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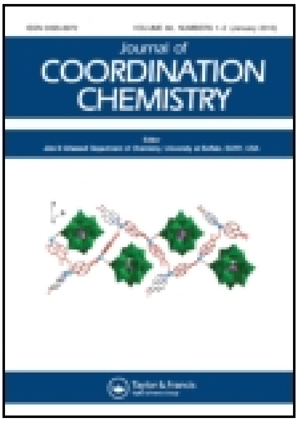

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Dinuclear Schiff-base copper(II) complexes with various bridging groups

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Dinuclear Schiff-base copper(II) complexes with various bridging groups

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Three new centrosymmetric dinuclear copper(II) complexes, $[Cu_2Cl_2(L^1)_2]$ (**1**), $[Cu_2(\mu_{1,3}\text{-NCS})_2(L^2)_2]$ (**2**), and $[Cu_2(\mu_{1,1}\text{-N}_3)_2(L^3)_2]$ (**3**), where L^1, L^2, and L^3 are the deprotonated forms of the Schiff bases 1-[(2-propylaminoethylimino)methyl]naphthalen-2-ol (HL^1), 1-[(3-methylaminopropylimino)methyl]naphthalen-2-ol (HL^2), and 2-[(2-isopropylaminoethylimino)methyl]phenol (HL^3), respectively, have been prepared and characterized by elemental analysis, IR spectra, and single-crystal X-ray crystallography. Each Cu is coordinated by the three donors of the Schiff bases and by two bridging groups, forming a square-pyramidal geometry.

Keywords: Schiff base; Copper complex; Dinuclear complex; Crystal structure

1. Introduction

Dinuclear complexes with bridging groups attract attention for their interesting structures and applications [1–3]. Design and construction of dinuclear complexes with Schiff bases are of particular interest in coordination and structural chemistry. Halide and pseudohalide groups can link two or more metals, yielding various polynuclear complexes [4–8]. In this study, three new dinuclear copper(II) complexes, $[Cu_2Cl_2(L^1)_2]$ (**1**), $[Cu_2(\mu_{1,3}\text{-NCS})_2(L^2)_2]$ (**2**), and $[Cu_2(\mu_{1,1}\text{-N}_3)_2(L^3)_2]$ (**3**), where L^1, L^2, and L^3 are deprotonated forms of 1-[(2-propylaminoethylimino)methyl]naphthalen-2-ol (HL^1), 1-[(3-methylaminopropylimino)methyl]naphthalen-2-ol (HL^2), and 2-[(2-isopropylaminoethylimino)methyl]phenol (HL^3) (scheme 1), respectively, were prepared and characterized.

2. Experimental

2.1. *Materials and measurements*

Starting materials, reagents, and solvents were purchased from commercial suppliers and purified before use. Elemental analyses were performed on a Perkin-Elmer 240C

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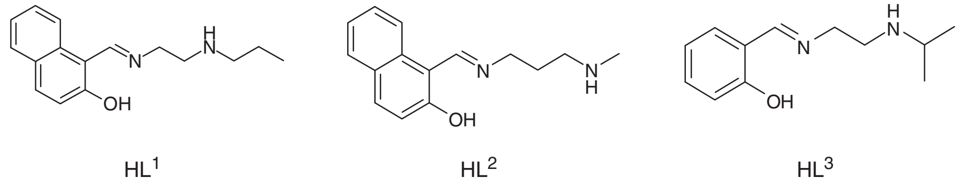

Scheme 1. The Schiff bases.

elemental analyzer. IR spectra were recorded on a Jasco FT/IR-4000 spectrometer as KBr pellets from 4000 to 200 cm^{-1}. Electronic spectra of the complexes in acetonitrile were recorded on a Hitachi U-3501 spectrophotometer.

