Synthesis and characterization of a chiral dimeric copper(II) complex: Crystal structure of [Cu$_2$(*m*Cl)$_2$(HL)$_2$]·H$_2$O(H$_2$L = *S*-(−)-2-[(2-hydroxy-1-phenyl-ethylimino)-methyl]-phenol)

CHULLIKKATTIL P PRADEEP, PANTHAPALLY S ZACHARIAS* and SAMAR K DAS*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India
e-mail: skdsc@uohyd.ernet.in

Abstract. Synthesis and characterization of an optically active binuclear dichloro-bridged copper(II) complex [Cu$_2$(*m*Cl)$_2$(HL)$_2$]·H$_2$O **1** (H$_2$L = *S*-(−)-2-[(2-hydroxy-1-phenyl-ethylimino)-methyl]-phenol) of a Schiff-base derived from salicylaldehyde and (*S*)-(+)-2-phenylglycinol are described. Compound **1** crystallizes in the orthorhombic chiral $P2_12_12_1$ space group with $Z = 4$, $a = 10\cdot21(2)$, $b = 11\cdot574(3)$, $c = 25\cdot364(9)$. Each copper shows square pyramidal geometry with O$_2$NCl$_2$ coordination and the Cu$_2$Cl$_2$ core geometry adopts a butterfly shape. Crystals of **1** were further characterized by elemental analysis, IR, UV–visible and EPR spectroscopy and circular dichroism (CD) studies.

Keywords. Dinuclear copper(II) complex; crystal structure; chiral properties.

1. Introduction

Binuclear complexes of copper have received much attention because of their relevance to the type 3 copper found in multicopper-containing proteins such as the tyrosinase, hemocyanins and copper oxidases.[1] There are many reports on modelling the copper dinuclear active sites of these proteins.[2] Many of these proteins are believed to contain the copper ions in dissymmetric ligand arrangements and therefore modelling the structural aspects of this dissymmetric ligand environment around copper is currently of great interest.[3–6] Chiral dinuclear complexes of copper(II) have received special attention because of their importance in molecular self-recognition.[5,6] In our continued efforts to synthesize complexes of optically active Schiff-bases,[7] we have prepared a dichloro-bridged dinuclear copper(II) complex [Cu$_2$(*m*Cl)$_2$(HL)$_2$]·H$_2$O **1** (H$_2$L = *S*-(−)-2-[(2-hydroxy-1-phenyl-ethylimino)-methyl]-phenol) of a chiral Schiff-base prepared from salicylaldehyde and (S)-(+)-2-phenylglycinol. We report here the synthesis, structural characterization and properties of the chiral complex **1**.

2. Experimental

2.1 *Physical measurements*

Microanalytical (C, H, N) data were obtained with a Flash EA 1112 Series CHNS analyser. A Shimadzu 3101-PC UV/Vis/NIR spectrophotometer was used to record the electronic spectra. Infrared spectra were collected by using KBr pellets on a Jasco-5300 FT-IR spectrophotometer. The CD spectra were measured with a Jasco J-810 spectropolarimeter. EPR spectra were recorded on a Jeol JES-FA200 spectrometer.

2.2 *Synthesis of the enantiopure ligand H$_2$L*

Synthesis and characterization of the ligand H$_2$L (*S*-(−)-2-[(2-hydroxy-1-phenyl-ethylimino)-methyl]-phenol) have been reported earlier.[7]

2.3 *Synthesis of 1*

CuCl$_2$·2H$_2$O (0·179 g, 1 mmol) was added to a methanolic solution of the ligand H$_2$L (0·241 g, 1 mmol). The mixture was stirred at room temperature in air overnight. The resultant green solution was evaporated to dryness using a rotavapor and vacuum pump. The green coloured solid thus obtained was recrystallized from ethanol. Yield was 163 mg (47%).

Analysis: Calc. for C$_{30}$H$_{30}$N$_2$O$_5$Cl$_2$Cu$_2$: C, 51·73; H, 4·34; N, 4·02%. Found C, 53·26; H, 4·2; N, 4·09%.

