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Syntheses and Crystal Structures of $[Ni(IIP)_2]$ and $[Cu_2(PMP)_2(\mu_{1,1}\text{-}N_3)_2] \cdot MeOH$ (IIP = 2-Iminomethyl-4,6-Diiodophenolate, PMP = 2-[(2-Phenylaminoethylimino)methyl]phenolate)[1]

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Abstract—A new centrosymmetric mononuclear nickel(II) complex, $[Ni(IIP)_2]$ (**I**), and a new end-on azido-bridged dinuclear copper(II) complex, $[Cu_2(PMP)_2(\mu_{1,1}\text{-}N_3)_2] \cdot MeOH$ (**II**) (IIP = 2-iminomethyl-4,6-diiodophenolate, PMP = 2-[(2-phenylaminoethylimino)methyl]phenolate), have been prepared from similar tridentate Schiff bases derived from N-phenylethane-1,2-diamine with 3,5-diiodosalicylaldehyde and salicylaldehyde, respectively. The complexes were characterized by elemental analysis, infrared spectra, and single-crystal X-ray diffraction. Complex **I** crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 4.936(1)$, $b = 11.779(3)$, $c = 15.789(4)$ Å, $\beta = 90.722(3)°$, $V = 918.0(4)$ Å^3, $Z = 2$, $R_1 = 0.0267$, and $wR_2 = 0.0546$. Complex **II** crystallizes in the orthorhombic space group $Pna2_1$ with unit cell dimensions $a = 23.370(2)$, $b = 12.210(1)$, $c = 11.438(1)$ Å, $V = 3263.8(5)$ Å^3, $Z = 4$, $R_1 = 0.0461$, and $wR_2 = 0.0891$. The Ni atom in **I** is in a square planar coordination, and the Cu atoms in **II** are in square pyramidal coordination.

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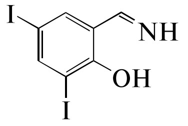
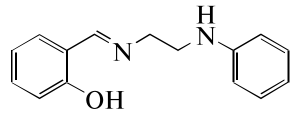
INTRODUCTION

Metal complexes with Schiff bases have been received considerable attention for their importance in the fields of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures [1–5]. Nickel and copper complexes with Schiff base ligands been proved to possess interesting biological, catalytic, and magnetic properties [6–10]. During the search of literature, we found that a large number of complexes with the tridentate Schiff bases derived from salicylaldehyde and its derivatives with versatile organic amines had been reported. Yet, to the best of our knowledge, no complexes have been reported for the tridentate Schiff bases 2,4-diiodo-6-[(2-phenylaminoethylimino)methyl]phenol (HIMP) and 2-[(2-phenylaminoethylimino)methyl]phenol (HPMP). As an extension of the work on the Schiff base complexes [11–13], we report in this paper the syntheses and crystal structures of two new nickel(II) and copper(II) complexes, $[Ni(IIP)_2]$ (**I**) and $[Cu_2(PMP)_2(\mu_{1,1}\text{-}N_3)_2] \cdot MeOH$ (**II**) (IIP = 2-iminomethyl-4,6-diiodophenolate, PMP = 2-[(2-phenylaminoethylimino)methyl]phenolate.



(HIMP)



(HPMP)

EXPERIMENTAL

Materials and measurements. Commercially available 3,5-diiodosalicylaldehyde, salicylaldehyde, and N-phenylethane-1,2-diamine were purchased from Aldrich and used without further purification. Other solvents and reagents were made in China and used as received. C, H, and N elemental analyses were performed with a PerkinElmer elemental analyser. The infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm^{-1} region. Thermal stability analysis was performed on a PerkinElmer Pyris Diamond TG-DTA thermal analyses system.

Synthesis of the Schiff base HIMP. 3,5-Diiodosalicylaldehyde (1.0 mmol, 0.374 g) and N-phenylethane-1,2-diamine (1.0 mmol, 0.136 g) were dissolved in EtOH (20 mL) with stirring. The mixture was stirred for about 30 min at room temperature to give a

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yellow solution. The solvent was evaporated to give yellow gummy product of HIMP. The yield was 98%.

For $C_{15}H_{14}N_2OI_2$

anal. calcd., %:	C, 36.6;	H, 2.9;	N, 5.7.
Found, %:	C, 36.5;	H, 2.9;	N, 5.6.