2.2. *Preparation of the Schiff bases*

The Schiff bases HL^1–HL^3 were prepared according to the literature method [9] to give yellow gummy products. For HL^1: Yield: 93%. Characteristic IR data (cm^{-1}): 1626 (vs). Anal. Calcd for $C_{16}H_{20}N_2O$: C, 75.0; H, 7.9; N, 10.9. Found (%): C, 74.8; H, 8.0; N, 10.8. For HL^2: Yield: 95%. Characteristic IR data (cm^{-1}): 1627 (vs). Anal. Calcd for $C_{15}H_{18}N_2O$: C, 74.4; H, 7.5; N, 11.6. Found (%): C, 74.3; H, 7.5; N, 11.8. For HL^3: Yield: 92%. Characteristic IR data (cm^{-1}): 1623 (vs). Anal. Calcd for $C_{12}H_{18}N_2O$: C, 69.9; H, 8.8; N, 13.6. Found (%): C, 69.6; H, 8.9; N, 13.7%.

2.3. *Preparation of $[Cu_2Cl_2(L^1)_2]$ (1)*

A methanolic solution (10 mL) of $CuCl_2 \cdot 2H_2O$ (0.1 mmol, 17.0 mg) was added with stirring to a methanolic solution (10 mL) of HL^1 (0.1 mmol, 25.6 mg). The mixture was stirred at room temperature for 30 min to give a clear blue solution. X-ray quality blue block-shaped single crystals were formed by slow evaporation of the solution in air for a few days. Yield: 62%. Selected IR data (cm^{-1}): 1618 (vs), 1186 (m), 458 (w), 393 (w). UV-Vis (acetonitrile): [nm (ε, $(mol\,L^{-1})^{-1}cm^{-1}$)]: 365 ($3.5 \times 10^3$), 619 (271). Anal. Calcd for $C_{32}H_{38}Cl_2Cu_2N_4O_2$: C, 54.2; H, 5.4; N, 7.9. Found (%): C, 53.9; H, 5.5; N, 8.1.

2.4. *Preparation of $[Cu_2(\mu_{1,3}\text{-}NCS)_2(L^2)_2]$ (2)*

A methanolic solution (10 mL) of $Cu(CH_3COO)_2 \cdot H_2O$ (0.1 mmol, 19.9 mg) was added with stirring to a mixture of a methanolic solution (10 mL) of HL^2 (0.1 mmol, 24.2 mg) and ammonium thiocyanate (0.1 mmol, 7.6 mg). The final mixture was stirred at room temperature for 30 min to give a clear deep blue solution. X-ray quality blue block-shaped single crystals were formed by slow evaporation of the solution in air for a few days. Yield: 53%. Selected IR data (cm^{-1}): 2109 (vs), 1618 (vs), 1189 (m), 462 (w), 400 (w). UV-Vis (acetonitrile): (nm (ε, $(mol\,L^{-1})^{-1}cm^{-1}$)): 361 ($3.1 \times 10^3$), 615 (253). Anal. Calcd for $C_{32}H_{34}Cu_2N_6O_2S_2$: C, 52.9; H, 4.7; N, 11.6. Found (%): C, 53.1; H, 4.8; N, 11.4.

2.5. *Preparation of [$Cu_2(\mu_{1,1}\text{-}N_3)_2(L^3)_2$] (3)*

Complex **3** was prepared by the same method as described for **2**, with HL^2 replaced by HL^3 (0.1 mmol, 20.6 mg), and ammonium thiocyanate replaced by sodium azide (0.1 mmol, 6.5 mg). X-ray quality blue block-shaped single crystals were obtained. Yield: 72%. Selected IR data (cm^{-1}): 2093 (vs), 1615 (vs), 1182 (m), 483 (w), 412 (w). UV-Vis (acetonitrile): (nm (ε, $(mol\,L^{-1})^{-1}cm^{-1}$)): 379 ($3.3 \times 10^3$), 611 (282). Anal. Calcd for $C_{24}H_{34}Cu_2N_{10}O_2$: C, 46.4; H, 5.5; N, 22.5. Found (%): C, 46.2; H, 5.6; N, 22.3.

2.6. *X-ray crystallography*

Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART 1000 CCD area-detector with Mo-Kα radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program [10], and multi-scan absorption corrections were performed using SADABS [11]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares using SHELXTL [12]. All non-hydrogen atoms were refined anisotropically. The amino hydrogen atoms in the complexes were located in difference Fourier maps and refined isotropically, with N–H distances restrained to 0.90(1) Å. All other hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms.