UV/Vis (MeOH): $\boldsymbol{l}_{\max}$, nm (å, $M^{-1}cm^{-1}$): 682·00 (172), 372·00 (9567), 271·00 (23649), 223 (44250).

IR (KBr): 1626·14, 1541·26, 1467·96, 1442·88, 1294·35, 1199·83, 1149·68, 1126·53, 1068·66, 1006·93, 945·20, 896·98, 761·95, 700·22, 590·27, 528·54, 430·16 cm^{-1}.

2.4 *X-ray crystallography*

Single crystals of the complex **1** were grown by slow evaporation of an ethanol solution. Unit cell determination and data collection were performed on an Enraf–Nonius Mach3 single crystal diffractometer using graphite monochromated Mo-K$_{\boldsymbol{a}}$ radiation ($\boldsymbol{l} = 0.71013$ Å). An empirical absorption correction was applied to the data, based on the $\boldsymbol{y}$-scans of three reflections.[8] Programs of WinGX[9] were used for data reduction and absorption correction. The structure was solved by direct methods and refined on F^2 by full-matrix least squares procedures using SHELX-97 programs.[10] The absolute configuration for the compound molecule was successfully determined by refining the Flack parameter (0·034(19)).[11] Additional details of the data collection parameters and refinement are collected in table 1. CCDC-255828 contains the supplementary crystallographic data for complex **1**. This can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

3. Results and discussion

The dinuclear copper complex **1** is synthesized in moderate yield by mixing equimolecular amounts of $CuCl_2 \cdot 2H_2O$ and the ligand H_2L in a methanolic solution as shown in the following equation:

$$2CuCl_2 \cdot 2H_2O + 2\ H_2L \rightarrow [(HL)Cu(\boldsymbol{m}Cl)_2Cu(HL)] + 2HCl + 4H_2O. \quad (1)$$
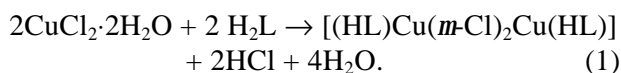
Single crystals of **1** are obtained by recrystallization from ethanol, and crystal structure of the complex **1** has been determined by means of single-crystal X-ray diffraction analysis. Table 2 displays its selected bond distances and angles.

The complex crystallizes in a noncentrosymmetric orthorhombic chiral space group $P2_12_12_1$ with four molecules per unit cell. The unit cell also contains four water molecules. The thermal ellipsoid plot for the molecular structure of complex **1** is presented in

figure 1. Each complex is hydrogen-bonded to one water molecule. The structure consists of dimeric Cu_2Cl_2 $(HL)_2$ units with a central non-planar Cu_2Cl_2 ring. The dihedral angle between the planes defined by Cu1, Cl1, Cl2 and Cu2, Cl1, Cl2 is 25.8°. Each Cu atom is penta-coordinated with distorted square-pyramidal geometry. Generally, the dichloro-bridged square-pyramidal copper complexes with square pyramid geometry exhibit three different geometries with regard to the relative arrangement of square pyramids, viz. perpendicular bases (type I), parallel bases (type II) and coplanar bases (type III).[12] The asymmetric arrangement of the Cu_2Cl_2 moiety in complex **1** belongs to type II. In the crystal structure, two penta-coordinated copper complexes with square-pyramidal geometry share a base to apex edge so that the Cl atom, situated at the vertex of one base, becomes the apex of the other square pyramid and vice versa for the other Cl-bridging ligand (figure 2). Analysis of the shape-determining angles using the approach of Reedijk *et al*[13] yields a $\hat{o}$ value of 0·1528 for Cu1 and 0·2878 for Cu2, indicating that the distortion is more towards square pyramidal. There is evidence for the involvement of imidazole and phenoxide ligands around the copper centres in oxyhemocyanins in square-pyramidal geometry.[14] Within the asymmetric $Cu(\boldsymbol{m}Cl)_2Cu$ core, the Cu–Cu distance is 3·381 Å, the two shorter Cu(1)–Cl(1) and Cu(2)–Cl(2) distances are 2·245(4) and 2·267(2)Å, the two longer Cu(1)–Cl(2) and Cu(2)–Cl(2) distances are 2·8802(17) and 2·6874(15)Å; and Cu(1)–Cl(1)–Cu(2) and Cu(1)–Cl(2)–Cu(2) angles are 86·03(5) and

