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Crystal structure and spectroscopic studies of bis[*N*-(2-iodo)-naphthaldiminato]copper(II)

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Abstract

The Schiff base complex bis[*N*-(2-iodo)-naphthaldiminato]copper(II) $[\mathrm{Cu}(\mathrm{C}_{17}\mathrm{H}_{11}\mathrm{NOI})_2]$ (**1**) has been studied by elemental analysis, IR techniques and the structure of the compound has been examined crystallography. The compound **1** crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.229(2)$ Å, $b = 15.840(4)$ Å, $c = 11.389(3)$ Å, $\beta = 104.49(2)°$ ($R = 0.053$ for 2507 reflections $[I > 2\sigma(I)]$). It has crystallographic inversion symmetry. Two bidentate Schiff base ligand **1** coordinate to the Cu atom in a square–planar arrangement. The Cu–N and Cu–O distances are 1.990(2) and 1.896(2) Å, respectively.

Keywords: Schiff base ligand; Complex; Spectroscopic study; Crystal structure; Inversion symmetry

1. Introduction

2-Hydroxy Schiff base ligands and their copper(II) complexes play a major role in both the synthesis and structural research [1]. Schiff base complexes have continued to play the role of one of the most important stereochemical models in main group and transition metal coordination chemistry with their easy preparation diversition and structural variation [2]. There have been many crystal structure determinations of 2:1 complexes between copper(II) and planar bidentate ligand (*N*-(2-iodo)-naphthaldimine) with two O and two N donor atoms. The geometry of the immediate coordination sphere is usually planar. An additional point of interest is the packing of these essentially planar molecules. In order to investigate distortions in the geometry and the mode of packing, in this paper, we have determined the structures of the complexes CuL^2, where L is *N*-(2-iodo)-naphthaldimine.

2. Experimental

2.1. Reagent and technique

2-Hydroxy-1-naphthaldehyde, 2-iodoaniline, methanol and CDCl_3 were purchased from Merck (Germany). Ethanol and acetonitrile were purchased from Aldrich Chemical Co. 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-analyser. Infrared absorption spectra were obtained from a

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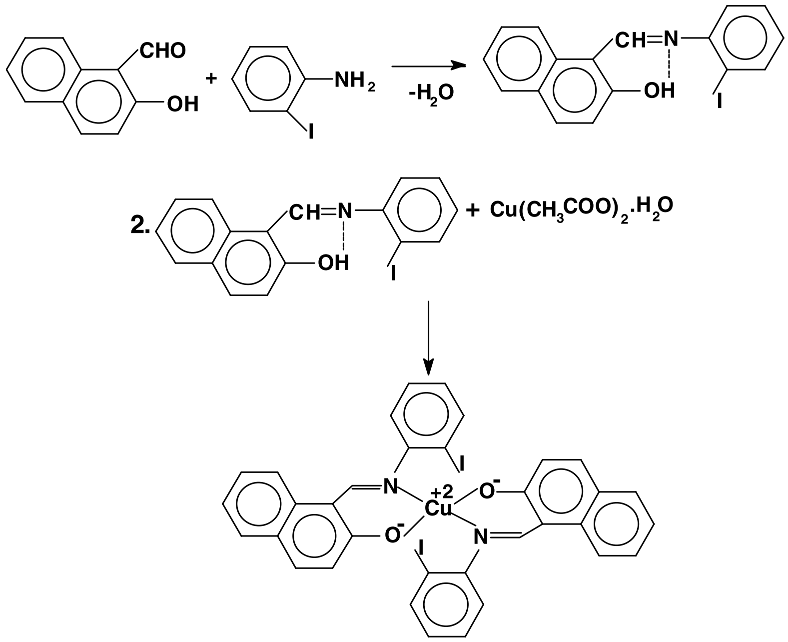

Fig. 1. Reaction scheme and chemical structure.

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 ($CDCl_3$ as internal standard).