3. Results and discussion

3.1. *Synthesis*

The Schiff bases HL^1–HL^3 were readily prepared by the condensation of 2-hydroxy-1-naphthaldehyde with *N*-propylethane-1,2-diamine, 2-hydroxy-1-naphthaldehyde with *N*-methylpropane-1,3-diamine, and salicylaldehyde with *N*-isopropylethane-1,2-diamine, respectively, in methanol, with high yields and purity. The Schiff bases were yellow gummy products and soluble in methanol, ethanol, acetonitrile, and chloroform. Complex **1** was prepared by the reaction of equimolar quantities of HL^1 with copper chloride in methanol; complexes **2** and **3** were prepared by the reaction of equimolar quantities of the Schiff bases with copper acetate and ammonium thiocyanate or sodium azide in methanol. The air-stable blue crystals of the complexes are soluble in DMF, DMSO, methanol, ethanol, and acetonitrile. The molar conductance values of the complexes measured in methanol at $10^{-3}\,mol\,L^{-1}$ are 15, 21, and 27 $\Omega^{-1}cm^2mol^{-1}$, indicating non-electrolytes in solution [13].

3.2. *Structure description of the complexes*

The molecular structures of **1**, **2**, and **3** are shown in figures 1, 2, and 3, respectively. A summary of crystal data for the complexes is listed in table 1, and selected bond lengths and angles are listed in table 2. Complexes **1**, **2,** and **3** are centrosymmetric chloro-, $\mu_{1,3}$-thiocyanato-, and $\mu_{1,1}$-azido-bridged dinuclear copper(II) compounds, in which the Cu's are five-coordinate square-pyramidal. In **1**, the basal plane of the square-pyramidal is defined by the NNO donor set of L^1, and by one Cl^-, with mean deviation

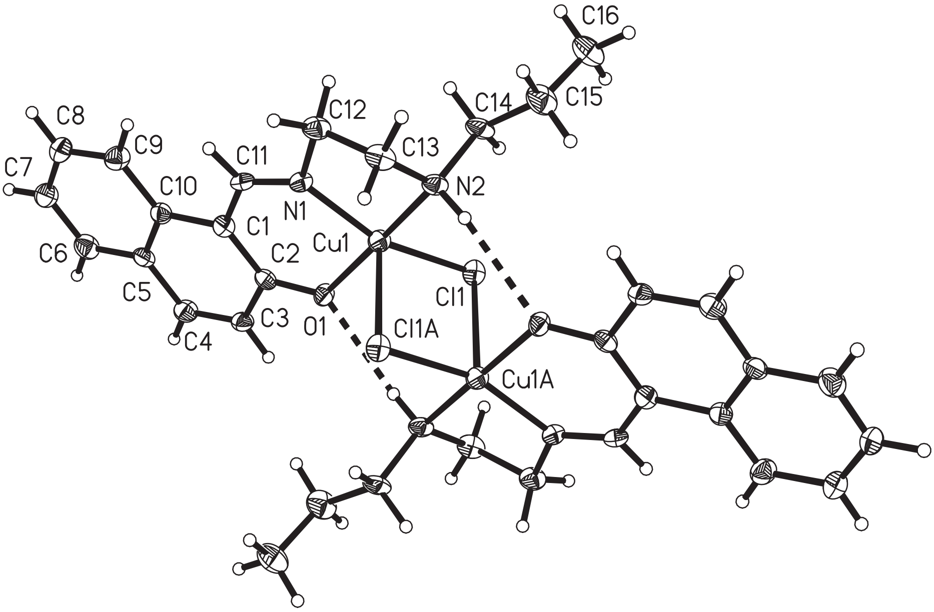

Figure 1. Molecular structure of **1**. Displacement ellipsoids are drawn at the 30% probability level. Atoms labeled with the suffix A or unlabeled are at the symmetry position 1−*x*, −*y*, −*z*.