Table 1. Crystallographic data for **1**

Empirical formula	$C_{30}H_{30}Cl_2Cu_2N_2O_5$
Formula weight	696·54
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
$\boldsymbol{l}$ (Å)	0·71073
a (Å)	10·21(2)
b (Å)	11·574(3)
c (Å)	25·364(9)
U (Å^3)	2998(6)
Z	4
$\hat{i}$ (mm^{-1})	1·638
T (°C)	25
Independent reflections	3856
R_{int}	0·0000
Obs reflections $[F > 4\acute{o}\ (F)]$	2882
$R_1{}^a\ [F > 4\acute{o}\ (F)]$	0·0362
$wR_2{}^b$	0·0707

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bwR_2 = [\Sigma\{w(F_o{}^2-F_c{}^2)^2\}/\Sigma\{w(F_o{}^2)^2\}]^{1/2}$

81·16(6)° respectively. In this context, it is worth mentioning that a number of dichloro-bridged dicopper complexes have been reported in the literature and many of these are structurally characterized.[15]

The compound shows high intensity IR bands around 1626 cm^{-1}, typical of conjugated C=N stretching. The carbon–oxygen stretch at 1541 cm^{-2} indicates a nonbridging phenolate ligand.

The absorption spectrum of **1** in MeOH is shown in figure 3. A broad *d–d* band (dashed line, figure 3) is obtained in the visible region (at 682 nm), a feature characteristic of many Cu(II) systems. The band at

372 nm might be assigned to a metal-to-ligand charge-transfer (MLCT) transition. The sharp peaks in the 200–290 nm range of the electronic spectrum are due
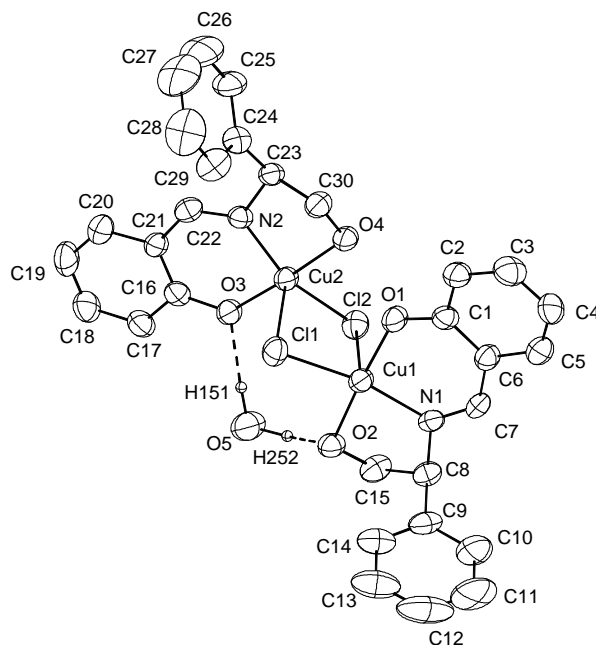

Figure 1. Thermal ellipsoid plot (50% probability) and atom labelling for **1**. Hydrogen atoms are omitted for clarity except water hydrogens. The hydrogen bonding parameters for the solvent water are O5–H151····O3 0·99 1·84 2·783(5) 158·3; O5–H2H2····O2 1·00 1·76 2·641(7) 143·4.

Table 2. Selected bond lengths [Å] and angles [°] for **1**.