2.2. Preparation of bis[N-(2-iodo)-naphthaldiminato]copper(II)

N-(2-iodo)-Naphthaldimine was prepared by condensation of 2-hydroxy-1-naphthaldehyde (0.01 mol, 1.72 g) and 2-iodoaniline (0.01 mol, 2.19 g) 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, mp 150 °C, 3.01 g (77%) yields. Found: C, 54.65; H, 3.44; N, 3.65, $C_{17}H_{12}NOI$: C, 54.71; H, 3.24; N, 3.75%. IR (KBr, cm^{-1}): ν(Ar–H) 3062–3064 m, ν(C=N) 1624 s, ν(C=C) 1610 s, ν(C–O) 1326 s. ^1H NMR ($CDCl_3$); δ ppm, 15.24 (s, 1H, NH); 9.32 (s, 1H, CH=N); 6.82–8.14 (m, 12H, Ar–H). MS (EI) *m/z*: (%) 373 (M^+) 100 base peak; 374 $(M+1)^+$ 17.5; 375 $(M+2)^+$ 1.7; 372 $(M-1)^+$ 87; 356 (M–OH) 12.1; 204 ($M-C_6H_5I^+$) 1.1; 128 ($C_{10}H_8^+$) 3.8; 246 (M–I) 10.95; 77 ($M-C_6H_5^+$) 2.92 and 76 ($M-C_6H_4^+$) 5.5 [3]. After recrystallization, yellow crystals were harvested and dried in vacuo. $[Cu(CH_3COO)_2]\cdot H_2O$ (0.001 mol, 0.199 g) in methanol (50 ml) and *N*-(2-iodo)-naphthaldimine (0.002 mol, 0.744 g) 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, 0.609 g (65%) yields (Fig. 1). Found: C, 50.10; H, 2.81; N, 3.23, $C_{34}H_{22}N_2O_2I_2Cu$; C, 50.49; H, 2.72; N, 3.47%. Crystals suitable for X-ray diffraction were obtained by slow evaporation from a saturated ethanol solution.

2.3. X-ray structure determination

A crystal with dimensions of $0.10 \times 0.15 \times 0.05\ mm^3$ for **1** was mounted on a Rigaku AFC7-S diffractometer employing graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å) [4]. Experimental conditions of **1** are summarized in Table 1. Cell parameters were determined by the least-squares refinement on the setting angles of 25 reflections [$10.4° < \theta < 19.2°$] for **1** carefully centred on the diffractometer.

Table 1
Crystal and experimental data

Compound	$C_{34}H_{22}N_2O_2I_2Cu$
Color/shape	Black/prismatic
Formula weight	807.88
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell constants	$a = 8.229(2)$ Å $b = 15.840(4)$ Å $c = 11.389(3)$ Å $\beta = 104.49(2)°$
Cell volume	1437.3(6) $Å^3$
Formula units/unit cell	4
D_x	1.867 g cm^{-3}
μ (Mo K_α)	1.020 mm^{-1}
Diffractometer/scan	Rigaku AFC7-S/ω–2θ
λ (Mo K_α)	0.71073 Å
Crystal size	0.10 × 0.15 × 0.05 mm^3
T	293 K
Standard reflections	3
F (000)	782
Range of h, k, l	$0 \leq h \leq 9$ $0 \leq k \leq 18$ $-13 \leq l \leq 13$
Number of reflections measured	2812
Number of reflections used	2507
Number of parameters	185
R	0.053
R_w	0.112
Goodness-of-fit	1.025
$(\Delta/\sigma)_{max}$	0.012
$(\Delta/\rho)_{max}$	0.56 e $Å^{-3}$
$(\Delta/\rho)_{min}$	−0.40 e $Å^{-3}$

