

Synthesis, characterization and crystal structures of 2,4-di(2-aminopyridine)-6-methylpyrimidine (dapmp), [Cu(dapmp)Cl₂] and [Cu(dapmp)(CH₃COO)₂] · H₂O

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Abstract

The new ligand dapmp (**1**) has been synthesized and the reactions of CuCl₂ · 2H₂O and Cu(CH₃COO)₂ · H₂O with the new ligand in methanol afforded two crystalline polymorphic forms: [Cu(dapmp)Cl₂] (**2**) and [Cu(dapmp)(CH₃COO)₂] · H₂O (**3**), where dapmp = 2,4-di(2-aminopyridine)-6-methylpyrimidine. Single crystal X-ray diffraction showed that (**1**) and (**2**) are each connected by hydrogen bonding to form a one-dimensional supermolecular compound and (**3**) is connected by hydrogen bonding to form a three-dimensional supermolecular compound.

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Keywords: New ligand; Copper(II) complex; Crystal structure; One-dimensional supermolecular; Three-dimensional supermolecular; Hydrogen bonds

1. Introduction

In recent years, the synthesis of multidentate N-donor ligands has attracted considerable interest [1,2], mainly because they can be used to design multinuclear metal compounds, coordination polymers and supermolecular compounds, which play a very important role in biological systems, magnetic materials, electronic materials, optical materials and other fields [3–7]. In the present paper, we describe a new multidentate N-donor ligand 2,4-di(2-aminopyridine)-6-methylpyrimidine (dapmp), which can exhibit several coordination modes: anti–anti–anti–anti, syn–syn–syn–syn, anti–syn–syn–anti, anti–syn–syn–syn and syn–syn–syn–anti (see Scheme 1).

Herein we report the anti–anti–anti–anti configuration of dapmp, in which the chain is formed by hydrogen bonding. The crystal structures of its copper(II) complexes with the all-*anti* conformation of the chelating ligand are presented.

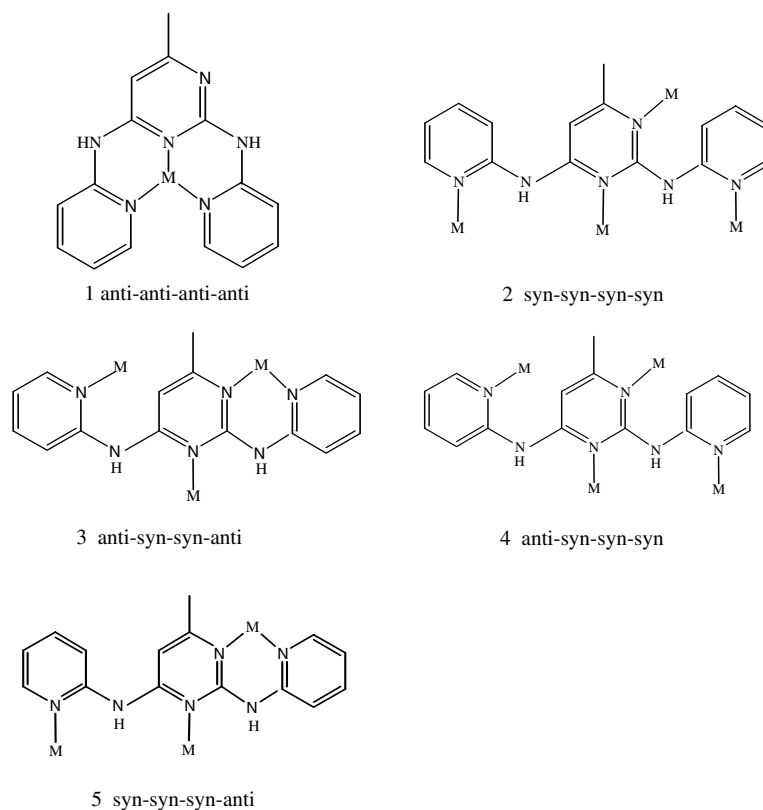
2. Experimental

2.1. Materials and physical measurements

All reagents were commercial grade and were used as received. Infrared spectra on KBr pellets were recorded on a Nicolet 170SX FT-IR spectrophotometer in the range 4000–400 cm⁻¹. NMR spectra were recorded using a VARIAN INOVA400MHZ spectrometer. Electronic spectra were recorded on a Cary 300 Bio UV–visible spectrophotometer. Elemental analyses were determined with a Perkin–Elmer model 240C instrument. FAB-MS