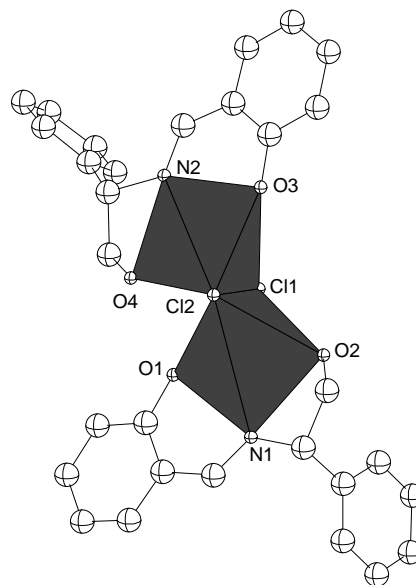|	
Cu(1)–O(1)	1·901(4)
Cu(1)–N(1)	1·949(5)
Cu(1)–O(2)	1·996(3)
Cu(1)–Cl(1)	2·245(4)
Cu(1)–Cl(2)	2·8802(17)
Cu(2)–O(3)	1·895(4)
Cu(2)–N(2)	1·933(4)
Cu(2)–O(4)	2·037(4)
Cu(2)–Cl(2)	2·267(2)
Cu(2)–Cl(1)	2·6874(15)
N(2)–C(22)	1·291(6)
N(2)–C(23)	1·496(6)
N(1)–C(7)	1·281(7)
O(1)–Cu(1)–N(1)	93·19(19)
O(1)–Cu(1)–O(2)	174·81(16)
N(1)–Cu(1)–O(2)	82·94(18)
O(1)–Cu(1)–Cl(1)	92·29(15)
N(1)–Cu(1)–Cl(1)	165·64(12)
O(2)–Cu(1)–Cl(1)	92·28(14)
O(3)–Cu(2)–N(2)	94·74(19)
O(3)–Cu(2)–O(4)	176·70(15)
N(2)–Cu(2)–O(4)	82·64(18)
O(3)–Cu(2)–Cl(2)	93·65(16)
N(2)–Cu(2)–Cl(2)	159·43(12)
O(4)–Cu(2)–Cl(2)	88·18(15)
O(3)–Cu(2)–Cl(1)	93·80(12)
N(2)–Cu(2)–Cl(1)	102·03(12)
O(4)–Cu(2)–Cl(1)	88·73(11)
Cl(2)–Cu(2)–Cl(1)	96·10(5)
Cu(1)–Cl(1)–Cu(2)	86·03(5)
Cu(2)–Cl(2)–Cu(1)	81·16(6)
C(22)–N(2)–C(23)	120·9(4)
C(22)–N(2)–Cu(2)	124·9(4)
C(23)–N(2)–Cu(2)	113·9(3)
C(30)–O(4)–Cu(2)	108·2(3)
C(7)–N(1)–C(8)	120·2(4)
C(7)–N(1)–Cu(1)	125·6(3)
C(8)–N(1)–Cu(1)	114·2(3)
C(16)–O(3)–Cu(2)	126·5(3)
C(1)–O(1)–Cu(1)	126·8(3)
C(15)–O(2)–Cu(1)	108·7(3)

Figure 2. The relative arrangement of square pyramid moieties around the copper atoms showing base-to-apex edge sharing.