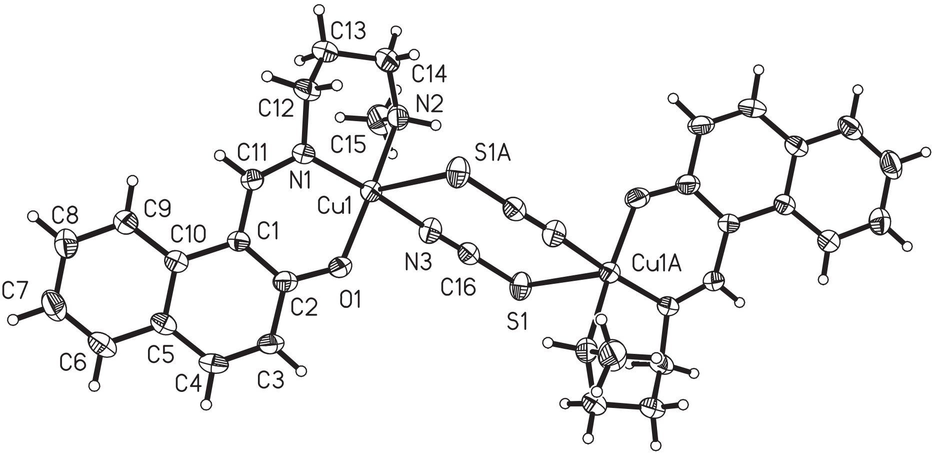

Figure 2. Molecular structure of **2**. Displacement ellipsoids are drawn at the 30% probability level. Atoms labeled with the suffix A or unlabeled are at the symmetry position −*x*, 1−*y*, −*z*.

from plane of 0.241(2) Å; the apical position is occupied by another symmetry-related Cl^-. In **2**, the basal plane of the square-pyramidal coordination is defined by the NNO donor set of L^2, and by one thiocyanate nitrogen atom, with mean deviation from plane of 0.057(2) Å; the apical position is occupied by a symmetry-related thiocyanate sulfur. In **3**, the basal plane of the square pyramid is defined by the NNO donor set of L^3, and by one azide nitrogen atom, with mean deviation from plane of 0.045(2) Å; the apical position is occupied by a symmetry-related azide nitrogen atom. The thiocyanate

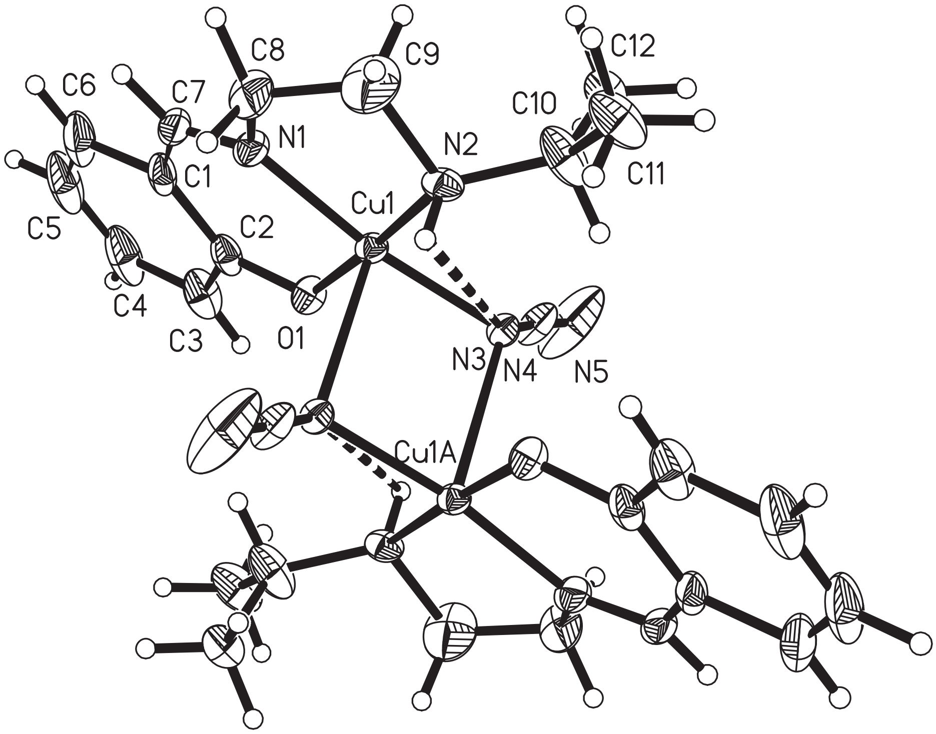

Figure 3. Molecular structure of **3**. Displacement ellipsoids are drawn at the 30% probability level. Atoms labeled with the suffix A or unlabeled are at the symmetry position $-x$, $2-y$, $1-z$.

