Synthesis and crystal structure of bis[2-[N-(2-chlorophenyl) formimidayl]-1-naphtholato]-(6Cl)copper(II)

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The title compound, bis[2-[*N*-(2-chlorophenyl)formimidayl]-1-naphtholato]-(6Cl) copper(II), [Cu(C₁₇H₁₁NOCl)₂] (1) was synthesized and its crystal structure was determined. The Compound **1** is monoclinic, space group $P2_1/c$ with a = 9.146(3) Å, b = 18.724(3) Å, c = 16.230(2) Å, $\beta = 96.46(1)^\circ$, V = 2761.8(11) Å³, Z = 4, $D_c = 1.503$ g cm⁻³, μ (Mo K α) = 1.020 mm⁻¹, R = 0.0606 for 2361 reflections [$I > 2\sigma(I)$]. In the title compound, the Cu atom is coordinated by an N₂O₂ donor set from the imine-phenol ligand in a slightly distorted square planar coordination geometry, with the two phenolate O atoms being deprotonated. The Cu–O bond lengths are 1.878(4) and 1.889(4) Å, the Cu–N bond lengths are 1.980(5) and 1.985(5) Å. The angles O1–Cu–N1 and O2–Cu–N2 are 90.96(19) and 90.72(19)°, respectively.

KEY WORDS: Schiff base complex; crystal structure; coordination geometry; ¹H NMR; square planar.

Introduction

The chemistry of metal complexes with Schiff base ligands and their applications have aroused considerable attention, mainly because of preparative accessibility, diversity, and structural variability. For example, there has been interest in copper(II) imine-phenols because of their color isomerism, conformational influences, and their potential as radiopharmaceuticals.^{1–7} The development of a ⁶²Zn/⁶²Cu-radionuclide generator increases the potential utility of Cu-labelled radiopharmaceuticals as imaging agents in positron emission tomography (PET). ⁶²Cu–PTSM [PTSM is pyruvaldehyde bis(4-methylthiosemicarbazone)], a neutral and lipophilic copper(II) complex, has been investigated as a potential Cu tracer for imaging the heart and brain.⁸ Additionally, neutral and lipophilic complexes of ⁶⁷Cu with a series of tetredentate Schiff base N₂O₂ ligands have also been evaluated as to their potential as cerebral blood-flow imaging agents.

In this paper, we report the results of the reaction of copper(II) with the bidentate ligand N-(2-chloro)-naphthaldimine, forming the title complex and determine its crystal structure by X-ray diffraction. The similar crystal structure bis[2-[N-(4-chlorophenyl)formimidayl]-1-naphtholato]-(8Cl)copper(II) has been determined previosly.⁹

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Experimental

Synthesis of 1

N-(2-chloro)-naphthaldimine was prepared by condensation of naphthaldehyde (0.861 g,0.005 mol) and 2-chloroaniline (0.638 g, 0.005 mol) in 100 mL of ethanol. The reaction mixture was stirred for 4 h and then placed in a freezer for 18 h. The yellow precipitate was collected by filtration and then washed with cold ethanol. m.p. 137°C, 1.325 g (88%) yields. Found: C, 72.32; H, 4.32; N, 4.9, C₁₇H₁₂NOCl; C, 72.47; H, 4.29; N, 4.97 (all values are given as percentages). IR (KBr, cm^{-1}): $\nu(Ar-H)$ $3072 \text{ m}, \nu(C=N) 1621 \text{ s}, \nu(C=C) 1600 \text{ s}, \nu(C=O)$ 1422 s, 1381 s. ¹H NMR (CDCl₃); δ ppm, 15.22 (s, 1H, OH); 9.18 (d, 1H, CH=N, ${}^{3}J_{\text{NHCH}} =$ 7.32 Hz); 8.22-6.90 (m, 12H, Ar-H). After recrystallization, yellow crystals were harvested and dried in vacuo. $[Cu(CH_3COO)_2] \cdot H_2O$ (0.199 g, 0.001 mol) in methanol (50 mL) and N-(2-chloro)naphthaldiminato (0.564 g, 0.002 mol) in acetonitrile (75 mL) were mixed and heated at 333 K for 1 h. The solution was filtered and the filtrate kept in a beaker at 277 K for crystallization. Black crystals started appearing after 3-4 days and were then collected by filtration, 0.689 g (90%)vields (Fig. 1). Found: C, 76.88; H, 4.90; N, 11.23,



Fig. 1. Reaction scheme.