Table 2
Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	x	y	z	B_{eq} ($Å^2$)
Cu1	0.0000(0)	0.0000(0)	0.0000(0)	2.14(2)
I1	−0.2636(1)	−0.0540(2)	0.1906(1)	5.97(2)
O1	−0.1508(3)	−0.0033(9)	−0.1560(2)	3.15(4)
N1	−0.1268(2)	0.0953(1)	0.0484(1)	2.39(4)
C1	−0.2467(3)	0.0572(1)	−0.2095(2)	3.05(6)
C2	−0.3134(3)	0.0430(2)	−0.3377(2)	3.24(5)
C3	−0.4221(4)	0.1016(2)	−0.4052(3)	4.37(7)
C4	−0.4634(2)	0.1766(2)	−0.3548(2)	3.72(6)
C5	−0.5799(3)	0.2341(2)	−0.4262(2)	3.60(7)
C6	−0.6140(4)	0.3075(2)	−0.3825(3)	5.11(9)
C7	−0.5466(2)	0.3289(1)	−0.2638(2)	4.82(7)
C8	−0.4232(2)	0.2708(1)	−0.1846(2)	3.58(6)
C9	−0.3911(3)	0.1933(2)	−0.2324(2)	2.91(5)
C10	−0.2829(4)	0.1319(2)	−0.1594(3)	4.62(7)
C11	−0.2303(3)	0.1427(2)	−0.0302(2)	3.19(6)
C12	−0.1010(3)	0.1135(1)	0.1747(2)	2.70(5)
C13	−0.0162(5)	0.1976(3)	0.2205(3)	6.80(9)
C14	0.0169(3)	0.2055(2)	0.3412(3)	4.21(7)
C15	−0.0203(4)	0.1467(2)	0.4217(2)	5.51(9)
C16	−0.1006(3)	0.0749(2)	0.3765(3)	4.78(8)
C17	−0.1346(3)	0.0576(2)	0.2548(2)	3.14(5)

$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$.

Standard reflections (110, 200, 210) were measured every 150 reflections. A total of 2812 reflections was recorded, with indices of $h_{min} = 0$, $h_{max} = 9$, $k_{min} = 0$, $k_{max} = 18$, $l_{min} = -13$, $l_{max} = 13$. Data reduction and corrections for absorption and crystal decomposition (1.2%) were carried out using the TEXAN Single Crystal Structure Analysis Software [5]. The structure was solved by SHELXS-97 [6] and refined with SHELXL-97 [7]. 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. H atom displacement parameters were restricted to be 1.2 U_{eq} of the parent atom. Fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are given for in Table 2. Bond distances and bond angles for **1** are listed in Table 3. An ORTEP view of the molecular structure of **1** is given in Fig. 2 [8].

3. Results and discussion

3.1. Spectroscopic study

The IR spectrum of the *N*-(2-iodo)-naphthaldimine reveals a band at 3415 cm^{-1} due to ν(O–H) [9]. This band is absent in the title copper(II) complex **(1)**, indicating coordination through deprotonated phenolic OH group. The ν(C=N) band appears at 1602–1605 cm^{-1} in the metal complex as compared to that at 1624 cm^{-1} in Schiff base. This decrease (19–22 cm^{-1}) indicates the coordination of nitrogen of azomethine group with the metal ion. The strong ligand band at 1326 cm^{-1} appears at 1309 cm^{-1} in the complex, thus showing a shift towards lower regions by 17 cm^{-1}. This band is characteristic of ν(C–O) and its shift further supports the formation of the M–O bond [10–12]. The title compound **1** also show

Table 3
Bond lengths (Å), angles (°) and torsion angles (°)

