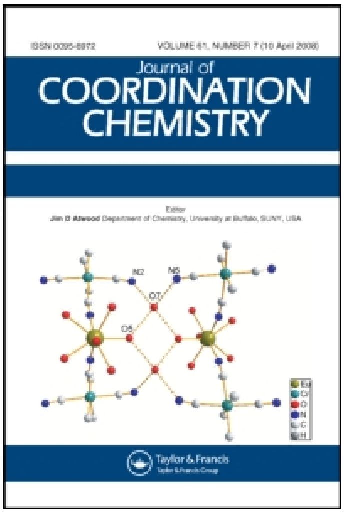

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The synthesis, electrochemical properties and structural characterization of *bis*(*N*-(4-dimethylaminophenyl)-3,5-di-*tert*-butylsalicylaldiminato)copper(II)

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A Cu(II) complex of a Schiff base obtained by the condensation of *N*,*N*-dimethyl-1,4-phenylenediamine with 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde has been synthesized and characterized. The structure of the complex was determined by single-crystal X-ray methods. The four-coordinate Cu(II) ion possesses a compressed tetrahedral coordination environment.

Keywords: Schiff base; Salicylaldimine; Copper(II) complex; Crystal structure; Electrochemistry

1. Introduction

Considerable attention has been paid to the chemistry of metal complexes of Schiff bases containing nitrogen and other donors [1–4]. This may be attributed to their stability, biochemical and analytical uses, and potential applications in fields such as oxidation catalysis, electrochemical and molecular materials with nonlinear optical properties, and therapeutic applications [5–9]. It is known that some Schiff base complexes show antifungal activity, which is increased by the presence of hydroxy groups in the ligand. Thus, it was thought worthwhile to synthesize complexes of Schiff bases with hydroxy substituents on phenyl and heterocyclic rings [10, 11]. Intra-molecular electron transfer is a fundamental chemical phenomenon and relates specifically to redox processes which occur in both natural and synthetic electron transfer systems [12]. The ability of metal ions to control the oxidation potentials

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of organic molecules by complexation has a significant role in biological electron transfer processes, molecular electronics and catalysis [13]. Furthermore, Schiff base complexes have been used as models for the metal sites in metallo-proteins and -enzymes [14–18].

Herein, we report the synthesis and structural characterization of a Cu(II) Schiff base complex, bis(*N*-(4-dimethylaminophenyl)-3,5-di-*tert*-butylsalicylaldiminato)-copper(II). In order to obtain more detailed information about the coordination mode of the ligands, a single-crystal X-ray determination has been carried out for the complex.

2. Experimental

2.1. *Materials and methods*

All solvents, *N*,*N*-dimethyl-1,4-phenylenediamine and $Cu(OAc)_2 \cdot H_2O$ (reagent grade, Aldrich) were used without further purification. 3,5-Di-*tert*-butylsalicylaldehyde was prepared from commercially available 2,4-di-*tert*-butylphenol according to a literature procedure [19]. NMR spectra were recorded at 297 K on Varian spectrometer at 400 MHz (^{1}H) and 100.56 MHz (^{13}C). Elemental analyses were carried out by the analytical service of TÜBİTAK. Magnetic susceptibilities were determined on a Sherwood Scientific MK1 balance at 20°C using $Hg[Co(SCN)_4]$ as calibrant; diamagnetic corrections were calculated from Pascal's constants [20]. Electronic spectra were recorded on a Schimadzu 1601 PC spectrophotometer. Voltammetric experiments were performed using an Metrohm 694 VA apparatus. The three electrode system comprised a 2 mm Pt disc working electrode, an Ag/AgCl reference electrode and a Pt wire counter electrode. The working electrode was polished with 0.05 µm alumina prior to each experiment. Throughout the experiment oxygen-free nitrogen was bubbled through the solution. Voltammetric experiments were performed at room temperature.