 $C_{34}H_{22}N_2O_2Cl_2Cu$; C, 77.42; H, 4.84; N, 11.29 (all values are given as percentages). Crystals suitable for X-ray diffraction were obtained by slow evaporation from a saturated ethanol solution.

Reagents and techniques

2-Hydroxy-1-naphthaldehyde, 2-chloroaniline, methanol, and CDCl₃ were purchased from Merck (Germany). Ethanol and acetonitrile were purchased from Aldrich Chemicals. The melting point was measured on a Gallonkamp apparatus using a capillary tube. The elemental analyses were performed on a LECO CHNS-932 C-, H-, N-analyzer. Infrared absorption spectra were obtained from a Mattson 1000 FTIR spectrometer in KBr discs and reported in cm⁻¹. Proton (400 MHz) NMR spectra were recorded with a Bruker DPX FT-NMR spectrometer (CDCl₃ as internal standard).

The X-ray data collection was performed on a Rigaku AFC7-S diffractometer employing graphite-monochromatized Mo K α radiation ($\lambda =$ 0.71073 Å).¹⁰ The details of the X-ray data collection, structure solution, and structure refinement were given in Table 1 and the fractional atomic coordinates of all nonhydrogen atoms were refined with anisotropic atomic displacement parameters. Data reduction and corrections for absorption and crystal decomposition (1.2%) were carried out using the TEXAN Single Crystal Structure Analysis Software.¹¹ The structure was solved by SHELXS-97¹² and refined with SHELXL-97.¹³ The positions of H atoms bonded to C atoms were calculated (C—H distance 0.93 Å), and included in the structure factor calculation using a riding model. The final fractional atomic coordinates and thermal parameters were given in Table 2. Bond distances and angles are listed in Table 3 and an ORTEP view of the molecular structure is given in Fig. 2.¹⁴

Results and discussion

Recently, the crystal structures of bis [*N*-(2-bromo-4-methylphenyl)-naphthaldiminato]

	Table 1.	Crystal D	ata and Str	ucture Refin	nement for 1
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Compound

Color/shape

CCDC deposit no.

Crystal size, mm3

Formula weight

Table 2. Tractional Atomic Constraints for T

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Index 2. Tractional Atomic Constraints for T

Isotropic Displacement F

Constraints for T

Constraints for T

Constraints for T

Constraints for T

State 2. Tractional Atomic Constraints for T

Isotropic Displacement F

Constraints for T

Constra

Temperature, K	295(2)
Crystal system	$P2_{1}/c$
Space group	Monoclinic
Unit cell dimensions	a = 9.146(3) Å
	b = 18.724(3) Å
	c = 16.230(2) Å
	96.46(1)°
Volume, Å ³	2761.8(11)
Ζ	4
Density, g cm ⁻³	1.503
Absorption coefficient, mm ⁻¹	1.020
Diffractometer	Rigaku AFC7-S
Scan	$\omega/2\theta$
θ range for data collection, deg	2.63-27.41
F (000)	1276
Reflections collected	5629
Independent reflections	5100
Observed reflections (R_{int})	2361 (0.0813)
Data/restraints/parameters	2361/0/360
Goodness of fit on F^2	1.002
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0606, wR2 = 0.1507
R indices (all data)	R1 = 0.1667, wR2 = 0.1979
Largest diff. peak and hole, e $Å^{-3}$	0.356 and -0.398

copper(II) $[Cu(C_{18}H_{13}NOBr)_2]^{15}$ and bis[N-(2iodo)-naphthaldiminato]copper(II) $[Cu(C_{17}H_{11} NOI)_2]^{16}$ were reported. These similar compounds have crystallographic inversion symmetry and the copper(II) ion is in a pseudo-octahedral environment if bromine or iodine is included in the description.