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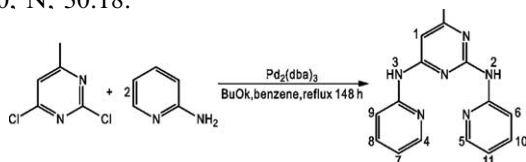


Scheme 1. Coordination modes for the ligand dapmp.

mass spectra were obtained with a JEOL HX-110 HF double focusing spectrometer operating in the positive ion detection mode. TGA analyses were recorded with a NETZSCH STA 449C microanalyzer in an atmosphere of nitrogen at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$.

2.2. Synthesis of 2,4-di(2-aminopyridine)-6-methylpyrimidine (dapmp, **1**)

2,4-Dichloro-6-methylpyrimidine (5.0 g, 31.1 mmol) and 2-aminopyridine (6.0 g, 72.9 mmol) were added to 100 ml dry benzene in a 200 ml flask. Then 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 the solution 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. Compound **1** was obtained as a white powder in 64% yield (8.7 g). *Anal.* Calc. for $\text{C}_{15}\text{H}_{14}\text{N}_6$: C, 64.47; H, 5.070; N, 30.18.



Found: C, 64.46; H, 4.891; N, 29.56%. IR (KBr, cm^{-1}): $\nu = 3176(\text{w}), 3028(\text{w}), 1599(\text{s}), 1569(\text{m}), 1505(\text{m}), 1466(\text{m}), 1425(\text{s}), 1358(\text{s}), 1299(\text{m}), 1248(\text{vw}),$

1218(w), 1149(w), 1048(w), 987(m), 773(s), 709(m), 617(vw). MS (FAB) m/z (%) 279.2 (dapmp). $^1\text{H NMR}$ (CDCl_3): $\delta = 7.14(\text{s}, 1\text{H}, 1\text{-H}), 9.63(\text{s}, 1\text{H}, 2\text{-H}), 9.44(\text{s}, 1\text{H}, 3\text{-H}), 8.37(\text{d}, 1\text{H}, ^3J = 4.8\text{ Hz}, 4\text{-H}), 8.37(\text{d}, 1\text{H}, ^3J = 4.8\text{ Hz}, 5\text{-H}), 8.33(\text{d}, 1\text{H}, ^3J = 3.6\text{ Hz}, 6\text{-H}), 6.92(\text{dt}, 1\text{H}, ^3J = 7.6\text{ Hz}, ^4J = 3.6\text{ Hz}, 7\text{-H}), 6.93(\text{dt}, 1\text{H}, ^3J = 7.6\text{ Hz}, ^4J = 2.4\text{ Hz}, 8\text{-H}), 7.37(\text{d}, 1\text{H}, 9\text{-H}), 7.68(\text{dt}, 1\text{H}, ^3J = 7.8\text{ Hz}, ^4J = 2.0\text{ Hz}, 10\text{-H}), 7.62(\text{dt}, ^4J = 2.0\text{ Hz}, 11\text{-H}), 2.42(\text{s}, 3\text{H}, \text{CH}_3)$ ppm.

2.3. Synthesis of $[\text{Cu}(\text{dapmp})\text{Cl}_2]$ (**2**)

A solution of the ligand dapmp (61.2 mg, 0.22 mmol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (34.1 mg, 0.2 mmol) in methanol (15 ml) were mixed together and stirred for 3 h. The green solution was filtered. Suitable X-ray quality crystals were obtained by slow evaporation of this green solution. Yield: 42%. *Anal.* Calc. for $[\text{Cu}(\text{C}_{15}\text{H}_{14}\text{N}_6)\text{Cl}_2]$: C, 43.65; H, 3.419; N, 20.36. Found: C, 43.46; H, 3.485; N, 20.12%.

