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CONSTRUCTION OF CHLORIDO-BRIDGED DINUCLEAR COPPER(II) COMPLEXES WITH SIMILAR TRIDENTATE SCHIFF BASES

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Two new chlorido-bridged dinuclear copper(II) complexes $[Cu_2Cl_2(L^1)_2]$ (**1**) and $[Cu_2Cl_2(L^2)_2]$ (**2**), where L^1 and L^2 are the deprotonated form of Schiff bases 2-[1-(2-morpholin-4-ylethylimino)ethyl]phenol (HL^1) and 2-[1-(2-piperidin-1-ylethylimino)ethyl]phenol respectively, are prepared and structurally characterized by elemental analysis, IR spectra, and single crystal X-ray crystallography. Complex **1** crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 8.0816(2)$ Å, $b = 19.1780(3)$ Å, $c = 9.6757(3)$ Å, $\beta = 106.465(2)°$, $V = 1438.13(6)$ Å^3, $Z = 2$, $R_1 = 0.0409$, and $wR_2 = 0.1085$. Complex **2** crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 7.7640(10)$ Å, $b = 19.930(3)$ Å, $c = 9.628(2)$ Å, $\beta = 103.890(3)°$, $V = 1446.2(4)$ Å^3, $Z = 2$, $R_1 = 0.0634$, and $wR_2 = 0.1316$. Each Cu atom in the complexes is coordinated by three donor atoms of the Schiff bases and by two bridging Cl atoms, forming square pyramidal geometry. The Cl anions are preferred bridging groups for the construction of dinuclear copper complexes with tridentate Schiff bases.

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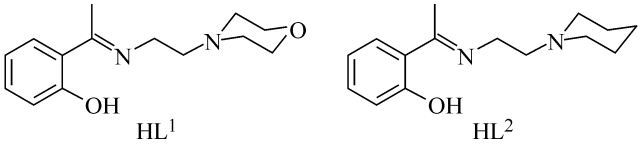
Dinuclear complexes with bridging groups are currently attracting much attention for their interesting structures and wide applications [1-3]. The Schiff bases derived from salicylaldehyde and its derivatives are a kind of versatile ligands in coordination chemistry. The rational design and construction of dinuclear complexes with Schiff bases are of particular interest in coordination and structural chemistry. As is well known, halide and pseudohalide groups can link two or more metal atoms, yielding various polynuclear complexes [4-8]. In this paper, two new dinuclear Schiff base copper(II) complexes with chloride bridges $[Cu_2Cl_2(L^1)_2]$ (**1**) and $[Cu_2Cl_2(L^2)_2]$ (**2**), where L^1 and L^2 are the deprotonated form of Schiff bases 2-[1-(2-morpholin-4-ylethylimino)ethyl]phenol (HL^1) and 2-[1-(2-piperidin-1-ylethylimino)ethyl]phenol (HL^2) (Scheme 1) respectively, were successfully prepared and characterized.



Scheme 1. Schiff bases

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Experimental. Materials and measurements. Starting materials, reagents and solvents (analytical grade) were purchased from commercial suppliers and used without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were recorded on a Jasco FT/IR-4000 spectrometer as KBr pellets in the range 4000-200 cm^{-1}. Single crystal structural X-ray diffraction was carried out on a Bruker SMART 1000 CCD area diffractometer.

Synthesis of the Schiff bases. The Schiff bases were synthesized by the same method as described here. To the methanolic solution (50 ml) of 2-acetylphenol (1.0 mmol each) was added a methanolic solution (50 ml) of amines (1.0 mmol each) under stirring. The mixtures were stirred for 30 min at room temperature to give a yellow solution. The solvent was evaporated to give a gummy product of the Schiff bases.

For HL^1: Yield 87%. Characteristic IR data: 1612 cm^{-1}. Anal. Calc. for $C_{14}H_{20}N_2O_2$: C, 67.7%; H, 8.1%; N, 11.3%. Found: C, 67.5%; H, 8.2%; N, 11.2%. For HL^2: Yield 91%. Characteristic IR data: 1612 cm^{-1}. Anal. Calc. for $C_{15}H_{22}N_2O$: C, 73.1%; H, 9.0%; N, 11.4%. Found: C, 73.2%; H, 9.0%; N, 11.2%.

Synthesis of the complexes. $[Cu_2Cl_2(L^1)_2]$ (**1**): To the methanolic solution (10 ml) of HL^1 (0.025 g, 0.1 mmol) was added a methanolic solution (10 ml) of $CuCl_2{\cdot}2H_2O$ (0.017 g, 0.1 mmol) under stirring. The mixture was stirred for 30 min at room temperature to give a blue solution. After keeping the solution in air for a few days, blue block-shaped crystals of **1**, suitable for the X-ray crystal structural determination, formed at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated, washed three times with methanol and dried in air. Yield 61%. Characteristic IR data (cm^{-1}): 1600 (s), 1235 (m). Anal. Calc. for $C_{28}H_{38}Cl_2Cu_2N_4O_4$: C, 48.6%; H, 5.5%; N, 8.1%. Found: C, 48.3%; H, 5.7%; N, 8.2%.