Cu1–O1	1.896(2)	Cu1–N1	1.990(2)
I1–C17	2.097(2)	O1–C1	1.293(3)
N1–C11	1.306(3)	N1–C12	1.431(3)
C1–C2	1.443(3)	C1–C10	1.378(4)
C2–C3	1.382(4)	C3–C4	1.398(4)
C4–C5	1.421(4)	C4–C9	1.398(3)
C5–C6	1.322(5)	C6–C7	1.370(3)
C7–C8	1.495(3)	C8–C9	1.395(3)
C9–C10	1.434(4)	C10–C11	1.437(4)
C12–C13	1.534(5)	C12–C17	1.348(3)
C13–C14	1.339(5)	C14–C15	1.394(5)
C15–C16	1.351(5)	C16–C17	1.372(4)
O1–Cu1–N1	90.9(1)	Cu1–O1–C1	126.8(2)
Cu1–N1–C11	122.9(2)	Cu1–N1–C12	118.4(1)
C11–N1–C12	118.7(2)	O1–C1–C2	113.2(2)
O1–C1–C10	127.7(2)	C2–C1–C10	119.1(2)
C1–C2–C3	119.2(2)	C2–C3–C4	122.2(3)
C3–C4–C5	120.6(3)	C3–C4–C9	118.9(2)
C5–C4–C9	120.5(2)	C4–C5–C6	121.7(3)
C5–C6–C7	121.2(3)	C6–C7–C8	119.3(2)
C7–C8–C9	118.2(2)	C4–C9–C8	118.7(2)
C4–C9–C10	119.9(2)	C8–C9–C10	121.4(2)
C1–C10–C9	120.6(3)	C1–C10–C11	119.0(3)
C9–C10–C11	119.8(3)	N1–C11–C10	127.7(2)
N1–C12–C13	117.1(2)	N1–C12–C17	123.0(2)
C13–C12–C17	119.6(3)	C12–C13–C14	112.8(3)
C13–C14–C15	126.3(3)	C14–C15–C16	118.6(3)
C15–C16–C17	120.7(3)	I1–C17–C12	119.3(2)
I1–C17–C16	118.6(2)	C12–C17–C16	121.9(2)
N1–Cu1–O1–C1	22.1(2)	O1–Cu1–N1–C11	−18.6(2)
O1–Cu1–N1–C12	162.4(2)	Cu1–O1–C1–C2	164.9(2)
Cu1–O1–C1–C10	−11.9(4)	Cu1–N1–C11–C10	5.8(4)
C12–N1–C11–C10	−175.2(3)	Cu1–N1–C12–C13	113.4(2)
Cu1–N1–C12–C17	−60.8(3)	C11–N1–C12–C13	−65.7(3)
C11–N1–C12–C17	120.1(3)	O1–C1–C2–C3	178.0(2)
C10–C1–C2–C3	−4.9(4)	O1–C1–C10–C9	179.3(3)
O1–C1–C10–C11	−9.3(5)	C2–C1–C10–C9	2.6(4)
C2–C1–C10–C11	174.0(2)	C1–C2–C3–C4	3.3(4)
C2–C3–C4–C5	−178.0(3)	C2–C3–C4–C9	0.6(4)
C3–C4–C5–C6	−176.2(3)	C9–C4–C5–C6	5.2(4)
C3–C4–C9–C8	175.5(2)	C3–C4–C9–C10	−3.0(4)
C5–C4–C9–C8	−5.9(4)	C5–C4–C9–C10	175.7(3)
C4–C5–C6–C7	−4.4(5)	C5–C6–C7–C8	4.3(4)
C6–C7–C8–C9	−5.0(3)	C7–C8–C9–C4	5.8(3)
C7–C8–C9–C10	−175.8(2)	C4–C9–C10–C1	1.3(4)
C4–C9–C10–C11	−170.0(3)	C8–C9–C10–C1	−177.1(3)
C8–C9–C10–C11	11.6(4)	C1–C10–C11–N1	12.0(5)
C9–C10–C11–N1	−176.6(3)	N1–C12–C13–C14	−174.1(3)
C17–C12–C13–C14	0.4(5)	N1–C12–C17–I1	−9.6(3)
N1–C12–C17–C16	176.5(2)	C13–C12–C17–I1	176.3(2)
C13–C12–C17–C16	2.5(4)	C12–C13–C14–C15	−0.8(5)
C13–C14–C15–C16	−1.5(5)	C14–C15–C16–C17	4.4(5)
C15–C16–C17–I1	−178.9(3)	C15–C16–C17–C12	−4.9(5)