Synthesis of the Schiff base HPMP. Salicylaldehyde (1.0 mmol, 0.122 g) and N-phenylethane-1,2-diamine (1.0 mmol, 0.136 g) were dissolved in EtOH (20 mL) with stirring. The mixture was stirred for about 30 min at room temperature to give a yellow solution. The solvent was evaporated to give yellow gummy product of HPMP. The yield was 95%.

For $C_{15}H_{16}N_2O$

anal. calcd., %:	C, 75.0;	H, 6.7;	N, 11.7.
Found, %:	C, 74.8;	H, 6.8;	N, 11.5.

Synthesis of [Ni(IIP)$_2$] (I). A MeOH solution (5 mL) of nickel acetate (0.1 mmol, 24.9 mg) was added to a MeOH solution (10 mL) of HIMP (0.1 mmol, 49.2 mg) with stirring. The mixture was stirred for 30 min to give a red solution. The resulting solution was allowed to stand in air for a few days. Red block-shaped crystals suitable for X-ray single crystal analysis were formed at the bottom of the vessel. The isolated product was washed three times with cold EtOH, and dried in a vacuum over anhydrous $CaCl_2$. The yield was 21.0 mg (52% on the basis of HIMP).

For $C_{14}H_8N_2O_2I_4Ni$

anal. calcd., %:	C, 21.0;	H, 1.0;	N, 3.5.
Found, %:	C, 20.8;	H, 1.1;	N, 3.5.

Synthesis of [Cu$_2$(PMP)$_2$($\mu_{1,1}$-N$_3$)$_2$] · MeOH (II). A MeOH solution (5 mL) of copper acetate (0.1 mmol, 19.9 mg) was added to the mixture of a MeOH solution (10 mL) of HPMP (0.1 mmol, 24.0 mg) and sodium azide (0.1 mmol, 6.5 mg) with stirring. The mixture was stirred for 30 min to give a blue solution. The resulting solution was allowed to stand in air for a few days. Blue block-shaped crystals suitable for X-ray single crystal analysis were formed at the bottom of the vessel. The isolated product was washed three times with cold EtOH, and dried in a vacuum over anhydrous $CaCl_2$. The yield was 16.0 mg (44% on the basis of HPMP).

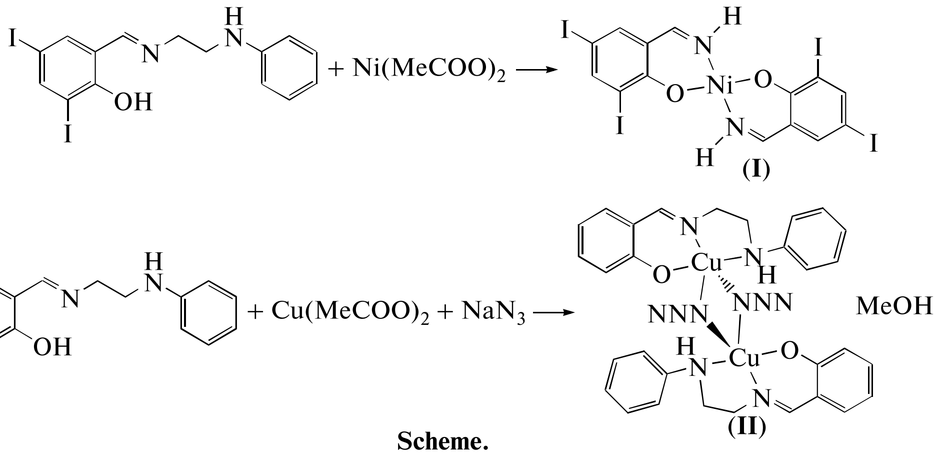
For $C_{31}H_{34}N_{10}O_3Cu_2$

anal. calcd., %:	C, 51.6;	H, 4.7;	N, 19.4.
Found, %:	C, 51.7;	H, 4.8;	N, 19.2.