$[Cu_2Cl_2(L^2)_2]$ (**2**): Complex **2** was synthesized by the similar method as that described for **1**, with HL^1 replaced by HL^2 (0.025 g, 0.1 mmol). The blue block-shaped single crystals of **2** were isolated, washed three times with methanol and dried in air. Yield 53%. Characteristic IR data (cm^{-1}): 1598 (s), 1231 (m). *Anal.* Calc. for $C_{30}H_{42}Cl_2Cu_2N_4O_2$: C, 52.3%; H, 6.1%; N, 8.1%. Found: C, 52.5%; H, 6.2%; N, 8.0%.

X-ray crystallography. Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART 1000 CCD area-detector diffractometer with MoK_α radiation (λ = 0.71073 Å). The collected data were reduced with the SAINT program [9], and multi-scan absorption correction was performed using the SADABS program [10]. The structures were solved by direct methods. The complexes were refined against F^2 by the full-matrix least-squares method using SHELXTL [11]. 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 ethylene group in **1** is disordered over two distinct sites with occupancies of 0.459(2) and 0.541(2). The crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Results and discussion. Chemistry. The HL^1 and HL^2 Schiff bases were synthesized by the reaction of equimolar quantities of 2-acetylphenol with 2-morpholin-4-ylethylamine and 2-piperidin-1-ylethylamine, respectively, in methanol. The elemental analysis data are in good agreement with the chemical formulas proposed for the compounds. Complexes **1** and **2** were synthesized by the reaction of the HL^1 and HL^2 Schiff bases with $CuCl_2{\cdot}2H_2O$ in methanol under ambient conditions.

Structure description of the complexes. Single crystal X-ray diffraction shows that the complexes are structurally similar to halido-bridged dinuclear copper(II) compounds (Fig. 1 for **1**, Fig. 2 for **2**). Each complex possesses a crystallographic inversion center symmetry, with the inversion center located at the midpoint of two Cu atoms. The Cu···Cu distances are 3.724(1) Å in **1** and 3.614(1) Å in **2**, which are within the values observed in the chlorido-bridged Schiff base copper(II) complexes deposited in CSD.

In the complexes, the Schiff bases behave as monoanionic and tridentate ligands that coordinate to Cu atoms through three NNO donor atoms. Each Cu atom in the complexes is five-coordinated in a square pyramidal geometry, with the basal plane defined by the NNO donor atoms of the correspondding Schiff base ligand and by one bridging Cl atom, and with the apical position occupied by the another bridging Cl atom. The average *trans* angles are 167.0(2)° in **1** and 168.2(2)° in **2**. The Cu atoms deviate from the least-squares planes defined by the four basal donor atoms by 0.161(1) Å for **1** and 0.197(1) Å for **2**, toward the apical donor atoms. In **1** and **2**, the coordinate bond lengths related to the Cu atoms are comparable to each

TABLE 1. Crystallographic Data and Refinement Parameters for the Complexes

Complex	**1**	**2**
Formula	$C_{28}H_{38}Cl_2Cu_2N_4O_4$	$C_{30}H_{42}Cl_2Cu_2N_4O_2$
M_r	692.6	688.7
T, K	298(2)	298(2)
Crystal shape/color	Block / blue	Block / blue
Crystal size, mm	0.18×0.17×0.17	0.23×0.20×0.20
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a, b, c, Å; β, deg	8.0816(2), 19.1780(3), 9.6757(3); 106.465(2)	7.7640(10), 19.930(3), 9.628(2); 103.890(3)
V, Å^3	1438.13(6)	1446.2(4)
Z	2	2
D_c, g·cm^{-3}	1.599	1.581
μ(MoK_α), mm^{-1}	1.706	1.691
F(000)	716	716
Independent/Observed reflections ($I \ge 2\sigma(I)$)	3111/2561	2717/1802
Min. and max. transmission	0.749 and 0.760	0.697 and 0.728
Parameters	191	182
Restraints	16	0
$GOOF$ on F^2	1.043	0.978
R_1, wR_2 [$I \ge 2\sigma(I)$][a]	0.0409, 0.1085	0.0634, 0.1316
R_1, wR_2 (all data)[a]	0.0504, 0.1151	0.1020, 0.1468

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[a] $R_1 = F_0 - F_c/F_0$, $wR_2 = [\sum w(F_0^2 - F_c^2)/\sum w(F_0^2)^2]^{1/2}$.

