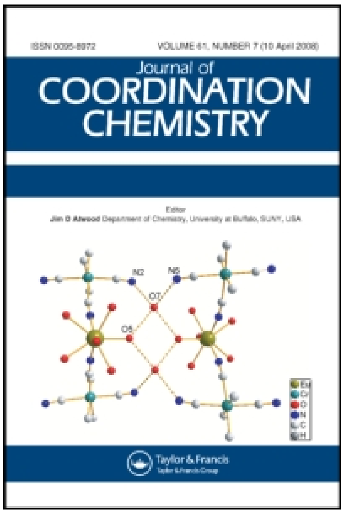

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Copper(II) complexes with tetradentate imine-phenols: synthesis, characterization and molecular structures

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Copper(II) complexes with tetradentate imine-phenols: synthesis, characterization and molecular structures

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Four copper(II) complexes of *N*,*N*′-bis(4-methoxysalicylidene)-1,2-diimino ethanemonohydrate (**1**), *N*,*N*′-bis(5-methoxysalicylidene)-1,2-diiminoethane (**2**), *N*,*N*′-bis(3-methoxysalicylidene)-2,2-dimethyl-1,3-diiminopropane (**3**) and *N*,*N*′-bis(4-methoxysalicylidene)-2,2-dimethyl-1,3-diiminopropane (**4**) have been prepared and characterized spectroscopically. The solid-state structures of the complexes were established by X-ray crystallography. Complexes **2**, **3** and **4** contain Cu(II) in a tetrahedrally distorted square planar environment with two phenolate O atoms being deprotonated. Complex **1** is five-coordinate and displays color isomerism.

Keywords: Copper; Imine-phenols; Molecular structures

1. Introduction

The role played by copper ions in the active sites of a large number of metalloproteins has stimulated efforts to characterize copper complexes as models for a better understanding of biological systems [1–3]. Transition metal complexes coordinated to tetradentate Schiff base ligands have been studied extensively, mainly because of their ease of preparation, flexibility and versatility in terms of chemical properties, geometry, coordination sites and ease of substitution. Among them, metal complexes of *N*,*N*′-bis(salicylidene)-1,2-diiminoethane (salen) and derivatives have been widely investigated for their color isomerism [4, 5], conformational influences [6–8] and oxidative catalysis [9–11]; copper complexes containing chelating diimine ligands find

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increasing use as catalysts in synthetic organic reactions [12, 13]. Considerable attention has also been directed towards the synthesis of copper(II) chelates in the field of nuclear medicine, following the development of the ^{62}Zn/^{62}Cu radionuclide generator, which has realized the potential of copper-labeled radiopharmaceutical imaging with positron emission tomography [14–16]. With this in mind, we have synthesized some related copper(II) complexes of tetradentate Schiff bases for structural studies [17–20]. We report here the synthesis and structural characterization by X-ray crystallography of four copper(II) complexes, Cu(II)-*N*,*N*′-bis(4-methoxysalicylidene)-1,2-diiminoethane 1-water (**1**), Cu(II)-*N*,*N*′-bis(5-methoxysalicylidene)-1,2-diiminoethane 1.5-water (**2**), Cu(II)-*N*,*N*′-bis(3-methoxysalicylidene)-2,2-dimethyl-1,3-diiminopropane 2-water (**3**) and Cu(II)-*N*,*N*′-bis(4-methoxysalicylidene)-2,2-dimethyl-1,3-diiminopropane 1-ethanol (**4**).

2. Experimental

All reagents were obtained from commercial sources and used without further purification. The alkylene diamines, copper(II) nitrate trihydrate, 3-, 4- and 5-methoxysalicylaldehyde were obtained from Aldrich.

Electronic spectra were recorded using a Hewlett Packard HP8452A diode array spectrometer, ^{1}H NMR spectra on a Bruker AC300 spectrometer and IR spectra (KBr pellets) using a Jasco FT/IR 300E spectrophotometer. Magnetic susceptibilities were measured on a Quantum Design MPMS5 magnetometer. Microanalyses were performed using a Perkin Elmer 2400 CHN elemental analyzer and copper analysis was carried out by iodometric titration [21]. Molar conductances (Λ_M) were measured with a Systronics 306 conductivity meter using ca 10^{-3} M solutions in MeOH.