2.2. N-*(4-dimethylaminophenyl)-3,5-di*-tert-*butylsalicylaldimine*

The ligand was synthesized by reaction of 5.0 mmol of 3,5-di-*tert*-butyl-2-hydroxybenzaldeyhde in 20 cm^3 of absolute ethanol and 5.0 mmol of *N*,*N*-dimethyl-1,4-phenylenediamine in 10 cm^3 of ethanol. The mixture was refluxed for 3 h, then cooled to room temperature. The orange solid was filtered off and recrystallized from CH_2Cl_2/EtOH (1 : 3) and dried under vacuum. Yield: 1.52 g (86%), m.p.: 102°C. Anal. Calcd for $C_{23}H_{32}N_2O$ (%): C, 78.36; H, 9.15; N, 7.95. Found: C, 79.74; H, 8.65; N, 8.10.

^{1}H NMR ($CDCl_3$, δ): 1.37 (s, 9H, C_6H_2–5–$C(CH_3)_3$); 1.52 (s, 9H, C_6H_2–3–$C(CH_3)_3$); 3.00 (s, 6H, N–CH_3); 6.77 (d, $J = 9.2$ Hz, 2H, N–C_6H_4); 7.22 (d, $J = 2.4$ Hz, 1H, HC–C_6H_2); 7.30 (d, $J = 4.8$ Hz, 2H, N–C_6H_4); 7.43 (d, $J = 2.0$ Hz, 1H, HC–C_6H_2); 8.66 (s, 1H, CH=N); 14.13 (s, 1H, C_6H_2–2–OH). ^{13}C NMR ($CDCl_3$, 100.56 MHz, δ): 158.23 (*C*H=N); 159.42; 149.89; 140.50; 137.87; 136.96; 127.34; 126.46; 122.34; 119.04; 113.15 (C_{aren}); 40.91 (N–CH_3); 35.33 and 34.43 ($C(CH_3)_3$); 31.80 and 29.76 ($C(CH_3)_3$).

2.3. Bis(N-(4-dimethylaminophenyl)-3,5-di-tert-butylsalicylaldiminato)copper(II)

To a solution of the ligand (705 mg, 2.0 mmol) in 20 cm^3 of hot methanol was added a solution of $Cu(OAc)_2 \cdot H_2O$ (200 mg, 1.0 mmol) dissolved in 20 cm^3 of hot methanol and the resulting solution was refluxed for 4 h. Volume was reduced to one half of the original and the solution cooled to 20°C to obtain a brown precipitate, which was filtered, washed with methanol, recrystallized from CH_2Cl_2/MeOH and dried under vacuum. Yield: 575 mg (75%); m.p.: 298°C; μ_{eff} 1.68 BM. Anal. Calcd for $C_{46}H_{62}CuN_4O_2$ (%): C, 72.07; H, 8.15; N, 7.31. Found: C, 72.28; H, 8.34; N, 7.25.

2.4. Crystal structure

A suitable crystal of the complex of dimensions of $0.42 \times 0.26 \times 0.17\ mm^3$ was mounted on a STOE IPDS 2 diffractometer employing graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). Crystallographic data were recorded at room temperature. A summary of crystallographic data and details of the structure refinement is given in table 1. Cell parameters were determined using X-AREA software [21] for setting angles of 60,178 reflections [$1.82° < \theta < 27.19°$]. Absorption correction was achieved by the integration method via X-RED software [21]. A total of 49,548 reflections was recorded, with $-23 \leq h \leq 23$, $-19 \leq k \leq 19$, $0.23 \leq l \leq 23$. The structure was solved by SHELXS97 [22] and refined by full-matrix least-square techniques on F^2 using the SHELXL97 program [23]. All non-hydrogen atoms were refined anisotropically and all

Table 1. Crystal data and refinement details for the complex.