TABLE 2. Selected Bond Distances (Å) and Angles (deg) for the Complexes

			1		
Cu1–O1	1.895(2)	O1–Cu1–N1	90.1(1)	O1–Cu1–N2	157.2(1)
Cu1–N2	2.073(3)	N1–Cu1–N2	85.5(1)	O1–Cu1–Cl1	90.6(1)
Cu1–Cl1A	2.832(1)	N1–Cu1–Cl1	176.8(1)	N2–Cu1–Cl1	95.1(1)
Cu1–N1	1.972(3)	O1–Cu1–Cl1A	106.8(1)	N1–Cu1–Cl1A	89.7(1)
Cu1–Cl1	2.280(1)	N2–Cu1–Cl1A	95.4(1)	Cl1–Cu1–Cl1A	87.1(1)
			2		
Cu1–O1	1.888(4)	O1–Cu1–N1	90.5(2)	O1–Cu1–N2	156.8(2)
Cu1–N2	2.044(4)	N1–Cu1–N2	85.0(2)	O1–Cu1–Cl1A	89.7(1)
Cu1–Cl1A	2.287(2)	N1–Cu1–Cl1A	179.6(1)	N2–Cu1–Cl1A	94.7(1)
Cu1–N1	1.966(4)	O1–Cu1–Cl1	108.2(1)	N1–Cu1–Cl1	93.0(1)
Cu1–Cl1	2.692(2)	N2–Cu1–Cl1	94.8(1)	Cl1–Cu1–Cl1A	87.3(1)

other and also comparable to the corresponding values observed in other similar chlorido-bridged copper(II) complexes with Schiff bases [4, 12-16].

Coordination number 5 for copper(II) complexes is very common. The question arises as to whether the coordination polyhedra around the Cu atoms can be described as a distorted square pyramid or a trigonal bipyramid. Further information can be obtained by determining the structural index τ that 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 the metal atom [17].

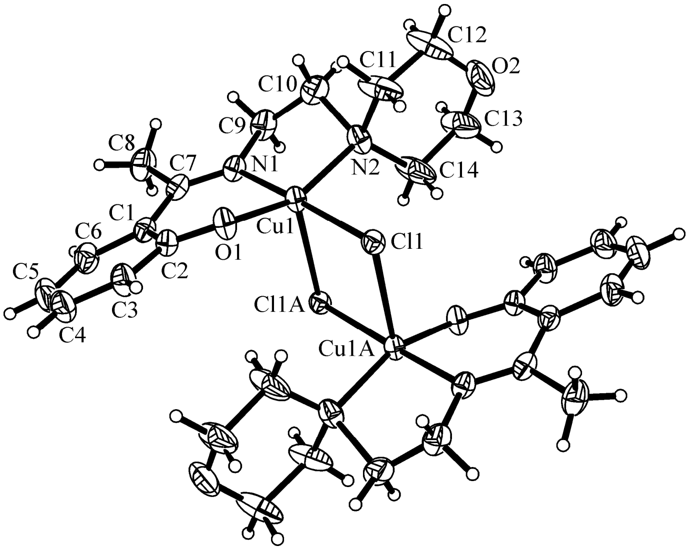

Fig. 1. Perspective view of the molecular structure of **1** with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Only the major component of the disordered group is shown.

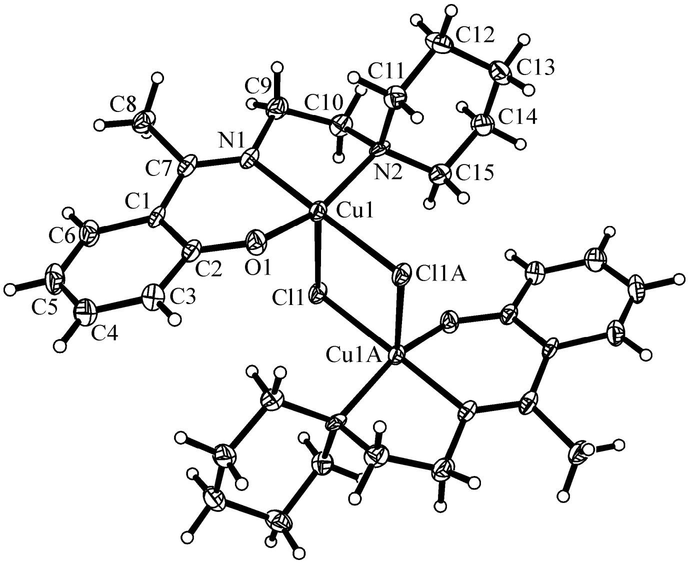

Fig. 2. Perspective view of the molecular structure of **2** with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

The τ values are 0.33 in **1** and 0.38 in **2**. From the τ values it can be concluded that Cu atoms in the complexes adopt a distorted square pyramidal coordination.

IR spectra. In the IR spectra of the complexes, the strong absorption bands at *ca.* 1600 cm^{-1} can be assigned to the azomethine stretching frequencies of the Schiff base ligands, whereas for the free Schiff bases the corresponding bands are observed at 1612 cm^{-1} for HL^1 and HL^2. The shift of these bands towards lower frequencies on complexation suggests the coordination to Cu atoms through the imine N atoms. The ν(C–O) mode is present as middle bands at 1235 cm^{-1} for **1** and 1231 cm^{-1} for **2**. The weak bands indicative of the Cu–O, Cu–N, and Cu–Cl bonds are located in the region 550-300 cm^{-1}.

Conclusions. The present paper reports the synthesis and crystal structures of two new chlorido-bridged dinuclear copper(II) complexes with similar tridentate Schiff bases. The Cl anions are preferred bridging groups for the construction of dinuclear copper(II) complexes with Schiff bases. The present dinuclear copper(II) complexes may serve as interesting magnetic materials.

Supplementary information. CCDC-825212 (**1**) and 825213 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdccam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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