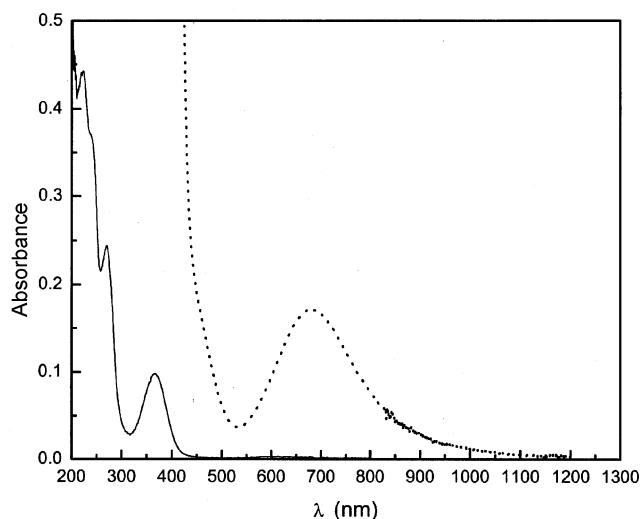**Figure 3.** Electronic spectra of **1** in methanol solution (solid line: 1×10^{-5} M and dashed line: 1×10^{-3} M).
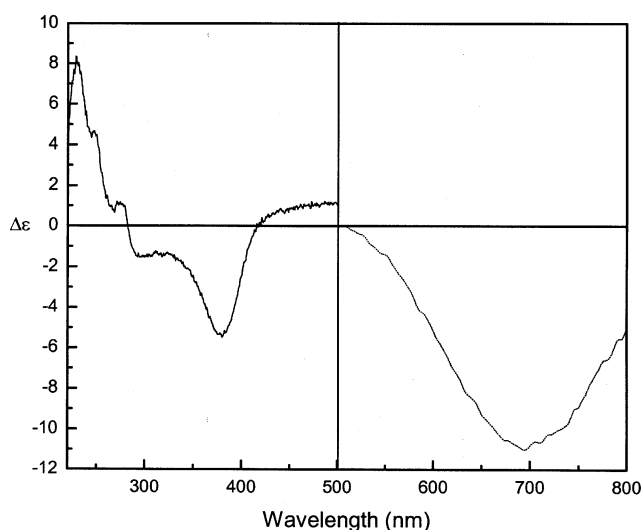

Figure 5. EPR spectrum of **1** in methanol solution at liquid nitrogen temperature.

Figure 4. Circular dichroism spectra of **1** in methanol solution (solid line: 1×10^{-5} M and dashed line: 1×10^{-3} M).

to intraligand charge transfer (ILCT) transitions, judging from their molar extinction coefficient values.

Optical activity of the dimeric copper complex **1** is induced by the enantiopure ligand H_2L (=S-(−)-2-[(2-hydroxy-1-phenyl-ethylimino)-methyl]-phenol). The circular dichroism (CD) spectrum of the ligand, H_2L, has been reported earlier[7] and shows a negative band around 315 nm. The CD spectrum of complex **1**, as expected, exhibits negative bands at 372 nm (MLCT), 682 nm (*d–d*) and in the UV region (ILCT) as shown in figure 4.
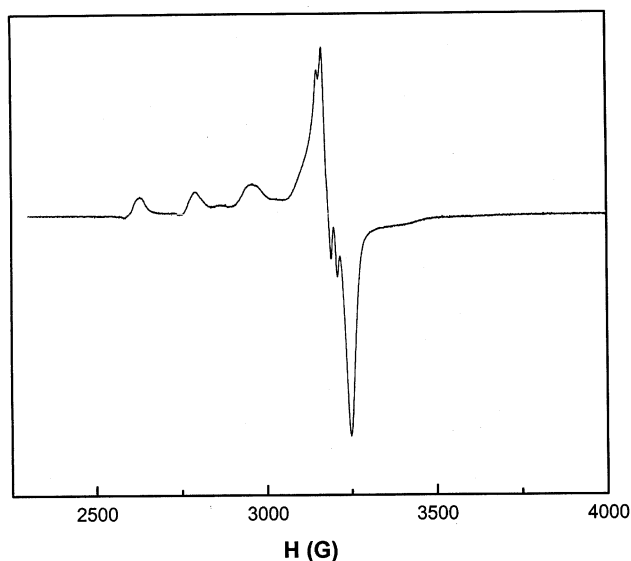
EPR spectrum of **1** in frozen methanol is displayed in figure 5. This is typical of a monomeric tetragonal Cu(II) complex with a $d_{x^2-y^2}$ ground-state doublet. This experiment suggests that the *bis*(*μ*-halo)-bridged structure, $[(HL)Cu(\mu Cl)_2Cu(HL)]$, is dissociated in solution presumably due to additional coordination by the solvent molecules. Similar behaviour has been observed for the other chloro-bridged dimeric copper complexes.[16] This observation is consistent with the fact that chloride bridges are weak in the crystalline state of **1** in terms of Cu–Cl distances (2·8802(16), 2·6872(15)). Thus the copper dimer complex **1** is readily dissociable in solution. The *g* values ($g_{\parallel}$ = 2·288, $g_{\perp}$ = 2·063, $A_{\parallel}$ = 164 G) are comparable with those of other dinuclear Cu(II) complexes.[16,17] Interestingly, the nitrogen superhyperfine splitting is observed in the $g_{\perp}$ region ($A_{\perp}^{N}$ = 16·5 G) as shown in figure 5.