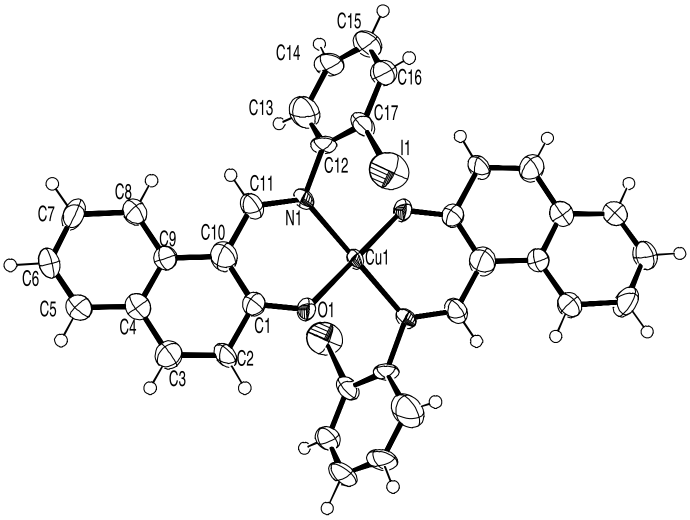

Fig. 2. The molecular structure of the title compound **1**. The displacement ellipsoids are plotted at the 50% probability level [8].

some new bands at 540–500 and 390–340 cm^{-1} which can be assigned to ν(Cu–N) and ν(Cu–O), respectively [13].

3.2. Crystallographic study

Because of their preparative accessibility and structural variability, a great number of Schiff base complexes of copper have been the subject of extensive studies [2]. Despite this, there are a few reported X-ray crystal structures of naphthalenic Schiff base-copper compounds [14,15].

Table 4
Bond lengths (Å) in some similar copper(II) complexes

	C–O	C=N	Cu–N	Cu–O
I[a]	1.293(6)	1.295(6)	1.990(4)	1.880(4)
II[b]	1.318(6)	1.291(6)	2.019(4)	1.879(4)
III[c]	1.303(5)	1.288(5)	1.965(3)	1.889(3)
IV[d]	1.323(4)	1.279(4)	1.939(3)	1.883(2)
V[e]	1.296(7)	1.296(6)	1.980(5)	1.878(4)
V[f]	1.293(3)	1.306(3)	1.990(2)	1.896(2)

[a] Bis[*N*-(2-bromo-4-methylphenyl)-naphthaldiminato]copper (II) [16].

[b] Bis[*N*-(4-bromophenyl)-salicylaldimine]copper (II) [17].

[c] {2-[2-(Salicylideneaminometyl)phenyl-iminometyl]phenolato(2-)-*N*,*N*′,O,O′}-copper (II) [18].

[d] [*N*,*N*′-Bis(salicylidene)-1,2-diimino-2-methylpropane]copper(II) [19].

[e] Bis[2-[*N*-(2-chlorophenyl)formimidayl]-1-naphtholato]-(6Cl)copper(II) [20].

[f] Present work.

The title compound bis[*N*-(2-iodo)-naphthaldiminato]copper(II), $[Cu(C_{17}H_{11}NOI)_2]$ has crystallographic inversion symmetry. The coordination of the copper(II) ion is necessarily planar by symmetry. A strictly planar or slightly distorted *trans* configuration is a characteristic for transition metal complexes of copper(II) with a CuN_2O_2 coordination sphere. In the title compound, the copper(II) ion is bonded to the O and N donor atoms of the two ligand molecules in a *trans* arrangement. The Cu–N and Cu–O distances are 1.990(2) and 1.896(2) Å, respectively. The O–Cu–N angle is 90.9(1)°. The Cu–N distances range from 1.930 to 2.020 Å, while the Cu–O distances have values between 1.870 and 1.920 Å in copper complexes [16–20]. The Cu–N and Cu–O values in the title compound agree with those in other complexes. In Table 4 the bond lengths of several complexes of N-substituted salicylaldimines and naphthaldimines are compared with our values. The copper(II) ion is in a pseudo-octahedral environment if iodine is included in the description. The non-bonded Cu···I distance is 3.536(1) Å. The title molecule is not planar; the copper(II) ion lies 0.157(1) Å below the plane formed by the Cu1, O1, C10, C11 and N1 atoms. The two Schiff base moieties, **A** (O1, C1–C11) and **B** (N1, C12–C17, I1), are inclined at an angle of 56.9(3)° with respect to one another, which is mainly the twist about N1–C12 [66.5(2)°].

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···C11 and Cu1···C10 with values of 3.746(3) and 3.312(3) Å, respectively.

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