In the title compound, however, the two bidentate ligands are coordinated as chelates to copper(II) and a slightly distorted square planar composed of two imine **N** atoms and two phenol O atoms. The Cu–O1 and Cu–O2 bond lengths are 1.878(4) and 1.889(4) Å, respectively, while the Cu–N1 and Cu–N2 bond lengths are 1.980(5) and 1.985(5) Å, respectively. The Cu–N and Cu–O values in the title compound agree with those in other naphthalenic complexes. The Cu–N distances range from 1.970 to 2.010 Å, while the Cu–O distances have values between 1.870 and 1.920 Å in (1,2-naphthaldiminato) copper complexes.^{15–18}

Table	2.	Fractional	Atomic	Coordinates	(Å)	and	Equivalent
		Isotropic D	isplacem	ent Parameter	s (Å ²) for	1

	x	у	Z	$U_{eq}{}^a$
Cu1	-0.00626(8)	0.34157(4)	0.69207(5)	0.0420(3)
Cl1	-0.3264(2)	0.29509(11)	0.75162(12)	0.0752(6)
Cl2	-0.0548(2)	0.36418(12)	0.91021(13)	0.0731(6)
01	0.0443(5)	0.4388(2)	0.6994(3)	0.0548(12)
02	-0.0241(4)	0.2434(2)	0.6663(3)	0.0512(12)
N1	-0.1833(5)	0.3636(3)	0.6144(3)	0.0402(12)
N2	0.1477(5)	0.3206(3)	0.7852(3)	0.0418(12)
C1	0.0010(6)	0.4920(3)	0.6518(4)	0.0437(15)
C2	0.0827(4)	0.5565(2)	0.6649(3)	0.0503(17)
C3	0.0426(4)	0.6150(2)	0.6199(3)	0.0526(18)
C4	-0.0826(4)	0.6158(2)	0.5576(3)	0.0456(16)
C5	-0.1160(4)	0.67867(17)	0.51198(19)	0.0587(19)
C6	-0.2356(4)	0.68008(17)	0.45388(19)	0.062(2)
C7	-0.3215(4)	0.61898(17)	0.43920(19)	0.065(2)
C8	-0.2895(4)	0.55539(17)	0.48231(19)	0.0545(18)
C9	-0.1645(4)	0.55266(17)	0.54341(19)	0.0428(15)
C10	-0.1218(6)	0.4881(3)	0.5908(4)	0.0383(14)
C11	-0.2070(4)	0.4250(2)	0.5786(3)	0.0391(14)
C12	-0.2815(4)	0.3066(2)	0.5909(3)	0.0394(14)
C13	-0.3051(3)	0.28389(17)	0.5075(2)	0.0494(17)
C14	-0.3942(3)	0.22635(17)	0.4856(2)	0.0567(19)
C15	-0.4619(3)	0.18906(17)	0.5456(2)	0.063(2)
C16	-0.4415(3)	0.20979(17)	0.6275(2)	0.0567(18)
C17	-0.3512(3)	0.26854(17)	0.6483(2)	0.0463(16)
C18	0.0638(7)	0.1912(3)	0.6885(4)	0.0406(14)
C19	0.0280(5)	0.1237(2)	0.6519(2)	0.0576(18)
C20	0.1142(5)	0.0654(2)	0.6722(2)	0.0560(18)
C21	0.2444(5)	0.0704(2)	0.7290(2)	0.0484(16)
C22	0.3326(4)	0.00881(17)	0.74602(19)	0.063(2)
C23	0.4580(4)	0.01367(17)	0.79955(19)	0.070(2)
C24	0.4984(4)	0.07788(17)	0.83769(19)	0.064(2)
C25	0.4125(4)	0.13827(17)	0.82159(19)	0.0533(18)
C26	0.2809(4)	0.13571(17)	0.76718(19)	0.0389(14)
C27	0.1867(6)	0.1973(3)	0.7488(4)	0.0383(14)
C28	0.2169(5)	0.2609(2)	0.7954(2)	0.0412(15)
C29	0.1975(5)	0.3770(2)	0.8406(2)	0.0424(15)
C30	0.3341(4)	0.40669(17)	0.8345(2)	0.0606(19)
C31	0.3861(4)	0.46418(17)	0.8862(2)	0.070(2)
C32	0.2994(4)	0.48743(17)	0.9476(2)	0.069(2)
C33	0.1646(4)	0.45564(17)	0.9551(2)	0.062(2)
C34	0.1139(4)	0.40043(17)	0.9006(2)	0.0468(16)