2.4. Synthesis of $[\text{Cu}(\text{dapmp})(\text{CH}_3\text{COO})_2] \cdot \text{H}_2\text{O}$ (**3**)

A solution of the ligand dapmp (61.2 mg, 0.22 mmol) and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (39.9 mg, 0.2 mmol) in methanol (15 ml) were mixed together and stirred for 3 h. The blue-green solution obtained was filtered, from which X-ray quality crystals were obtained by slow evapora-

Table 1
Data collection and processing parameters for dapmp (1), [Cu(dapmp)Cl₂] (2) and [Cu(dapmp)(CH₃COO)₂] · H₂O (3)

	(1)	(2)	(3)
Empirical formula	C ₁₅ H ₁₄ N ₆	C ₁₅ H ₁₄ Cl ₂ CuN ₆	C ₁₉ H ₂₂ CuN ₆ O ₅
Formula weight	278.32	412.76	477.97
Temperature (K)	295(2)	150(1)	150(1)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	9.8006(4)	10.2639(2)	11.2417(5)
<i>b</i> (Å)	16.2106(6)	18.8819(4)	11.6485(5)
<i>c</i> (Å)	17.2988(7)	8.6769(2)	15.5540(8)
β (°)	91.539(1)	105.233(1)	101.856(1)
Volume (Å ³)	2747.3(2)	1622.52(6)	1996.9(2)
<i>Z</i>	8	4	4
<i>D</i> _{calc} (g/cm ³)	1.346	1.690	1.590
Absorption coefficient (nm ⁻¹)	0.087	1.685	1.140
<i>F</i> (000)	1168	836	988
Crystal size (mm)	0.20 × 0.12 × 0.10	0.20 × 0.15 × 0.12	0.12 × 0.12 × 0.08
θ range for data collection (°)	1.72–27.50	2.06–27.50	2.05–27.50
Limiting indices	−12 ≤ <i>h</i> ≤ 12, −21 ≤ <i>k</i> ≤ 21, −22 ≤ <i>l</i> ≤ 18	−11 ≤ <i>h</i> ≤ 13, −24 ≤ <i>k</i> ≤ 23, −11 ≤ <i>l</i> ≤ 10	−13 ≤ <i>h</i> ≤ 14, −14 ≤ <i>k</i> ≤ 15, −20 ≤ <i>l</i> ≤ 20
Reflections collected	21870	17432	19501
Independent reflections	6307	3716	4579
Absorption correction	semi-empirical	semi-empirical	semi-empirical
Maximum and minimum transmission	0.9914 and 0.9828	0.827 and 0.707	0.9143 and 0.8753
Refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6307/0/379	3716/0/218	4579/0/288
Goodness-of-fit on <i>F</i> ²	1.026	1.128	1.068
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0667, 0.1503	0.0481, 0.1129	0.0443, 0.1042
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1532, 0.1861	0.0817, 0.1440	0.0584, 0.1108
Largest difference peak and hole (e Å ⁻³)	0.243 and −0.253	1.011 and −0.826	0.492 and −0.369

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

Table 2
Selected bond lengths (Å) and bond angles (°) of dapmp (1), Cu(dapmp)Cl₂ (2) and [Cu(dapmp)(CH₃COO)₂] · H₂O (3)