X-ray structure determination. Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART 1K area-detector with MoK_α radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program [14], and multi-scan absorption corrections were performed using the SADABS program [15]. The structures of the complexes were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL [16]. All of the non-hydrogen atoms were refined anisotropically. The imino H atoms in **I** and the amino H atoms in **II** were located from difference Fourier maps and refined isotropically, with N–H distances restrained to 0.90(1) Å. The remaining H atoms were placed in idealized positions and constrained to ride on their parent atoms. The crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 825216 (**I**) and 867494 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The complexes **I** and **II** were readily prepared by the similar synthetic procedure, as shown in Scheme. It is interesting that for the preparation of **I**, the starting material HIMP was changed to HUP during the coordination.



Scheme.

Table 1. Crystallographic and experimental data for the complexes **I** and **II**

Parameter	Value	
	I	**II**
Fw	802.5	721.8
Crystal shape/color	Block/red	Block/blue
Crystal size, mm	0.20 × 0.20 × 0.18	0.23 × 0.21 × 0.21
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pna2_1$
a, Å	4.936(1)	23.370(2)
b, Å	11.779(3)	12.210(1)
c, Å	15.789(4)	11.438(1)
β, deg	90.722(3)	90
V, Å^3	918.0(4)	3263.8(5)
Z	2	4
$\mu(\mathrm{Mo}K_\alpha)$, mm^{-1}	7.791	1.352
ρ_{calcd}, g cm^{-3}	2.903	1.469
$F(000)$	724	1488
$T_{\min}$, $T_{\max}$	0.3048, 0.3345	0.7462, 0.7644
Reflections measured	7095	13865
Unique reflections (R_{int})	1981	6857
Observed reflections ($I \geq 2\sigma(I)$)	1559	4778
Parameters	109	425
Restraints	1	4
Goodness of fit on F^2	1.079	1.000
R_1, wR_2 ($I \geq 2\sigma(I)$)*	0.0267, 0.0546	0.0461, 0.0891
R_1, wR_2 (all data)*	0.0402, 0.0609	0.0800, 0.1022
Largest diff. peak and hole, e Å^{-3}	1.150 and –0.768	0.343 and –0.279

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

The molecular structure of the complex **I** is shown in Fig. 1. The compound is a centrosymmetric mononuclear nickel(II) complex, with the Ni atom located at the inversion center. The Ni atom in the complex is coordinated by two phenolate O and two imine N atoms from two IIP ligands, forming a square planar geometry. The Ni–O and Ni–N bond lengths in the complex are comparable to the corresponding values observed in other Schiff base nickel(II) complexes with square planar geometies [17, 18]. In the crystal structure of the complex, molecules are linked through intermolecular N(1)–H(1)···I2^i (N(1)–H(1) 0.90(1), H(1)···I(2) 3.07(5), N(1)···I(2) 3.775(4) Å, N(1)–H(1)···I(2) 137(5)°; symmetry code: ^{i} $1 - x$, $-1/2 + y$, $1/2 - z$) hydrogen bonds, forming layers parallel to the yz plane, as shown in Fig. 2.

The molecular structure of the complex **II** is shown in Fig. 3. The compound contains an end-on azido-bridged dinuclear copper(II) complex molecule and a methanol molecule of crystallization. The intramolecular Cu···Cu distance is 3.339(1) Å, indicating there exists strong metallophilic interaction. Each Cu atom in the complex is in a square-pyramidal coordination, with the phenolate O, imine N, and amine N atoms of the PMP ligand and one azide N atom defining the basal plane, and with the other azide N atom occupying the apical position. The deviations of the Cu(1) and Cu(2) atoms from the least-squares planes defined by the basal donor atoms are 0.101(2) and 0.140(2) Å, respectively. The azide ligands adopt end-on bridging mode. Significant distortion of the square pyramid is revealed by bond lengths and angles among the apical and basal donor atoms. The apical Cu–N bond lengths are much longer than usual; the other bond lengths are within normal ranges and comparable to the corresponding values observed in other Schiff base copper(II) complexes with azide bridges [19–21]. The bridging azide groups are nearly linear and show bent coordination with Cu atoms (N(5)N(6)N(7) 178.0(6)°, Cu(1)N(5)N(6) 128.2(3)°, N(8)N(9)N(10) 175.8(6)°, Cu(2)N(8)N(9) 124.3(4)°).