^{*a*} U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. $U_{eq} = (1/3) \sum_{i} \sum_{j} U_{ij} a_i^* a_i^* a_i \cdot a_j$.

The Cu atom is displaced by 0.020(2) Å above the best coordination plane (O1, O2, N1, N2). N1 and O2 are on the same side of the plane as Cu at distances of 0.191(2) and 0.201(2) Å, respectively, while N2 and O1 are on the opposite side at distances of 0.194(3) and 0.204(2) Å, respectively. The nonbonded Cu ··· Cl1 and Cu ··· Cl2

C-1 01	1.070(4)	C-1 02	1.000(4)
	1.8/8(4)	Cu1-02	1.889(4)
Cu1-N1	1.980(5)	Cu1-N2	1.985(5)
Cl1-C17	1.739(4)	C12 - C34	1.708(4)
01-C1	1 206(7)	02 - C19	1 201(7)
	1.290(7)	02-018	1.291(7)
N1-C11	1.296(6)	N2-C28	1.287(6)
N1-C12	1.418(6)	N2-C29	1.428(6)
C1 - C10	1 412(8)	C18 - C27	1 / 10(8)
	1.424(7)		1.410(0)
C1-C2	1.424(7)	C18-C19	1.418(7)
C2-C3	1.344(7)	C19-C20	1.365(7)
C3-C4	1.440(7)	C20-C21	1.425(7)
C4-C0	1.404(5)	$C_{21} - C_{26}$	1 205(5)
C4-C9	1.404(3)	C21-C20	1.393(3)
C4–C5	1.406(5)	C21–C22	1.416(5)
C5-C6	1.362(5)	C22-C23	1.361(5)
C6-C7	1 393(5)	$C_{23}-C_{24}$	1 383(5)
C7 C9	1 205(5)	C24 C25	1 295(5)
0/-08	1.393(3)	C24-C23	1.565(5)
C8–C9	1.428(5)	C25-C26	1.411(5)
C9-C10	1.463(6)	C26-C27	1.451(6)
C10-C11	1 417(7)	C27-C28	1420(7)
C10 C11	1.417(7)	627 620	1.420(7)
C12-C17	1.385(5)	$C_{29}-C_{34}$	1.375(5)
C12-C13	1.413(5)	C29-C30	1.382(5)
C13-C14	0.373(5)	C30-C31	1.414(5)
C14-C15	1 398(5)	$C_{31} - C_{32}$	1 /11(5)
C14 C15	1.370(5)	631 632	1.411(5)
C15-C16	1.578(5)	C32-C33	1.380(5)
C16-C17	1.394(5)	C33–C34	1.405(5)
01-Cu1-N1	90.96(19)	Ω^2 —Cu1—N1	00.00(10)
	90.90(19)		(10, 70, 10)
OI-CuI-N2	89.09(19)	02-Cul-N2	90.72(19)
O1-Cu1-O2	166.4(2)	N1-Cu1-N2	170.0(2)
C1-O1-Cu1	130.6(4)	C18-O2-Cu1	129.8(4)
C11-N1-C12	118 5(5)	C11-N1-Cu1	123 6(4)
C12 N1 $Cu1$	117.6(2)	C_{28} N2 C_{20}	116 2(5)
	117.0(3)	C20-N2-C29	110.5(5)
C28-N2-Cu1	124.5(4)	C29—N2—Cu1	118.9(3)
01-C1-C10	122.9(6)	01-C1-C2	116.3(5)
C10-C1-C2	120.8(5)	C3 - C2 - C1	120.2(3)
C_{2} C_{3} C_{4}	122 5(3)	$C_{0}-C_{4}-C_{5}$	122.6(4)
	122.3(3)	C) C4 C3	122.0(4)
C9-C4-C3	118.3(2)	C5-C4-C3	119.2(2)
C6-C5-C4	119.4(2)	C5-C6-C7	119.8(2)
C6-C7-C8	122.2(2)	C7–C8–C9	119.0(2)
