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Synthesis and Crystal Structures of *N*,*N'*-bis(5-methylsalicylidene)ethane-1,2-Diamine and Its Bromido-, Phenolato-, and Dicyanoamido-Cobridged Polymeric Copper(II) Complex[1]

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Abstract—A bis-Schiff base *N*,*N'*-bis(5-methylsalicylidene)ethane-1,2-diamine (H_2L) was prepared and characterized by elemental analysis, ^1H NMR and ^{13}C NMR spectra, MS, and single crystal X-ray diffraction (CIF file CCDC no. 1022761 (H_2L)). Reaction of the Schiff base with copper bromide and sodium dicyanoamide in methanol gave a novel bromido-, phenolato-, and dicyanoamido-cobridged polymeric copper(II) complex, $(\{Cu_2LBr[N(CN)_2]\}_2)_n$ (**I**). Structure of complex **I** was characterized by elemental analysis and single crystal X-ray diffraction (CIF file CCDC no. 1022762 (**I**)). The smallest repeat unit of complex **I** is a dicyanoamide bridged tetranuclear copper(II) complex moiety, $\{Cu_2LBr[N(CN)_2]\}_2$, in which there possesses a crystallographic inversion symmetry. The tetranuclear moieties are further linked through Br atoms, forming a zigzag chain. The chains are further linked by dicyanoamide ligands, forming a 2D network. One Cu atom in complex **I** is coordinated by two N and two O atoms of the Schiff base ligand and one Br atom, forming square pyramidal geometry. The other Cu atom is coordinated by two N atoms of the Schiff base ligand, two N atoms of dicyanoamide ligands, and one Br atom, forming square pyramidal geometry. The bromido-, phenolato-, and dicyanoamido-cobridged Cu···Cu distances are 4.823(2), 2.955(1), and 7.121(3) Å, respectively. The $[Cu_2L]$ units are linked by the bridging groups, to form 2D chains along the *xy* plane.

Keywords: Schiff base, copper complex, polynuclear complex, crystal structure

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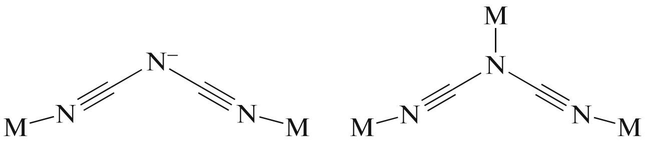
INTRODUCTION

Considerable attention has been focused on the polynuclear copper complexes due to their wide applications in magnetic fields [1–5]. The preferred way to construct polynuclear complexes is the use of suitable bridging groups, such as N_3^-, NCS^-, $N(CN)_2^-$, dicarboxylate, 4,4'-bipyridene, etc. [6–10]. Among the bridging groups, dicyanoamide anion is of great interest for its simple coordination modes:



In addition, polynuclear complexes constructed from halide salts are not uncommon [11–15]. Tetradentate Schiff bases derived from salicylaldehyde and its derivatives with diamines are important in coordination chemistry. The phenolate oxygen atoms of the Schiff bases usually act as bridging groups [16–20]. In the present work, a novel polynuclear complex bearing simultaneously bromide, phenolate and dicyanoamide bridging groups, was presented.

EXPERIMENTAL

General methods and materials. Starting materials, reagents and solvents were purchased from commercial suppliers and used as received. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Jasco FT/IR-4000 spectrometer as KBr pellets in the 4000–400 cm^{-1} region. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 900 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometer at 300

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and 75 MHz, respectively. HRMS data was obtained with ESI (electrospray ionization) mode. Single crystal structures were determined by Bruker D8 Venture single crystal diffraction.

Synthesis of *N,N′*-bis(5-methylsalicylidene)ethane-1,2-diamine (H_2L). 5-Methylsalicylaldehyde (2.72 g, 0.02 mol) and ethane-1,2-diamine (0.60 g, 0.01 mol) were mixed in methanol (30 mL). The mixture was stirred at ambient temperature for 30 min to give yellow solution. Then the solvent was evaporated to give yellow crystalline product with quantitative yield.