Chemical formula	$C_{46}H_{62}CuN_4O_2$
Colour/shape	Red/Prismatic
Formula weight	766.55
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell constants (Å, °)	$a = 18.4343(10)$
	$b = 15.0510(14)$
	$c = 18.4747(10)$
	$\beta = 114.845(4)$
V (Å^3)	4651.5(6)
Z (g cm^{-3})	4
Density	1.095
$F(000)$	1644
μ (Mo-Kα) (mm^{-1})	0.507
λ (Mo-Kα) (Å)	0.71073
Crystal size (mm^3)	$0.42 \times 0.26 \times 0.17$
T_{min}/T_{max}	0.854/0.917
Temperature (K)	293(2)
Unique reflections	8176
Independent/observed reflections	8176/3554
Data/restraints/parameters	8176/2/469
Final R indices [$I > 2\sigma(I)$]	$R = 0.068$; $R_w = 0.171$
R indices (all data)	$R = 0.180$; $R_w = 0.139$
Goodness-of-fit on F^2	0.903
Highest peak (e Å^{-3})	0.57
Deepest hole (e Å^{-3})	−0.43
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0790P)^2]$ where $P = [F_o^2 + F_c^2]/3$

hydrogen atoms except for H1 and H2, which are linked to C1 and C2 atoms, were refined with a riding model.

3. Results and discussion

3.1. *Spectroscopic and electrochemical characterization*

In the ^{1}H NMR spectrum of the ligand, chemical shifts of Ar–OH and CH=N protons are observed at 14.13 and 8.66 ppm, respectively. A strong band is observed in IR spectra at 1618 $\mathrm{cm^{-1}}$, attributed to C=N stretching, shifts to ca 1615 $\mathrm{cm^{-1}}$ in spectra of the Cu(II) complex, indicating coordination of the azomethine nitrogen atom to copper [24, 25]. The room temperature magnetic moment of the complex (1.68 BM) is quite low and can be attributed to the compressed tetrahedral *trans*-[$\mathrm{CuN_2O_2}$] coordination environment. In the electronic spectrum of the Schiff-base, recorded in chloroform solution, aromatic bands at 240–272 nm are attributed to a benzene $\pi \rightarrow \pi^*$ transition. The band at 390 nm is assigned to the imino $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transition [26]. The electronic spectrum of the complex was recorded in chloroform. Bands at 410–700 nm can be assigned to d → d or charge-transfer transitions [27].

Cyclic voltammetric studies were performed in DMSO under anaerobic conditions at a scan rate of 0.1 $\mathrm{V\,s^{-1}}$ over the potential range from −0.8 to +1.0 V *versus* Ag/AgCl. The ligand exhibits a *quasi*-reversible reduction peak at $Ep_\mathrm{c} = -0.31$ V and an oxidation peak at $Ep_\mathrm{a} = +0.76$ V, assigned to the phenolate/phenoxyl radical couple. The cyclic voltammogram of Cu(II) complex **2** in DMSO exhibits a reduction peak at $Ep_\mathrm{c} = +0.09$ V and an oxidation peak at $Ep_\mathrm{a} = +0.63$ V (peak separation $\Delta E_\mathrm{p} = 0.54$ V). The ratio of anodic to cathodic peak current ($I_\mathrm{pa}/I_\mathrm{pc}$) decreased at faster scan rates and the separation between peak potentials gradually increased with increasing scan rates. This is characteristic of a *quasi*-reversible one-electron process corresponding to the copper(II)/copper(I) couple [28].

3.2. *X-ray crystallography*

An ORTEP [29] view of the complex is shown in figure 1. The asymmetric unit consists of a single mononuclear complex. Selected bond distances, bond angles and torsion angles for the complex are given in table 2.