groups in **2** and azide groups in **3** are nearly linear and show bent coordination with Cu (in **2**, the angles N3–C16–S1, Cu1–N3–C16, and C16–S1-Cu1^{ii} are 178.8(3), 167.8(2), and 100.5(2)°; in **3**, the angles N3–N4–N5, Cu1–N3–N4, and Cu1^{iii}–N3–N4 are 176.4(6), 122.3(4), and 130.4(4)°; symmetry codes: (^{ii}) $-x$, $1-y$, $-z$; (^{iii}) $-x$, $2-y$, $1-z$). In the complexes, the deviations of Cu from the least-squares planes defined by the corresponding four basal donor atoms toward the apical donors are 0.154(2) (**1**), 0.155(2) (**2**), and 0.071(2) (**3**) Å. In **1** and **3**, there are two intramolecular N–H$\cdots$O (**1**) and N–H$\cdots$N (**3**) hydrogen bonds between the two [CuL] units (L = L^1 for **1**, L = L^3 for **3**). The Cu$\cdots$Cu distances are 3.251(1) Å in **1**, 5.791(2) Å in **2**, and 3.257(1) Å in **3**.

The question arises as to whether the coordination polyhedra around the five-coordinate Cu atoms can be described as distorted square pyramid or distorted trigonal bipyramid. Information can be obtained by determining the structural index τ [14] which represents the relative amount of trigonality (square pyramid, $\tau = 0$; trigonal bipyramid, $\tau = 1$); $\tau = (\beta - \alpha)/60°$, α and β being the two largest angles around copper. The values of τ are 0.26 for **1**, 0.13 for **2**, and 0.083 for **3**, indicating they are slightly distorted square-pyramidal coordination.

Close examination of the structures reveals that Cu–O and Cu–N bond lengths are comparable. All the coordinate bond lengths can be considered as normal by comparison with those reported in the dinuclear copper(II) complexes with Schiff bases [15–20].

Table 1. Crystal data for the complexes.

Complex	**1**	**2**	**3**
Formula	$C_{32}H_{38}Cl_2Cu_2N_4O_2$	$C_{32}H_{34}Cu_2N_6O_2S_2$	$C_{24}H_{34}Cu_2N_{10}O_2$
Molecular formula	708.6	725.8	621.7
Temperature (K)	298(2)	298(2)	298(2)
Crystal shape/color	Block/blue	Block/blue	Block/blue
Crystal size (mm^3)	0.30 × 0.27 × 0.27	0.17 × 0.13 × 0.12	0.27 × 0.23 × 0.23
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	*P*bca	$P2_1/n$
Unit cell dimensions (Å,°)			
a	6.663(5)	13.369(2)	9.497(1)
b	9.474(6)	12.996(2)	15.020(2)
c	24.006(16)	18.354(3)	10.409(1)
β	96.479(10)	90	108.554(2)
Volume ($Å^3$), *Z*	1505.6(18), 2	3188.9(10), 4	1407.6(3), 2
Calculated density ($g\,cm^{-3}$)	1.563	1.512	1.467
Absorption coefficient (Mo-Kα) (mm^{-1})	1.627	1.505	1.551
F(000)	732	1496	644
Data collected	2944	3306	3011
Unique data ($I \geq 2\sigma(I)$)	1807	2531	1690
Min. and max. transmission	0.641 and 0.668	0.784 and 0.840	0.679 and 0.717
Parameters	195	203	178
Restraints	1	1	7
Goodness-of-fit on F^2	1.014	1.020	1.028
R_1, wR_2 $[I \geq 2\sigma(I)]^a$	0.0733, 0.1118	0.0344, 0.0866	0.0550, 0.1230
R_1, wR_2 (all data)^a	0.1368, 0.1255	0.0498, 0.0960	0.1144, 0.1500
Largest difference peak and hole ($e\,Å^{-3}$)	0.470 and −0.594	0.350 and −0.249	0.690 and −0.441