C4 - C9 - C8	117.0(2)	C4 - C9 - C10	120 3(4)
C ⁰ C ⁰ C ¹⁰	122.7(2)		120.5(1)
C8-C9-C10	122.7(3)	CI=CI0=CII	121.5(5)
C1-C10-C9	118.0(5)	C11-C10-C9	120.4(5)
N1-C11-C10	128.0(4)	C17-C12-C13	117.2(4)
C17-C12-N1	122.1(4)	C13-C12-N1	120.5(4)
C14_C13_C12	120 4(2)	C13_C14_C15	120 6(2)
C14 C15 C12	120.4(2)	C15 C14 C15	120.0(2)
	120.0(2)		117.9(2)
C12-C17-C16	123.3(2)	C12-C17-Cl1	118.8(3)
C16-C17-Cl1	117.92(13)	O2-C18-C27	123.6(6)
02 - C18 - C19	116 8(5)	C27-C18-C19	119 5(5)
C_{20} C_{10} C_{1}	120.8(2)	C_{10} C_{20} C_{21}	121 4(2)
C20-C19-C1	120.8(3)	C19-C20-C21	121.4(3)
C26-C21-C22	121.7(4)	C26-C21-C20	119.1(2)
C22-C21-C20	119.3(2)	C23-C22-C21	119.4(2)
C22-C23-C24	120.5(2)	C23 - C24 - C25	120.5(2)
C24-C25-C26	121 1(2)	C21_C26_C25	116.9(2)
C_{24} C_{23} C_{20}	121.1(2)	C_{21} C_{20} C_{23}	110.9(2)
C21-C26-C27	120.0(4)	C25-C26-C27	125.1(5)
C18-C27-C28	122.1(5)	C18-C27-C26	119.1(5)
C28-C27-C26	118.8(4)	N2-C28-C27	126.6(4)
C34 - C29 - C30	120 1(4)	C34-C29-N2	121 2(4)
C30-C20-N2	118 6(4)	C_{20} C_{20} C_{21}	1207(2)
$C_{30} - C_{29} - N_{2}$	110.0(4)	$C_{29} = C_{30} = C_{31}$	120.7(2)
C32-C31-C30	118.4(2)	C33–C32–C31	120.4(2)
C32–C33–C34	119.7(2)	C29–C34–C33	120.7(2)
C29-C34-Cl2	121.2(3)	C33-C34-C12	118.17(13)
	x- /		



Fig. 2. The molecular structure of the Compound 1. The displacement ellipsoids are plotted at the 50% probability level.

distance are 3.302(1) and 3.642(1) Å, respectively. The Schiff base moieties **A** (O1, C1–C11) and **B** (N1, C12–C17, C11), and **C** (O2, C18–C29) and **D** (N2, C29–C34, C12) are inclined at an angle of 54.47(8) and 56.9(3)°, respectively, with respect to one another, which is mainly the twist about N1–C12 and N2–C29 [57.7(2)°] and [65.3(7)°] respectively.

Discrete monomeric molecules are held together in the crystal by van der Waals interactions. The minimum distances between two non-H atoms in neighbouring molecules are $C2 \cdots C11$, $C19 \cdots C28$, $Cu1 \cdots C10$, and $Cu1 \cdots C27$ with values of 3.770(3), 3.755(3), 3.309(3), and 3.300(3) Å, respectively.

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