2.1. *Preparation of ligands*

Schiff bases were prepared by condensation of methoxy-substituted salicylaldehydes and diamines following the procedure reported previously [17–20]. The reaction mixture in ethanol was stirred for 6 h and then placed in a freezer for 24 h. Yellow solids were collected by filtration and washed with cold ethanol. Purification was by recrystallization from absolute ethanol. Melting points, elemental analysis and ^{1}H NMR spectra were examined for chemical purity.

2.2. *Preparation of Cu(II) complexes*

All complexes were prepared following an identical procedure. To an ethanolic solution of the ligand, a solution of copper(II) nitrate trihydrate in a 1 : 1 mol ratio in the same solvent was added dropwise. The mixture was stirred at 333 K for 1.5 h. The solution was filtered and kept in a beaker at 277 K for crystallization. Green–blue crystals appeared after 3–4 days and were collected by filtration. Single crystals suitable for X-ray analyses were obtained from 95% ethanol on slow evaporation. Yields varied in the range 80–85%. Anal. Calcd for **1**(%): C, 52.95; H, 4.90; N, 6.86; Cu, 15.57. Found: C, 52.85; H, 4.97; N, 6.78; Cu, 15.42. Anal. Calcd for **2**(%): C, 51.81; H, 5.04; N, 6.72; Cu, 15.23. Found: C, 51.91; H, 5.11; N, 6.77; Cu, 15.09. Anal. Calcd for **3**(%): C, 53.85; H, 5.98; N, 5.98; Cu, 13.57. Found: C, 53.65; H, 6.08;

N, 6.05, Cu, 13.29. Anal. Calcd for **4**(%): C, 52.72; H, 6.28; N, 5.86; Cu, 13.28. Found: C, 52.61; H, 6.21; N, 5.92; Cu, 13.12.

2.3. *X-ray diffraction*

X-ray diffraction data were collected on a Siemens SMART CCD diffractometer equipped with a normal focus, 3 kW sealed X-ray source. Intensity data were collected in 1271 frames with increasing ω (0.3°/frame) and with a scan speed of 10.00 s/frame [22]. Unit cell dimensions were determined by a least-squares fit of 3068 reflections for **1**, 4722 reflections for **2**, 4601 reflections for **3** and 2746 reflections for **4**, with $5^\circ < 2\theta < 50^\circ$. Absorption correction was based on 4555 (for **1**), 4409 (for **2**), 4641 (for **3**) and 3391 (for **4**) symmetry-equivalent reflections using the SHELXTL-PC program package. The structures were solved by direct methods and refined on F^2 by a full-matrix least-squares procedure using SHELXTL-PLUS [23]. Scattering factors and anomalous dispersion correction terms were taken from *International Tables for X-ray Crystallography*. The quantity minimized was $\sum w(kF_o - F_c)^2$, with $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$. All H atoms included in the refinement were placed in idealized positions (C–H = 0.96 Å, and H–C–H = 109.4°) with U_{iso} constrained to 0.08 Å^2 after the non-H atoms were refined anisotropically.

3. Results and discussion

All of the Schiff bases act as tetradentate dibasic ONNO ligands and all of the complexes are soluble in common organic solvents. Conductivity values were in the range 9–20 $\Lambda_o\,\mathrm{mol^{-1}\,cm^{-1}}$, indicating nonelectrolytic behavior in solution. Magnetic moments at 298 K in the solid state are given in table 1, excluding diamagnetic corrections, and μ_{eff} values were calculated using the Curie equation [$\mu_{eff} = 2.828(\chi_M T)^{1/2}$]. Values are normal as found for monomeric copper(II) complexes [24, 25].

3.1. *Structures*

Perspective drawings of **1**–**4** with atom numbering schemes are shown in figures 1–4, respectively. Experimental data are summarized in table 1. Selected bond lengths and angles are listed in table 2.