Dapmp (1)		Cu(dapmp)Cl ₂ (2)		[Cu(dapmp)(CH ₃ COO) ₂] · H ₂ O (3)	
<i>Bond lengths</i>					
N(1)–C(1)	1.333(4)	Cu–N(5)	1.9666(3)	Cu–N(5)	1.978(2)
N(1)–C(5)	1.341(3)	Cu–N(3)	2.071(3)	Cu–N(3)	2.067(2)
N(2)–C(6)	1.375(3)	Cu–N(1)	1.974(3)	Cu–N(1)	1.975(2)
N(2)–C(5)	1.384(3)	Cu–Cl(1)	2.369(1)	Cu–O(3)	2.162(2)
N(6)–C(7)	1.350(4)	Cu–Cl(2)	2.417(1)	Cu–O(1)	1.996(2)
N(6)–C(6)	1.359(3)	N(1)–C(1)	1.358(5)	O(1)–C(16)	1.267(3)
N(12)–C(21)	1.367(4)	N(1)–C(5)	1.327(5)	O(2)–C(16)	1.244(3)
N(12)–C(22)	1.372(4)	N(3)–C(9)	1.361(4)	O(3)–C(18)	1.273(3)
N(12')–C(24)	1.354(4)	N(3)–C(6)	1.352(5)	O(4)–C(18)	1.242(3)
N(12')–C(22)	1.358(4)	N(5)–C(14)	1.347(5)	N(3)–C(6)	1.362(3)
C(7)–C(8)	1.362(4)	N(5)–C(10)	1.335(5)	N(6)–C(6)	1.343(3)
C(8)–C(9)	1.369(4)	N(6)–C(7)	1.358(5)	N(3)–C(9)	1.352(3)
<i>Bond angles</i>					
C(4)–C(5)–N(2)	124.8(3)	N(5)–Cu–N(1)	172.3(1)	N(5)–Cu–N(1)	172.84(9)
C(6)–N(2)–C(5)	129.9(2)	N(1)–Cu–N(3)	94.1(1)	N(5)–Cu–O(1)	89.80(9)
N(2)–C(6)–N(3)	119.9(2)	N(5)–Cu–N(3)	93.6(1)	N(5)–Cu–N(3)	93.27(9)
N(3)–C(9)–N(4)	118.9(3)	N(1)–Cu–Cl(1)	88.99(9)	N(1)–Cu–O(3)	88.62(8)
C(9)–N(4)–C(10)	128.3(2)	N(5)–Cu–Cl(1)	88.13(9)	O(1)–Cu–O(3)	121.54(8)
N(4)–C(10)–C(11)	123.3(3)	N(5)–Cu–Cl(2)	88.77(9)	N(3)–Cu–O(1)	139.58(8)
C(19)–C(20)–N(8)	124.1(3)	N(1)–Cu–Cl(2)	88.46(9)	N(1)–Cu–O(1)	88.24(8)
C(20)–N(8)–C(21)	130.9(3)	N(3)–Cu–Cl(2)	107.48(8)	N(1)–Cu–N(3)	92.68(9)
N(8)–C(21)–N(9)	119.7(3)	N(3)–Cu–Cl(1)	115.64(8)	N(5)–Cu–O(3)	86.53(8)
C(24)–N(10)–C(25)	129.1(2)	Cl(1)–Cu–Cl(2)	136.88(4)	N(3)–Cu–O(3)	98.88(8)

tion. Yield: 51%. *Anal. Calc.* for $[\text{Cu}(\text{C}_{15}\text{H}_{14}\text{N}_6)(\text{CH}_3\text{OO})_2] \cdot \text{H}_2\text{O}$: C, 47.75; H, 4.640; N, 17.58. Found: C, 47.92; H, 4.478; N, 17.71%.

2.5. Crystal structure determination

X-ray diffraction data were collected with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) on a BRUKER SMART APEXCCD diffractometer for compound **1**, on a NONIUS KaCCD diffractometer for complex **2** and on a BRUKER SMART APEXCCD diffractometer for complex **3**. The structures were solved by direct methods with the SHELXL-93 [8] program and refined by full-matrix least-squares methods on F^2 with SHELXTL-PC V 5.03 [9]. Crystal data and structure refinement details are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

3. Results and discussion

3.1. Description of structures

Fig. 1 shows the molecular packing of compound **1**. It can be seen that the ligand dapmp forms zigzag chains in the solid state, and the molecules are held together by a series of donor–acceptor (DA) double hydrogen bonds. Each molecule with the *all-anti* conformation is linked via two hydrogen bonds ($\text{N}(1) \cdots \text{N}(10)$ 3.104 \AA , $\text{N}(2) \cdots \text{N}(11)$ 3.107 \AA) with a centrosymmetrically related counterpart to form a dimer as depicted in Fig. 1. The structural characterization of such hydrogen-bonded dimeric compounds linked by self complementary donor–acceptor groups is well documented in organic chemistry [10–13]. The adjacent dapmp dimer units are interlaced and are connected by two hydrogen bonds ($\text{N}(7) \cdots \text{N}(4)$ 3.147 \AA , $\text{N}(8) \cdots \text{N}(5)$ 3.189 \AA), forming a one-dimensional supermolecular compound along the c axis (Fig. 1).