Some Cu(II) and Ni(II) complexes incorporating Schiff base ligands [30] have been known to exhibit flexibility from a square planar to a tetrahedral coordination environment by introducing various substituents, and show structural phase transitions on heating [31–36]. The structure of the present complex shows that the Cu(II) centre is coordinated to four atoms in a compressed tetrahedral *trans*-[$\mathrm{CuN_2O_2}$] coordination environment; this can be ascribed to the bulky substituents [*N*-(4-dimethylaminophenyl] of the ligands. Copper is bonded to two phenolate oxygen atoms (O1 and O2) and the two imino nitrogen atoms (N1 and N2). Cu–O1 and Cu–O2 distances are 1.875(4) and 1.882(4) Å, respectively, and are slightly different from the corresponding values (1.887(2) and 1.884(2) Å) in [37]. Cu–N1 and Cu–N2 bond lengths are 1.959(5) and 1.977(5) Å. The O1–Cu1–O2 bond angle is 144.2(2)° and the N1–Cu1–N2 bond angle 148.4(2)°, showing an angular deviation of 31.6° from an exact *trans* coordination,

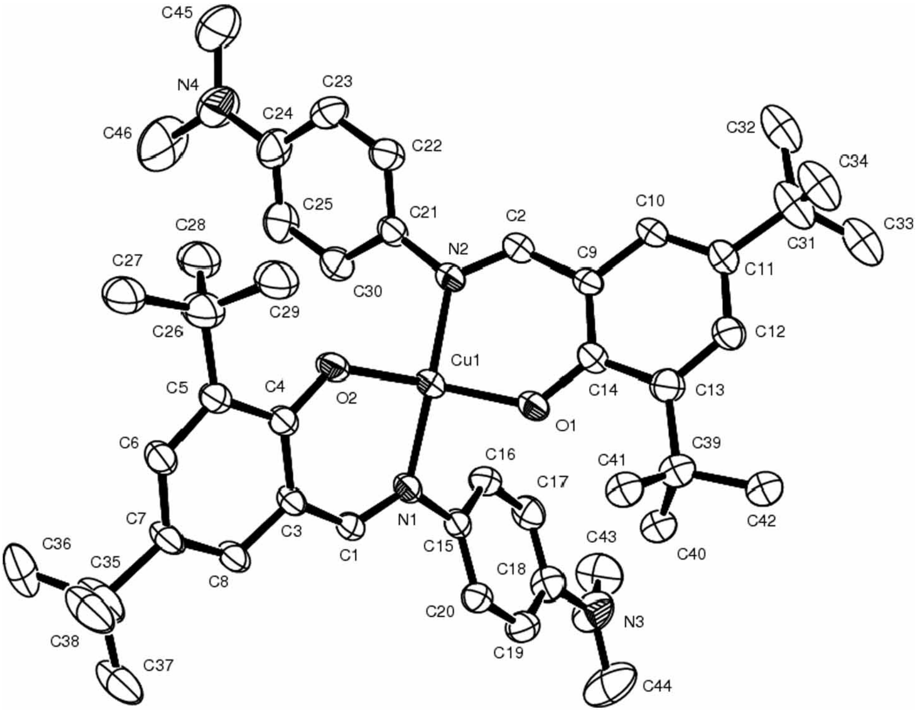

Figure 1. An ORTEP view of the complex with displacement ellipsoids plotted at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected geometrical parameters (Å, °) for the complex.

Bond lengths			
Cu1–O1	1.875(4)	Cu1–O2	1.882(4)
Cu1–N1	1.959(5)	Cu1–N2	1.977(5)
C1–N1	1.296(6)	C2–N2	1.314(6)
N1–C15	1.435(7)	N2–C21	1.418(7)
C3–C1	1.415(7)	C9–C2	1.426(8)
O1–C14	1.307(6)	O2–C4	1.318(6)
C18–N3	1.406(9)	N3–C44	1.425(10)
N3–C43	1.428(9)	C24–N4	1.390(9)
N4–C45	1.439(11)	N4–C46	1.426(11)
Bond angles			
O1–Cu1–O2	144.2(2)	O1–Cu1–N1	93.7(2)
N1–Cu1–O2	93.6(2)	N2–Cu1–O1	94.4(2)
O2–Cu1–N2	97.5(2)	N1–Cu1–N2	148.4(2)
Torsion angles			
O1–Cu1–O2–C4	–78.4(5)	N1–Cu1–O2–C4	22.9(4)
N2–Cu1–O2–C4	173.2(4)	O2–Cu1–O1–C14	−98.1(5)
N1–Cu1–O1–C14	160.6(5)	N2–Cu1–O1–C14	11.2(5)
O1–Cu1–N1–C1	128.5(4)	O2–Cu1–N1–C1	−16.4(4)
N2–Cu1–N1–C1	−127.0(5)	O1–Cu1–N1–C15	−47.3(4)
O2–Cu1–N1–C15	167.9(4)	N2–Cu1–N1–C15	57.2(5)
O1–Cu1–N2–C2	−4.0(5)	O2–Cu1–N2–C2	142.1(4)
N1–Cu1–N2–C2	−108.3(5)	O1–Cu1–N2–C21	177.4(4)
N1–Cu1–N2–C21	73.1(6)	Cu1–O2–C4–C3	−17.0(7)
Cu1–O1–C14–C9	−11.5(8)	Cu1–N1–C1–C3	5.3(8)