IR data (KBr; ν, cm^{-1}): 3439 w, 1636 s, 1586 m, 1491 s, 1371 w, 1282 m, 1231 m, 1157 w, 1037 s, 977 w, 942 w, 827 s, 777 w, 662 w, 567 w, 473 w. UV-Vis data (methanol; λ, nm (ε, L mol^{-1} cm^{-1})): 260 (1.88×10^4), 280 (8.21×10^3), 328 (7.28×10^3). HRMS (ESI): *m/z* calcd. for $C_{18}H_{20}N_2O_2$ $[M + H]^+$ 297.1598; found: 297.1593. ^{1}H NMR (300 MHz; d^6-DMSO; δ, ppm): 13.06 (s., 2H), 8.51 (s., 2H), 7.20 (s., 2H), 7.12 (d., 2H), 6.76 (d., 2H), 3.90 (s., 4H), 2.22 (s., 6H). ^{13}C NMR (75 MHz; DMSO-*d*^{6}; δ, ppm): 166.75, 158.21, 133.00, 131.47, 127.10, 118.24, 116.22, 58.92, 19.87. Yellow block-like single crystals were obtained by slow evaporation of a methanol solution of the compound.

For $C_{18}H_{20}N_2O_2$			
anal. calcd., %:	C, 72.9;	H, 6.8;	N, 9.5.
Found, %:	C, 73.1;	H, 6.7;	N, 9.3.

Synthesis of complex I. H_2L (0.296 g, 1.0 mmol), copper bromide (0.223 g, 1.0 mmol) and sodium dicyanamide (0.089 g, 1.0 mmol) and were mixed in methanol (30 mL). The mixture was stirred at ambient temperature for 30 min to give blue solution, which was filtered to avoid minor impurity, and kept still to slow evaporate of the solvent. A few days later, block-like single crystals were obtained by filtration. The yield was 38%.

IR data (KBr, ν, cm^{-1}): 1626 s, 1531 m, 1466 m, 1382 m, 1312 m, 1212 w, 1157 w, 1082 w, 967 w, 822 m, 552 w, 498 w. UV-Vis data (methanol; λ, nm (ε, L mol^{-1} cm^{-1})): 230 (2.85×10^4), 275 (1.55×10^4), 367 (6.13×10^3), 560 (538).

For $C_{20}H_{18}BrN_5O_2Cu_2$			
anal. calcd., %:	C, 42.3;	H, 3.2;	N, 12.3.
Found, %:	C, 42.1;	H, 3.3;	N, 12.5.

X-ray crystallography. Diffraction intensities for H_2L and complex **I** were collected at 298(2) K using a Bruker D8 Venture diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å). The collected data were reduced with SAINT [21], and multi-scan absorption correction was performed using SADABS [22]. Structures of H_2L and the copper complex were solved by direct method and refined against F^2 by full-matrix least-squares method using SHELXTL [23]. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1022761 (H_2L), 1022762 (**I**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The Schiff base H_2L was readily prepared by the condensation reaction of 2 : 1 molar ratio of ethane-1,2-diamine with 5-methylsalicylaldehyde in methanol at ambient condition. The copper complex was prepared by the one-pot reaction of H_2L, copper bromide and sodium dicyanamide in methanol. Complex **I** is soluble in methanol, ethanol, DMSO and DMF. The Schiff base and stable in air at room temperature. Elemental analyses of the compounds are in good agreement with the components determined by single crystal X-ray diffraction.

The medium and broad absorption at 3439 cm^{-1} in the spectrum of H_2L substantiates the presence of O–H group. The strong absorption bands at 1636 cm^{-1} for H_2L and 1626 cm^{-1} for complex **I** are assigned to the azomethine groups ν(C=N). The infrared spectrum of complex **I** displays absorption bands at 2313, 2235, and 2171 cm^{-1}, which are attributed to ν_s + ν_{as}(CN), ν_{as}(CN) and ν_s(CN) modes of the bridging dicyanamide ligand, respectively [24]. The ligand coordination to the metal centre is substantiated by two bands appearing at 552 and 498 cm^{-1} attributable to ν(Cu–N) and ν(Cu–O), respectively.