The bond length of $\text{N}(6)–\text{C}(7)$ 1.350(4) \AA is shorter than that of $\text{N}(12\text{C})–\text{C}(22\text{B})$ (1.358(4) \AA) while the angle of $\text{C}(5)–\text{N}(2)–\text{C}(6)$ ($129.9(2)^\circ$) is similar to that of $\text{C}(9)–\text{N}(4)–\text{C}(10)$ ($128.3(2)^\circ$). The three rings of the dapmp li-

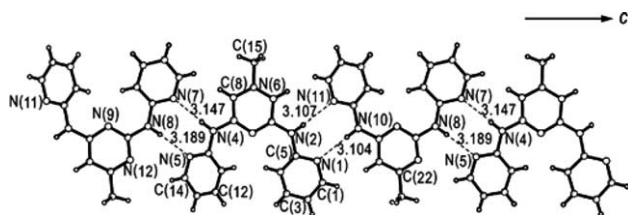


Fig. 1. An ORTEP diagram of dapmp (**1**), showing the interactions among the ligands. Thermal ellipsoids are at the 50% probability level.

gand are each planar and the dihedral angle between each pair of neighboring rings is 144.7° and 163.1° .

The crystal structure of complex **2** (Fig. 2) reveals that the coordination geometry around copper(II) is distorted trigonal bipyramidal with the monohelical dapmp ligand existing in an *all-anti* configuration. The equatorial sites consists of N(3), which comes from the pyrimidyl ring of the tridentate dapmp, and two Cl-donors, and the apical sites are occupied by N(1) and N(5) atoms of the pyridal rings. The bond angles $\text{Cl}(1)–\text{Cu}–\text{Cl}(2)$ ($136.88(4)^\circ$), $\text{N}(3)–\text{Cu}–\text{Cl}(1)$ ($115.64(8)^\circ$) and $\text{N}(3)–\text{Cu}–\text{Cl}(2)$ ($107.48(8)^\circ$) sum up to 360° and the Cu(II) atom lies in the equatorial plane. The average Cu–N bond length is observed to be 2.004 \AA while the Cu–Cl bond length is 2.393 \AA . The dihedral angle between the plane 1 (Cu, Cl(1), Cl(2), N(3)) and the plane 2 (N(3), N(6), C(6), C(7), C(8), C(9)) is 88.9° . The mononuclear unit is connected via two $\text{N}–\text{H} \cdots \text{Cl}$ hydrogen bonds ($\text{N}(4\text{B}) \cdots \text{Cl}(2\text{A})$ 3.225 \AA , $\text{Cl}(2\text{B}) \cdots \text{N}(4\text{A})$ 3.225 \AA) with a centrosymmetrically related counterpart to form a dimer as depicted in Fig. 3. The structural characterization of such hydrogen-bonded dimeric compounds linked by self complementary donor/acceptor groups is scarce for inorganic compounds. We are aware of only a few transition metal carboxylates of, e.g. zinc [14] and platinum [15] displaying pairs of symmetric $\text{C}=\text{O} \cdots \text{H}–\text{N}$ bridges, while here copper displays pairs of symmetric $\text{Cl} \cdots \text{H}–\text{N}$ bridges. The dimer is linked via another two $\text{Cl} \cdots \text{H}–\text{N}$ bridges to form a one-dimensional supermolecular chain along the c axis (Fig. 3).

Complex **3** has the same coordination configuration as **2**. The copper(II) atom is 5-coordinated with three N atoms from the ligand dapmp and two monodentate CH_3COO^- ligands in an approximately trigonal bipyramidal environment (Fig. 4). The basal plane is formed by two O atoms from CH_3COO^- and one N atom of the