whereas *cis* N1–Cu1–O2 and N2–Cu1–O1 angles are 93.6(2)° and 94.4(2)°. C1–N1 and C2–N2 imine bond lengths are 1.296(6) and 1.314(6) Å and are similar to those found in related complexes [38–40]. The angle between the planes formed by Cu, O1, N2, C2, C9, C14 and Cu, O2, N1, C1, C3, C4 atom groups is 52.2(2)° and the weighted average ring bond distances of these six membered rings are 1.708 and 1.669 Å, respectively. In addition, both average ring planes are separately adapted to nearly planar conformation, with O1 and O2 atoms having maximum deviations of 0.072(4) and −0.139(4) Å, respectively.

Crystal packing, shown in figure 2, consists of neutral, discrete mononuclear molecules. In the classical sense, intramolecular and intermolecular hydrogen bonds could not be detectable within the sums of van der Waals radii [41] and crystal packing is dominated by weak van der Waals forces. However, some intramolecular interactions which can be regarded as weak hydrogen bonds (table 3) are observed in the structure. These contribute to the stability of the crystal structure and are presumably responsible for the nature of the coordination environment.

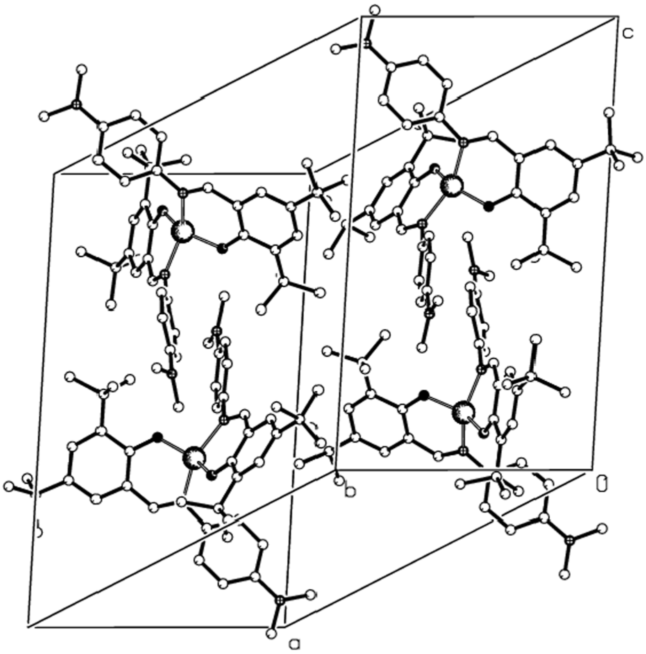

Figure 2. Crystal packing of the complex.

Table 3. Weak hydrogen bond geometries (Å, °) for the complex.

D–H···A	D–H	H···A	D···A	∠D–H···A
C28–H28C···O2	0.96	2.32	2.960(9)	124
C29–H29B···O2	0.96	2.30	2.953(10)	124
C40–H40C···O1	0.96	2.31	2.954(10)	124
C41–H41C···O1	0.96	2.36	2.997(8)	123

Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 284751. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223 336-033; E-mail: deposit@ccdc.cam.ac.uk).

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