Electronic spectra of H_2L and complex **I** were recorded in 10^{-5} M methanol. There are strong bands centered at 328 nm for H_2L and 367 nm for complex **I**, which can be assigned to the *n*–π* transition. The spectra showed weak and broad *d*–*d* electronic transitions at about 560 nm, which are assigned to $^2E_{g(D)} \rightarrow {}^2T_{2g(D)}$ [25]. The broadness of the bands is due to the ligand field and the Jahn–Teller effects. These absorptions prefer the distorted octahedral geometry for the Cu^{2+} ion. The intense bands observed at about 270–290 nm for H_2L and complex **I** are assigned to intraligand π–π* transitions.

The molecular structure of H_2L is shown in Fig. 1a. The compound possesses a crystallographic inversion center symmetry with the inversion center located at the midpoint of C(8) and C(8*A*) atoms (symmetry code for *A*: $1 - x, -y, 1 - z$). The bond length of C(7)–N(1) in the Schiff base is 1.276(2) Å, indicating it is a typical double bond. The intramolecular O(1)–

Table 1. Crystallographic data and structure refinements for H_2L and **I**

Parameter	Value	
	H_2L	**I**
Fw	296.36	567.38
Crystal shape; colour	Plate; light yellow	Block; blue
Crystal size, mm	0.33 × 0.28 × 0.07	0.20 × 0.20 × 0.17
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*
a, Å	7.3233(3)	12.2128(6)
b, Å	6.1007(2)	15.4193(7)
c, Å	35.4295(11)	22.0274(10)
V, Å^3	1582.9(1)	4148.0(3)
Z	4	8
$\mu(\mathrm{Mo}K_\alpha)$, cm^{-1}	0.082	4.005
$T_{\min}/T_{\max}$	0.9735/0.9943	0.5014/0.5492
ρ_{calcd}, g cm^{-3}	1.244	1.817
Reflections/parameters	1613/102	3862/271
Unique reflections (R_{int})	1303 (0.0208)	3369 (0.0431)
Restraints	0	12
Goodness of fit on F^2	1.044	1.040
R_1 ($I \geq 2\sigma(I)$)	0.0518	0.0295
wR_2 ($I \geq 2\sigma(I)$)	0.1381	0.0759
R_1 (all data)	0.0611	0.0362
wR_2 (all data)	0.1453	0.0802
$\Delta\rho_{\max}/\Delta\rho_{\min}$, e Å^{-3}	0.186/–0.162	0.602/–0.605

Table 2. Selected bond lengths (Å) and angles (deg) for H_2L and complex **I***

Bond	*d*, Å	Bond	*d*, Å
		H_2L	
C(7)–N(1)	1.276(2)	C(8)–N(1)	1.458(2)
		I	
C(8)–N(1)	1.273(4)	C(11)–N(2)	1.273(4)
C(9)–N(1)	1.468(4)	C(10)–N(2)	1.459(4)
Cu(1)–N(1)	1.901(2)	Cu(1)–N(2)	1.906(2)
Cu(1)–O(1)	1.908(2)	Cu(1)–O(2)	1.9057(19)
Cu(1)–Br(1)	2.8697(5)	Cu(2)–N(3)	1.972(3)
Cu(2)–N(5)	1.988(3)	Cu(2)–O(1)	2.042(2)
Cu(2)–O(2)	1.995(2)	Cu(2)–Br(1*B*)	2.5902(5)
Angles	**ω, deg**	**Angles**	**ω, deg**
		H_2L	
C(7)N(1)C(8)	118.1(2)		
		I	
C(8)N(1)C(9)	122.6(3)	C(10)N(2)C1(1)	122.2(3)
N(1)Cu(1)N(2)	86.43(10)	N(1)Cu(1)O(2)	170.48(10)
N(2)Cu(1)O(2)	95.56(9)	N(1)Cu(1)O(1)	95.91(9)
N(2)Cu(1)O(1)	167.84(10)	O(2)Cu(1)O(1)	80.25(9)
N(1)Cu(1)Br(1)	94.97(8)	N(2)Cu(1)Br(1)	94.84(8)
O(2)Cu(1)Br(1)	94.14(7)	O(1)Cu(1)Br(1)	96.83(7)
N(3)Cu(2)N(5)	88.73(12)	N(3)Cu(2)O(2)	158.32(11)
N(5)Cu(2)O(2)	92.85(10)	N(3)Cu(2)O(1)	93.85(10)
N(5)Cu(2)O(1)	152.25(10)	O(2)Cu(2)O(1)	75.00(8)
N(3)Cu(2)Br(1B)	98.04(9)	N(5)Cu(2)Br(1*B*)	104.65(9)
O(2)Cu(2)Br(1*B*)	102.45(6)	O(1)Cu(2)Br(1*B*)	102.33(6)

* Symmetry code: (*B*) $-1/2 + x$, $1/2 - y$, $1 - z$.