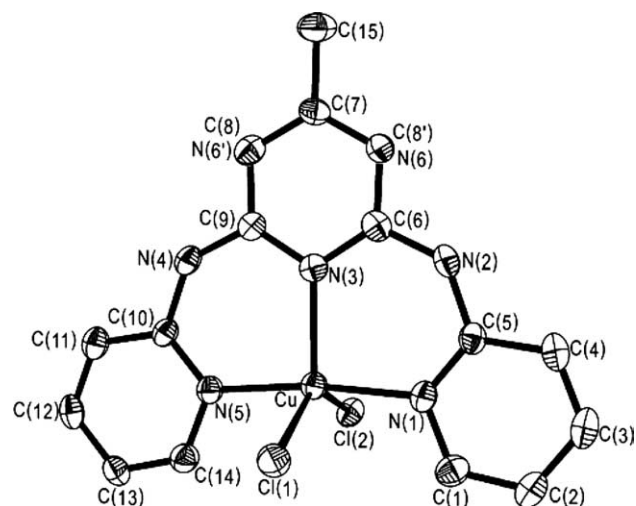


Fig. 2. The ORTEP drawing of $\text{Cu}(\text{dapmp})\text{Cl}_2$ (**2**). Thermal ellipsoids are drawn at the 50% probability level.

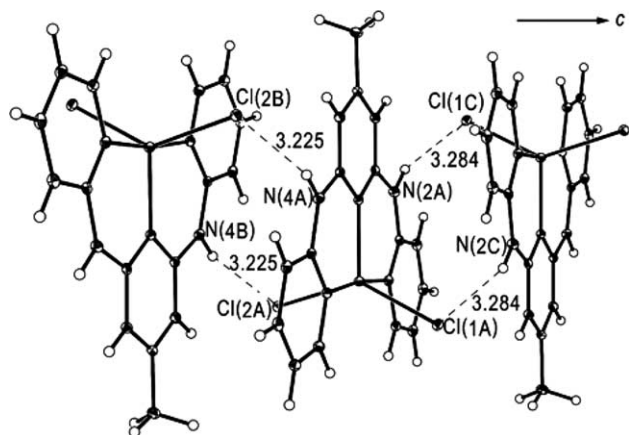


Fig. 3. The one-dimensional chains structure of Cu(dapmp)Cl₂ (2) formed by hydrogen-bonding interactions (dashed lines).

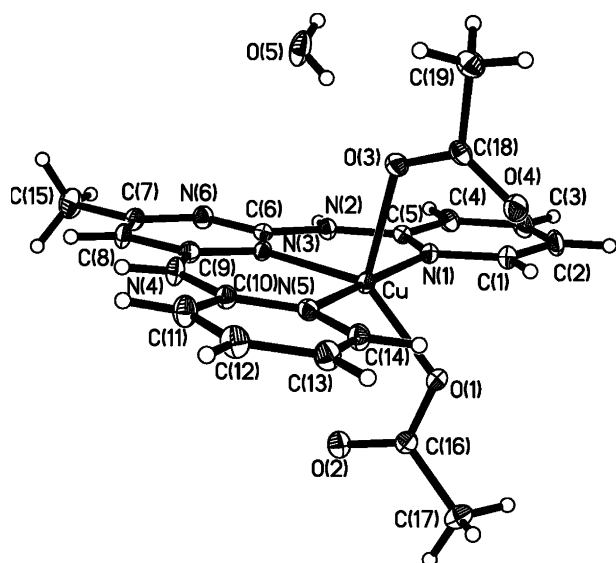


Fig. 4. The ORTEP drawing of [Cu(dapmp)(CH₃) · H₂O] (3). Thermal ellipsoids are drawn at the 50% probability level.

central pyrimidine, which is indicated by bond angle summation (360°) of O(1)–Cu–O(3) ($121.54(8)^\circ$), N(3)–Cu–O(1) ($139.58(8)^\circ$) and N(3)–Cu–O(3) ($98.88(8)^\circ$). The apical positions are occupied by two N atoms of terminal pyridine groups (N(1)–Cu–N(5) $172.84(9)^\circ$). The corresponding Cu–N_(dapmp) and Cu–O_(CH₃COO[−]) distances have the same magnitude, ranging from 1.975(2) to 2.067(2) Å. Within the acetate groups the C–O distances are greater for the strongly coordinated O atoms C(18)–O(3) and C(16)–O(1) (average 1.270 Å) than for the non-coordinated O atoms (average 1.243 Å). Intermolecular bonding of O(2) results in an intermediate C(16)–O(2) distance (1.244 Å). Both Cu–N bond lengths are typical of those found for the 5-coordinate Cu(II)-μ₂-pmae analogues [16]. Buckling of the tridentate dapmp ligand produces a dihedral angle between the two pyridyl rings of 10.5° . The Cu–O(3) bond has the longest distance (2.162(2) Å) in the 5-coordinated unit. The average

Cu–N bond length is observed to be 2.006 Å, which is similar to the average Cu–N bond length of **2**. The dihedral angle (84.6°) between the plane (Cu, O(1), O(3), N(3)) and the pyrimidine ring plane is smaller than that of **2** between the plane (Cu, Cl(1), Cl(2), N(3)) and the plane of the pyrimidine ring (88.9°).