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

3.3. *IR spectra*

IR spectra of the Schiff bases and complexes provide information about the metal–ligand bonding. The assignments are based on typical group frequencies. The weak and broad bands indicative of ν(O–H) of phenols of the free Schiff bases are located at 3370–3450 cm^{-1}, which are absent in the complexes, indicating coordination through the deprotonated forms of the Schiff bases. The middle and sharp absorptions at 3160–3290 cm^{-1} for the Schiff bases and the complexes can be assigned to ν(N–H). The intense absorption bands at 2109 cm^{-1} in **2**, and at 2093 cm^{-1} in **3**, are assigned to the stretching vibrations of thiocyanate and azide, respectively [21, 22]. Strong absorptions at 1623–1627 cm^{-1} in spectra of the Schiff bases are assigned to azomethine groups, ν(C=N), shifted to lower wavenumbers in the complexes, 1618 cm^{-1} for **1** and **2**, and 1615 cm^{-1} for **3**; the shift indicates coordination of the azomethine to Cu.

The close resemblance of the shape and the positions of the bands suggest similar coordination modes for the complexes, in accord with the structural features.

4. Conclusion

In this study, three new centrosymmetric dinuclear Schiff-base copper(II) complexes with halide and pseudohalide bridges were constructed and structurally characterized.

Table 2. Selected bond lengths (Å) and angles (°) for the complexes.

1			
Cu1–O1	1.886(3)	Cu1–N1	1.916(4)
Cu1–N2	2.004(4)	Cu1–Cl1	2.2621(17)
Cu1–Cl1^{i}	2.754(2)		
O1–Cu1–N1	91.58(15)	O1–Cu1–N2	173.49(17)
N1–Cu1–N2	85.63(17)	O1–Cu1–Cl1	91.61(11)
N1–Cu1–Cl1	157.80(14)	N2–Cu1–Cl1	93.19(14)
O1–Cu1–Cl1^{i}	92.20(12)	N1–Cu1–Cl1^{i}	101.98(13)
N2–Cu1–Cl1^{i}	82.65(15)	Cl1–Cu1–Cl1^{i}	99.85(5)
2			
Cu1–O1	1.9081(19)	Cu1–N1	1.957(2)
Cu1–N2	2.044(2)	Cu1–N3	1.985(2)
Cu1–S1^{ii}	2.838(2)		
O1–Cu1–N1	90.11(8)	O1–Cu1–N3	87.28(9)
N1–Cu1–N3	174.01(9)	O1–Cu1–N2	166.52(10)
N1–Cu1–N2	94.67(9)	N3–Cu1–N2	86.73(10)
O1–Cu1–S1^{ii}	102.52(10)	N1–Cu1–S1^{ii}	95.75(10)
N2–Cu1–S1^{ii}	89.57(10)	N3–Cu1–S1^{ii}	90.08(10)
3			
Cu1–O1	1.904(3)	Cu1–N1	1.923(5)
Cu1–N2	2.064(5)	Cu1–N3	1.974(4)
Cu1–N3^{iii}	2.486(5)		
O1–Cu1–N1	93.4(2)	O1–Cu1–N3	89.4(2)
N1–Cu1–N2	84.3(2)	N1–Cu1–N3	172.6(2)
O1–Cu1–N2	177.3(2)	N3–Cu1–N2	92.7(2)
O1–Cu1–N3^{iii}	96.8(2)	N1–Cu1–N3^{iii}	99.5(2)
N2–Cu1–N3^{iii}	84.9(2)	N3–Cu1–N3^{iii}	86.9(2)

Symmetry codes: (^{i}) $1-x$, $-y$, $-z$; (^{ii}) $-x$, $1-y$, $-z$; (^{iii}) $-x$, $2-y$, $1-z$.

The Schiff bases coordinate to Cu through the phenolate O, imine N, and amine N. Cu's are in distorted square-pyramidal coordination. The halide and pseudohalide groups readily bridge the CuL units, forming dinuclear structures of the complexes.

Supplementary material

Crystallographic data for the complexes have been deposited with the Cambridge Crystallographic Data Center (CCDC 804641 for **1**, 804642 for **2**, and 830435 for **3**).

Acknowledgments

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