dashed lines. H atoms and water molecules has been omitted

Fig. 5 The π–π stacking between neighbouring chains along a axis in **2**. Water molecules and H atoms on C atoms have been omitted
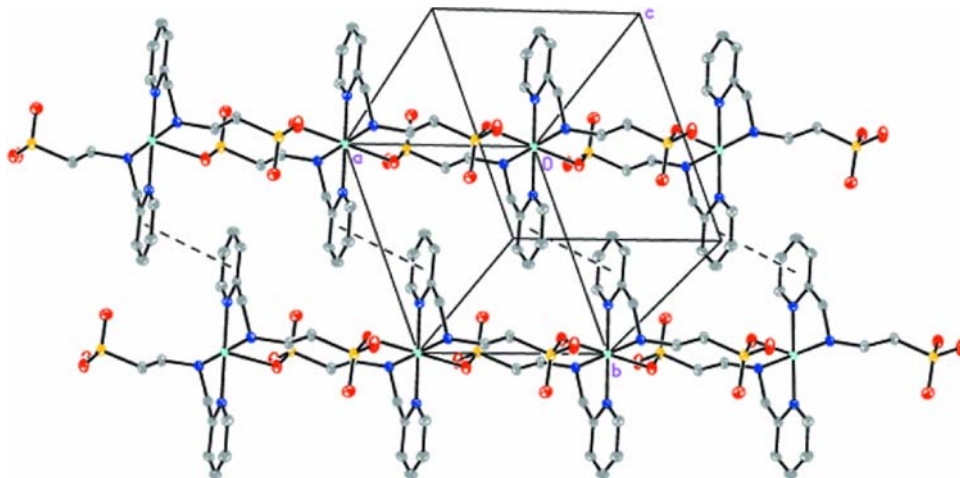
two pmt ligands and two water molecules. As shown in Fig. 2, the Cu^{II} atom is situated on a center of symmetry and is six-coordinated with four N atoms from two pmt ligands together with two sulfonate O atoms belonging to another two ligands, exhibiting a distorted octahedral geometry. Four N atoms occupy the equatorial plane and they are coplanar and O atoms locate on axial position. The distance of Cu–O bond [2.572(2) Å] is evidently longer than that of Cu–N bond [2.011(3) and 2.039(3) Å], showing the typical Jahn-Teller distortion effect for the Cu^{II} atom.

In complex **2**, the N atoms of each pmt ligand bond to one Cu^{II} atom, but its O atom coordinates to adjacent Cu^{II} atom. This original μ_2-bridging coordination mode leads to forming 12-membered $(–Cu–N–C–C–S–O–)_2$ rings between neighbouring Cu^{II} atoms. These interconnected rings create a one-dimensional linear chain propagating along the a axis in the triclinic unit cell, with a Cu⋯Cu distance of 7.617(2) Å.

Stronger π–π stacking interactions can be observed between the parallel pyridine rings of adjacent chains along a axis (Fig. 5). The interplanar average distance and ring-centroid separation distance are 3.455(4) and 3.710(6) Å, respectively. The chain structure is expanded into two-dimensional network in the ab plane by π–π stacking.

In addition, there exists weak hydrogen bonding interactions between lattice water molecules and pmt ligand. They connect together to form eight-membered (H–N–Cu–O–S–O–H–O) and 12-membered $(–O–S–O–H–O–H–)_2$ rings between adjacent chains (Fig. 6), which join the network into a three-dimensional supramolecular architecture.

Conclusions

In this paper, we report the syntheses and structures of a pair of new copper coordination isomers $[Cu(pmt)_2] \cdot 4H_2O$ (**1**), $\{[Cu(pmt)_2] \cdot 2H_2O\}_n$ (**2**). It is just

Fig. 6 The crystal packing for **2**, showing hydrogen bonds as dashed lines. H atoms bonded to C atoms have been omitted
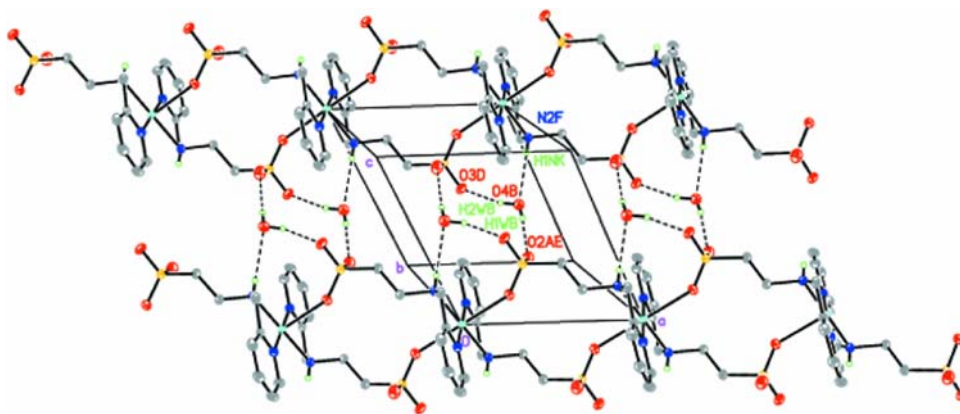
the using of different experimental methods that result in the pmt ligand coordinates to Cu^{II} atom in different modes: pmt in (**1**) can be described as N,N',O-tridentate chelating coordination, signed as "3" mode; pmt in (**2**) is N,N'-copper, O-another copper, marked as "2 + 1"mode. Both the hydrogen bonds and $\pi-\pi$ interactions make great contributions on stabilization the three-dimensional structure.

Supplementary Data

CCDC numbers 614217 and 629383 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Telephone: (44) 01223 762910; Facsimile: (44) 01223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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