In the crystal structure of the complex (Fig. 4), the methanol molecule is linked to the dinuclear copper complex molecule through intermolecular N(2)–H(2)···O(3) (N(2)–H(2) 0.90(1), H(2)···O(3) 1.98(2), N(2)···O(3) 2.871(6) Å, N(2)–H(2)···O(3) 174(6)°) hydrogen bond. In addition, the two [Cu(PMP)] units are further linked via intramolecular N(4)–H(4)···O(1) (N(4)–H(4) 0.90(1), H(4)···O(1) 1.97(2), N(4)···O(1) 2.849(5) Å, N(4)–H(4)···O(1) 164(5)°) hydrogen bond.

The middle and sharp band at 3298 cm^{-1} for **I** is assigned to the N–H streching vibration. The weak and broad band at 3435 cm^{-1} for **II** is assigned to the O–H streching vibration of the methanol molecule. The strong absorption bands at 1612 cm^{-1} for **I** and 1633 cm^{-1} for **II** are assigned to the azomethine groups, ν(C=N). The phenolate ν(Ar–O) in the complexes exhibit middle bands at 1206 cm^{-1} for **I** and 1197 cm^{-1} for **II**. The intense band at 2038 cm^{-1} for **II** is assigned to the stretching vibrations of the azide ligands. The weak bands located at the low numbers may be assigned to the ν(M–O) and ν(M–N).

Differential thermal (DT) and thermal gravimetric analyses (TGA) were conducted to examine the stability of the azido-bridged complex **II** (Fig. 5). The first step started at 91°C and was completed at 185°C, corresponding to the loss of the methanol molecule. The observed weight loss of 4.1% is close to the calculated value of 4.4%. The second step, from 185 to 285°C, corresponds to the loss of the terminal benzene groups of the Schiff base ligands and the azide ligands. The

Table 2. Selected bond lengths (Å) and angles (deg) for structures **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
	I		
Ni(1)–O(1)	1.833(3)	Ni(1)–N(1)	1.847(4)
	II		
Cu(1)–O(1)	1.919(3)	Cu(1)–N(1)	1.956(4)
Cu(1)–N(2)	2.034(4)	Cu(1)–N(5)	2.004(4)
Cu(1)–N(8)	2.507(4)	Cu(2)–O(2)	1.916(3)
Cu(2)–N(3)	1.930(4)	Cu(2)–N(8)	2.000(4)
Cu(2)–N(4)	2.083(4)	Cu(2)–N(5)	2.435(4)
Angle	ω, deg	Angle	ω, deg
	I		
O(1)Ni(1)N(1)	93.6(2)		
	II		
O(1)Cu(1)N(1)	92.25(15)	O(1)Cu(1)N(5)	89.03(15)
N(1)Cu(1)N(5)	173.96(18)	O(1)Cu(1)N(2)	173.29(15)
N(1)Cu(1)N(2)	84.32(15)	N(5)Cu(1)N(2)	93.80(16)
N(8)Cu(1)N(1)	103.63(16)	N(8)Cu(1)N(2)	96.31(16)
N(8)Cu(1)N(5)	82.26(16)	N(8)Cu(1)O(1)	90.09(16)
O(2)Cu(2)N(3)	92.86(16)	O(2)Cu(2)N(8)	93.26(15)
N(3)Cu(2)N(8)	173.60(17)	O(2)Cu(2)N(4)	164.13(16)
N(3)Cu(2)N(4)	82.14(17)	N(8)Cu(2)N(4)	91.46(16)
O(2)Cu(2)N(5)	108.53(14)	N(3)Cu(2)N(5)	95.62(16)
N(8)Cu(2)N(5)	84.23(16)	N(4)Cu(2)N(5)	87.01(15)