Table 3. Parameters between the planes for H_2L and complex **I***

Cg	Distance between ring centroids, Å	Dihedral angle, deg	Perpendicular distance of *Cg*(I) on *Cg*(J), Å	Perpendicular distance of *Cg*(J) on *Cg*(I), Å
		H_2L		
Cg(1)–*Cg*(1)^{i}	4.698	47	–2.0695	–4.4903
Cg(1)–*Cg*(1)^{ii}	4.834	47	2.2316	4.6525
		I		
Cg(2)–*Cg*(2)^{iii}	4.270	0	–3.7704	–3.7704
Cg(2)–*Cg*(3)^{iii}	4.205	6	3.7507	–3.6290
Cg(2)–*Cg*(4)^{iii}	3.9069	8	3.7349	–3.5891
Cg(2)–*Cg*(6)^{iii}	4.8676	14	3.8571	–3.1099
Cg(3)–*Cg*(4)^{iii}	3.7266	12	3.4446	3.5569
Cg(3)–*Cg*(6)^{iii}	4.3349	16	3.6359	3.0045
Cg(4)–*Cg*(4)^{iii}	4.9532	0	3.8710	3.8710
Cg(4)–*Cg*(5)^{iii}	4.7428	14	3.7300	2.9146
Cg(5)–*Cg*(6)^{iv}	4.8403	73	–0.4155	–4.7250
Cg(5)–*Cg*(6)^{iii}	4.6320	15	3.1046	3.3412

* Symmetry codes: ^{i} $1/2 - x$, $1/2 + y$, z; ^{ii} $3/2 - x$, $-1/2 + y$, z; ^{iii} $-x$, $1 - y$, $-z$; ^{iv} $1/2 + x$, $1/2 - y$, $-z$. *Cg*(1) is the centroid of C(1)–C(2)–C(3)–C(4)–C(5)–C(6) benzene ring of H_2L. *Cg*(2), *Cg*(3), *Cg*(4), *Cg*(5) and *Cg*(6) are the centroids of Cu(1)–N(1)–C(9)–C(10)–N(2), Cu(1)–O(1)–C(2)–C(1)–C(8)–N(1), Cu(1)–O(2)–C(13)–C(12)–C(11)–N(2), C(1)–C(2)–C(3)–C(4)–C(5)–C(6), and C(12)–C(13)–C(14)–C(15)–C(16)–C(17), respectively.