4. Conclusions

Copper-containing proteins are shown to contain the copper ions in dissymmetric ligand arrangements. We have described, for the first time, a chiral dichlorobridged dimeric copper(II) complex. Both copper centres adopt square-pyramidal geometry, which is also found in copper-containing oxyhemocyanins. The chirality of the complex is supported by circular dichroism studies.

Acknowledgements

References

1. Ochiai E I 1977 *Bioinorganic chemistry; An introduction* (Boston, MA: Allyn and Bacon) ch. 9
2. Sorrell T N 1989 *Tetrahedron* **45** 3
3. Telfer S G, Sato T, Harada T, Kuroda R, Lefebvre J and Leznoff D B 2004 *Inorg. Chem.* **43** 6168
4. Deschamps P, Kulkarni P P and Sarkar B 2003 *Inorg. Chem.* **42** 7366; Adams H, Fenton D E, McHugh P E and Potter T J 2002 *Inorg. Chim. Acta* **331** 117; Amudha P, Akilan P and Kandaswamy M 2000 *Polyhedron* **19** 1769; Amudha P, Thirumavalavan M and Kandaswamy M 1999 *Polyhedron* **18** 1363
5. Rowland J M, Olmstead M M and Mascharak P K 2002 *Inorg. Chem.* **41** 1545
6. Masood M A, Enemark E J and Stack T D P 1998 *Angew. Chem., Int. Ed.* **37** 928
7. Pradeep C P, Htwe T, Zacharias P S and Das S K 2004 *New. J. Chem.* **28** 735
8. North A C T, Philips D C and Mathews F S 1968 *Acta Crystallogr.* **A24** 351
9. Farrugia L J 1999 *J. Appl. Crystallogr.* **32** 837
10. Sheldrick G M 1997 SHELX-97, Structure Determination Software, University of Göttingen, Göttingen, Germany
11. Flack H D 1983 *Acta Crystallogr.* **A39** 876
12. Rodríguez M, Llobet A, Corbella M, Martell A E and Reibenspies J 1999 *Inorg. Chem.* **38** 2328
13. Addison A W, Rao T N, Reedijk J, Rijn J V and Verschoor G C 1984 *J. Chem. Soc., Dalton Trans.* 1349
14. Beinert H 1980 *Coord. Chem. Rev.* **33** 55; Amundson A R, Whelan J and Bosnick B 1977 *J. Am. Chem. Soc.* **99** 6730
15. Kapoor P, Pathak A, Kapoor R, Venugopalan P, Corbella M, Rodríguez M, Robles J and Llobet A 2002 *Inorg. Chem.* **41** 6153; Rodríguez M, Llobet A and Corbella M 2000 *Polyhedron* **19** 2483, and references cited therein; Sangeetha N R and Pal S 2000 *Polyhedron* **19** 1593
16. Brown S J, Tao X, Wark T A, Stephan D W and Mascharak P K 1988 *Inorg. Chem.* **27** 1581
17. Brown S J, Tao X, Stephan D W and Mascharak P K 1986 *Inorg. Chem.* **25** 3377