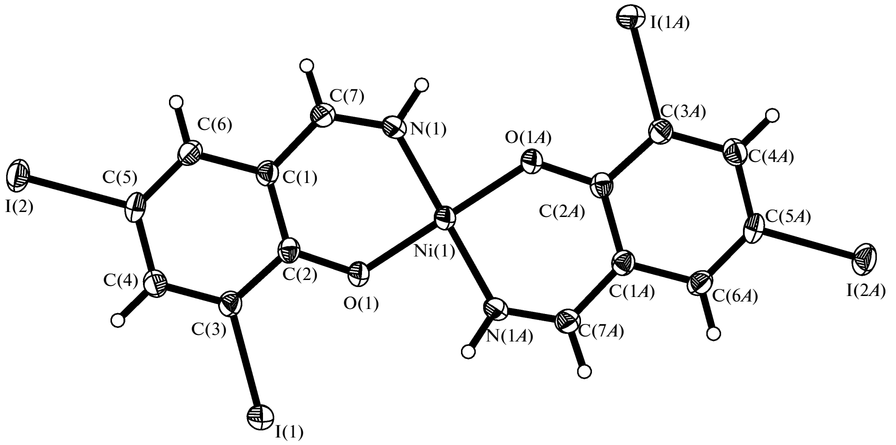


Fig. 1. Molecular structure of **I** at 30% probability displacement. Atoms labeled with the suffix *A* are at the symmetry position $-x, 1-y, -z$.

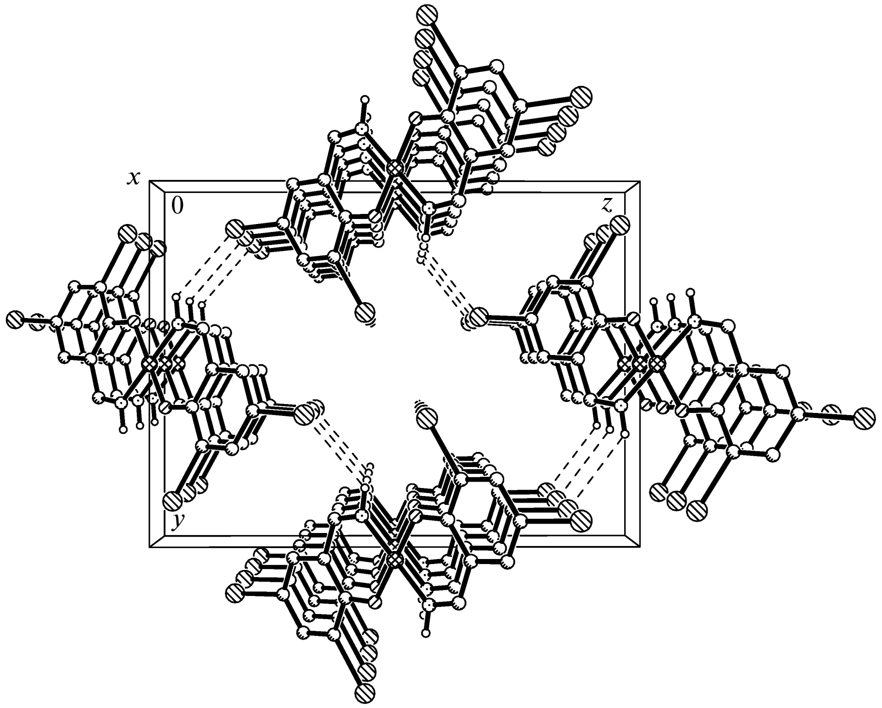


Fig. 2. Molecular packing structure of **I**, viewed along the *x* axis. Hydrogen bonds are shown as dashed lines.