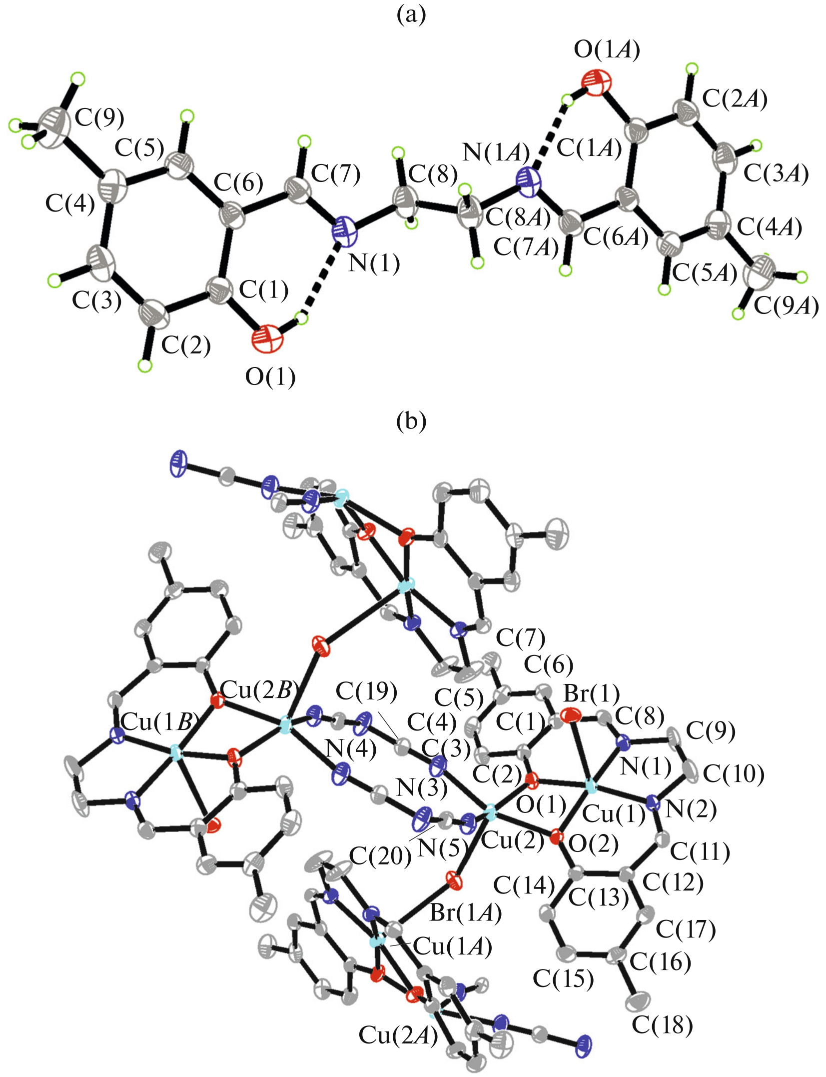

Fig. 1. A perspective view of the molecular structures: H_2L (a), **I** (b) with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. The symmetry positions: (*A*) $1 - x$, $-y$, $1 - z$ for H_2L and (*A*) $-x$, $1 - y$, $1 - z$; (*B*) $-1/2 + x$, $1/2 - y$, $1 - z$ for **I**. Hydrogen bonds for H_2L are shown as dashed lines.

H(1)···N(1) hydrogen bonds (O(1)–H(1) 0.82, H(1)···N(1) 1.88, O(1)···N(1) 2.610(2) Å, O(1)–H(1)···N(1) 148°) in the Schiff base molecule make *S*(6) ring motifs [26]. Moreover, there exists π···π interactions (Table 3) in the crystal packing (Fig. 2a).

The molecular structure of complex **I** is shown in Fig. 1b. The Schiff base ligand coordinates to the Cu atoms through the phenolate O and imino N atoms. The phenolate O atoms act as bridging groups, coordinating to two different Cu atoms. The dihedral angle between the two benzene rings is 15.9(3)°. The smallest repeat unit of complex **I** is a dicyanamide bridged tetranuclear copper(II) complex moiety, $\{Cu_2LBr[N(CN)_2]\}_2$, in which there exists a crystallographic inversion symmetry. The inversion center is located at the midpoint of the Cu(2) and Cu(2*A*) atoms (symmetry code for *A*: $-x$, $1 - y$, $1 - z$) which has a separation of 7.121(3) Å. The distance between Cu(1) and Cu(2) atoms is 2.955(1) Å. The Cu(1) atom is in a square pyramidal coordination with the basal plane defined by two phenolate O and two imino N atoms of the Schiff base ligand and with the apical position occupied by a Br atom. The square pyramidal geometry is slightly distorted, as evidenced by the bond lengths and angles related to Cu(1) atom. The bond lengths in the basal plane are within 1.90–1.91 Å, and the bond angles within the basal plane are in the range 80.25(9)°–95.91(9)°. The deviation of the basal angles from the ideal value of 90° is mainly caused by the strain created by the four-membered chelate ring Cu(1)–O(1)–Cu(2)–O(2) and the five-membered chelate ring Cu(1)–N(1)–C(9)–C(10)–N(2). The bond angles among the apical and the basal donor atoms are range from 94.14(7)° to 96.83(7)°.