The mononuclear units are bridged by two H₂O molecules via four hydrogen bonds to form a dimeric unit (Fig. 5). On the other hand, via two hydrogen bonds (O_{uncoord} ··· N(H), 2.806 Å), adjacent dimers are interconnected, giving rise to a one-dimensional supermolecular chain along the crystallographic *a* axis. It is worthy of note that the H₂O molecule binds the other uncoordinated O atom of CH₃COO[−] by hydrogen bonds (O(5) ··· O(4), 2.744 Å) in the *b*–*c* plane, and the neighboring chains are extended into a three-dimensional supermolecular structure.

3.2. Spectroscopic properties

The IR spectra of the complexes exhibit several characteristic strong bands. In complex **2**, the bands around 1598 and 1569 cm^{−1} in ligand dapmp (**1**), attributed to the C=N grouping, are shifted to 1651 and 1588 cm^{−1}, respectively, confirming the involvement of the ligand dapmp (**1**) in the copper complexation. In complex **3**, the corresponding bands are shifted to 1684 and 1642 cm^{−1}. The bands corresponding to $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ are at 1590 and 1397 cm^{−1} [17,18]. The $\Delta\nu$ of the complex are 193 cm^{−1} more than the corresponding values for CH₃COONa (164 cm^{−1}), indicating that the CH₃COO[−] group behaves as a monodentate ligand [18]. Other absorption peaks can also be assigned to the ligand dapmp (**1**). These are in good agreement with the crystallographic results. The electronic spectra of the two complexes in methanol at ambient temperature were measured. On the basis of high extinction coefficient, the bands at 49 505, 46 296 and 47 393 cm^{−1} can be ascribed to a π – π transition of the ligand in **1**, **2** and **3**, respectively. There are two bands 39 370 cm^{−1} (complex **2**)

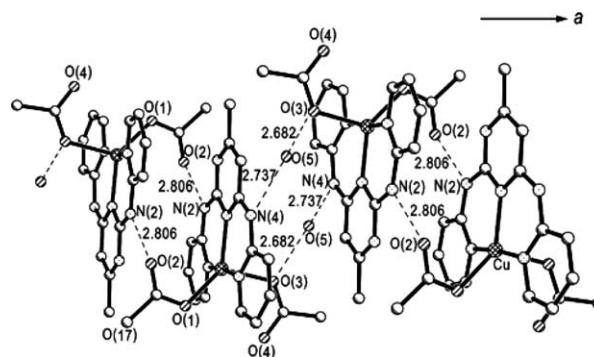


Fig. 5. The molecule packing of [Cu(dapmp)(CH₃) · H₂O] (3) formed by hydrogen-bonding interactions (dashed lines). For the interest of clarity, the hydrogen atoms are omitted.

and 39063 cm^{-1} (complex **3**) corresponding to a metal–ligand charge transfer transition. The shoulder band 32573 cm^{-1} is due to the d–d transition in **2** and the band 32468 cm^{-1} due to the d–d transition in **3**. In addition, there is a weak unresolved shoulder at 30581 cm^{-1} in **1**.

3.3. Thermogravimetric analysis

Thermogravimetric analysis of complex **3** was carried out to examine its thermal stability. The TGA curve shows that the first weight loss of 3.68%, which occurs between 80 and 105 °C, corresponds to the loss of an uncoordinated water molecule (calc.: 3.77%). Further decomposition begins at 175 °C and ends at 560 °C with residue CuO in 17.5% yield (calc.: 16.6%). Thermogravimetric analysis of complex **2** shows that the decomposition begins at 291 °C and ends at 690.2 °C with residue CuO in 20.2 yield (calc.: 19.4%).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 236246 for compound **1**, 236245 for compound **2** and 236244 for compound **3**. 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 <http://www.ccdc.cam.ac.uk>).

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