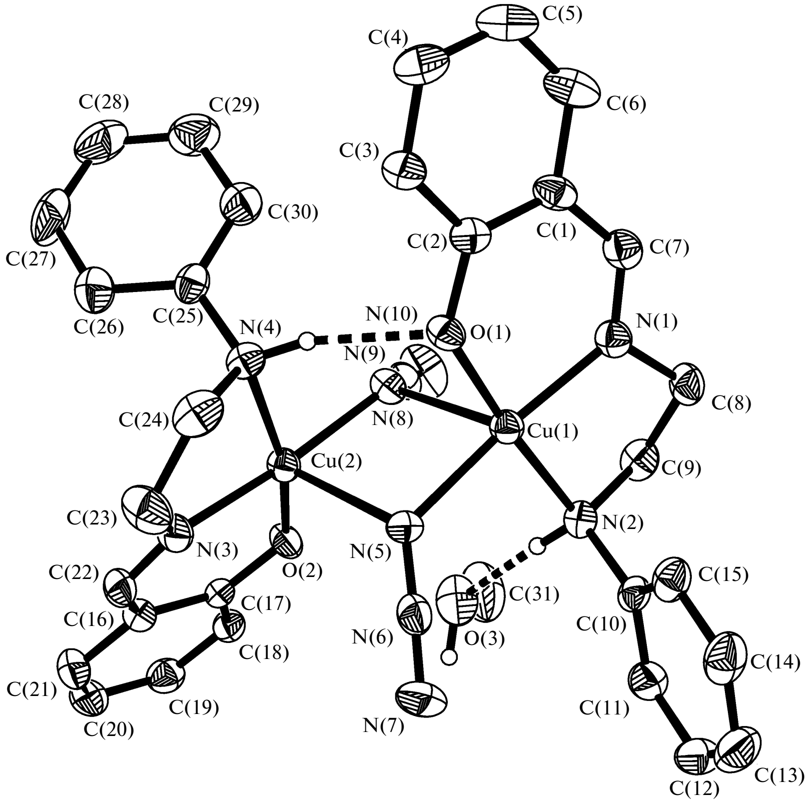


Fig. 3. Molecular structure of **II** at 30% probability displacement. Hydrogen bonds are shown as dashed lines.

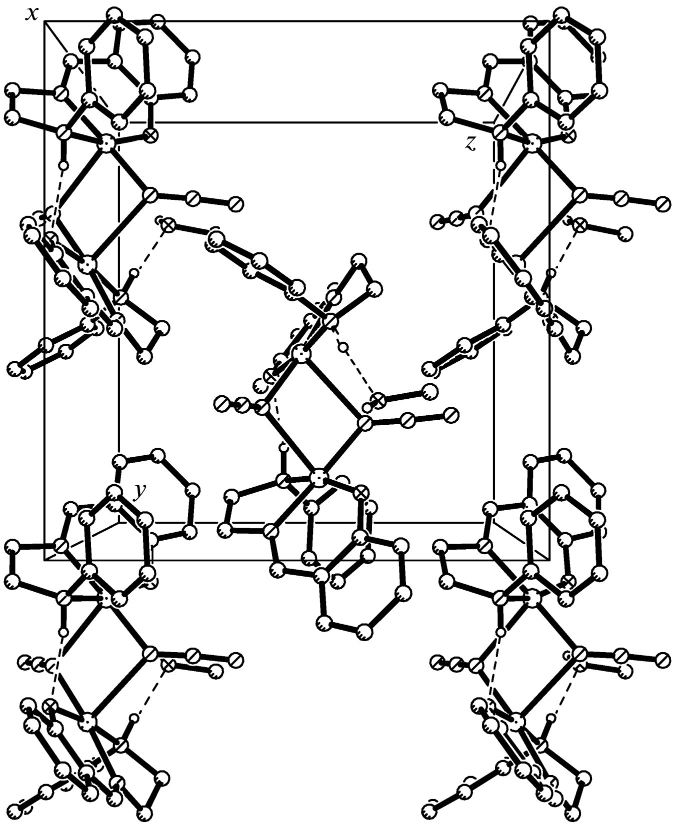


Fig. 4. Molecular packing structure of **II**, viewed along the *x* axis. Hydrogen bonds are shown as dashed lines.

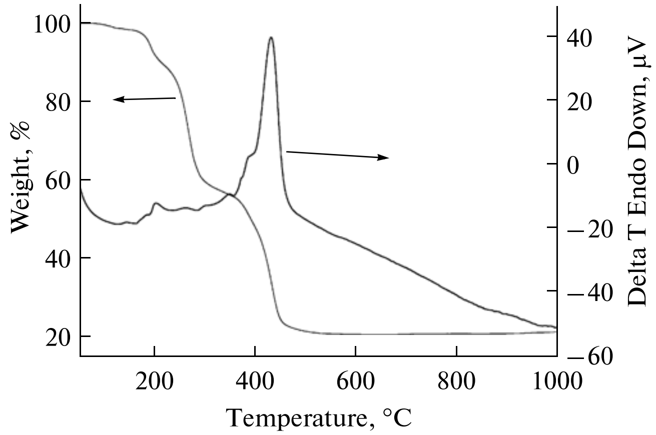


Fig. 5. DT-TGA curve of **II**.

observed weight loss of 33.4% in this step is close to the calculated value of 33.0%. The last step, from 285 to 563°C, corresponds to the loss of the remaining parts of the Schiff base ligands, and the formation of the final product (CuO). The observed weight loss of 42.0% in this step is close to the calculated value of 40.4%. The total weight loss of 79.5% is close to the calculated value of 78.0%.

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