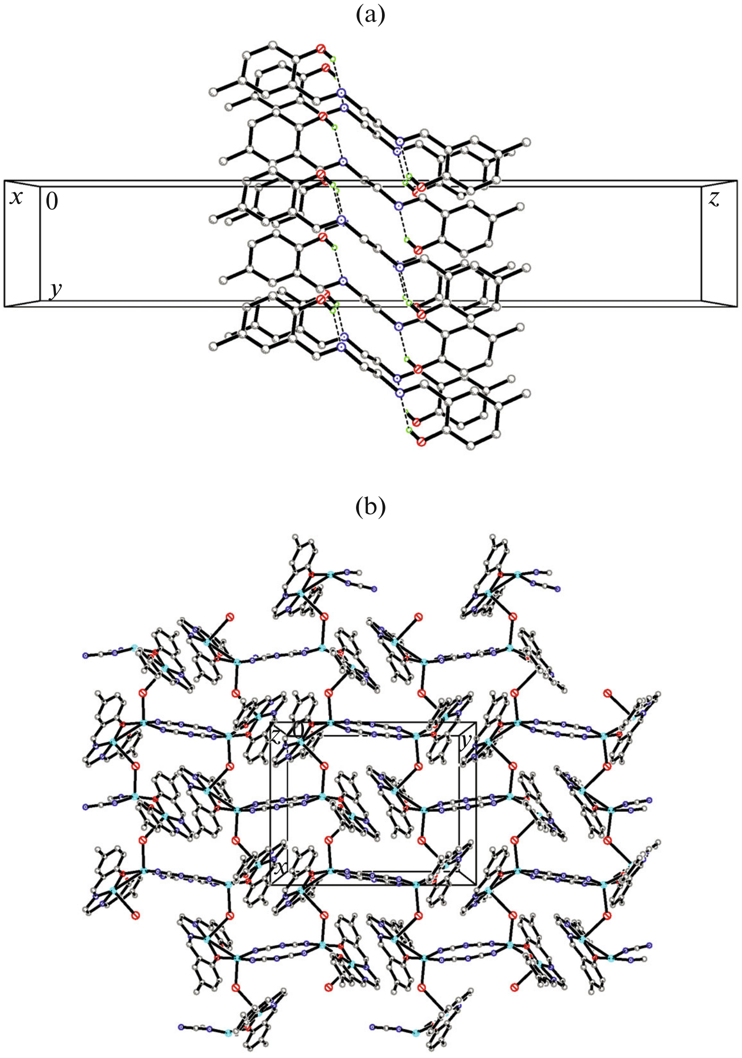

Fig. 2. Molecular packing diagrams: H_2L along the *x* axis (a), **I** along the *z* axis (b). Hydrogen bonds for H_2L are shown as dashed lines. Hydrogen atoms for **I** and hydrogen atoms unrelated to hydrogen bonding for H_2L are omitted for clarity.

The Cu(1) atom deviates from the least-squares plane defined by the four basal donor atoms by 0.172(2) Å. The Cu(2) atom is also in a square pyramidal coordination with the basal plane defined by two phenolate O atoms of the Schiff base ligand and two N atoms of the dicyanamide ligands and with the apical position occupied by a Br atom. The square pyramidal geometry is somewhat distorted, as evidenced by the bond lengths and angles related to the Cu(2) atom. The bond lengths in the basal plane are within 1.97–2.05 Å, and the bond angles within the basal plane are in the range 75.00(8)°–93.85(10)°. The deviation of the basal angles from the ideal value of 90° is mainly caused by the strain created by the four-membered chelate ring Cu(1)–O(1)–Cu(2)–O(2). The bond angles among the apical and the basal donor atoms are range from 98.04(9)° to 104.65(9)°. The Cu(2) atom deviates from the least-squares plane defined by the four basal donor atoms by 0.410(2) Å. In general, the coordinate bond lengths in complex **I** are comparable to those observed in the copper(II) complexes with Schiff bases [27–29].

The tetranuclear moieties are further linked through Br bridging atoms, forming a zigzag chain. The bromido-bridged Cu···Cu distance is 4.823(2) Å. The chains are further linked by dicyanamide ligands, forming a two-dimensional network (Fig. 2b). In addition, crystal of the complex is stabilized by π···π interactions (Table 3).

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