Complex **1** is centrosymmetric, the inversion center being located at the midpoint of the C1–C1a bond. The Cu(II) atom is five-coordinate and exhibits square pyramidal stereochemistry with two *cis* O and two *cis* N atoms forming the square plane. The structure of **1** is regular, as indicated by the trigonality index [26] τ of 0.0 [$\tau = (\beta - \alpha)/60$ where $\alpha = \beta =$ O1–Cu1–N1a = N1–Cu1–O1a = 168.3(2)°]. Although the base of the pyramid is planar, the bond angles deviate from the ideal value of 90° (table 2). The apical position is occupied by a water O atom. The Cu$\cdots$O′ apical bond [2.294(4) Å] is somewhat smaller than the reported value of 2.53 Å for Cu(II)-*NN*′-disalicylidenepropane-1,2-diaminecopper monohydrate [27]. The Cu(II) atom is displaced by 0.150 Å from the best plane of the N_2O_2 atoms towards water. These donor atoms deviate by ±0.375 Å from the least-squares basal plane. Ethylenediamine carbons C1 and C1a are displaced by 0.329 Å in opposite directions from the CuNN′ plane. The dihedral angle between the two CuON planes is 15.8°

Table 1. Summary of crystal data, data collection and structure refinement parameters.

	1	**2**	**3**	**4**
Chemical formula	$C_{18}H_{18}CuN_2O_4 \cdot H_2O$	$C_{18}H_{18}CuN_2O_4 \cdot 1.5H_2O$	$C_{21}H_{24}CuN_2O_4 \cdot 2H_2O$	$C_{21}H_{24}CuN_2O_4 \cdot C_2H_5OH$
Formula weight	407.9	416.9	468.0	478.0
Space group	*Pnma*	$C2/c$	$C2/c$	$P2_1/c$
a (Å)	8.7800(2)	21.3705(8)	23.7471(7)	9.6727(3)
b (Å)	27.0725(3)	8.3355(3)	9.5046(3)	17.4644(6)
c (Å)	7.4801(2)	21.5012(8)	21.0366(6)	13.8572(2)
β (°)		111.534(1)	112.896(1)	91.801(2)
V (Å^3)	1778.0(6)	3562.7(10)	4374.0(11)	2339.7(6)
Z	4	8	8	4
T (K)	293(2)	293(2)	293(2)	293(2)
D_{calc} (Mg m^{-3})	1.524	1.555	1.421	1.357
μ (mm^{-1})	1.260	1.262	1.038	0.968
$F(000)$	836	1728	1960	980
Trans. (min, max)	0.655, 0.893	0.711, 0.928	0.702, 0.928	0.726, 0.962
2θ range (°)	2.5–57.5	2.5–57.1	2.5–57.3	2.5–57.7
No. measured ref.	6390	7842	10 088	6491
No. unique ref.	2195	4204	5131	5523
No. obs. ref.	1080 [$>3\sigma(I)$]	2522 [$>3\sigma(I)$]	2543 [$>3\sigma(I)$]	1697 [$>3\sigma(I)$]
R, R_w	0.0468, 0.0387	0.0378, 0.0417	0.0505, 0.0516	0.0644, 0.0645
GOF	1.08	1.16	0.97	1.62

$R = [\sum ||F_o| - |F_c|| / \sum |F_o|]$. $R_w = [\sum \omega(|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2}$.
$\mathrm{GOF} = [\sum \omega(|F_o| - |F_c|)^2 / (N_o - N_p)]^{1/2}$.

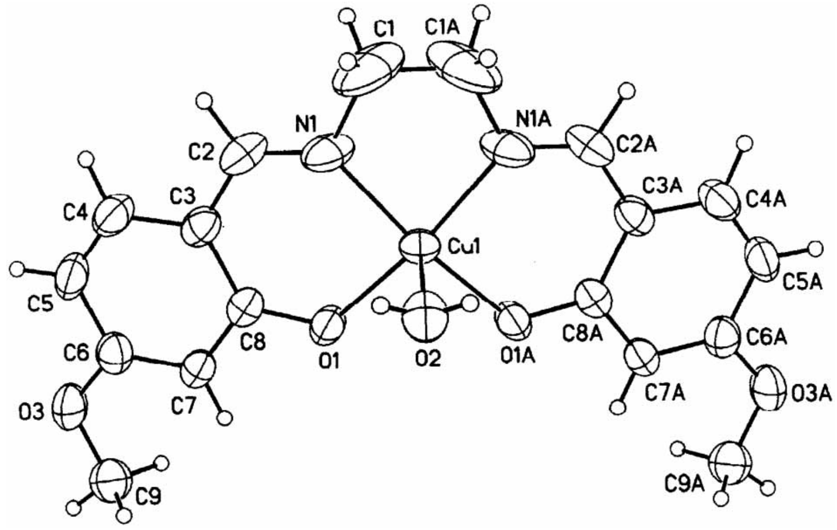

Figure 1. Structure and atom labeling scheme for **1**.

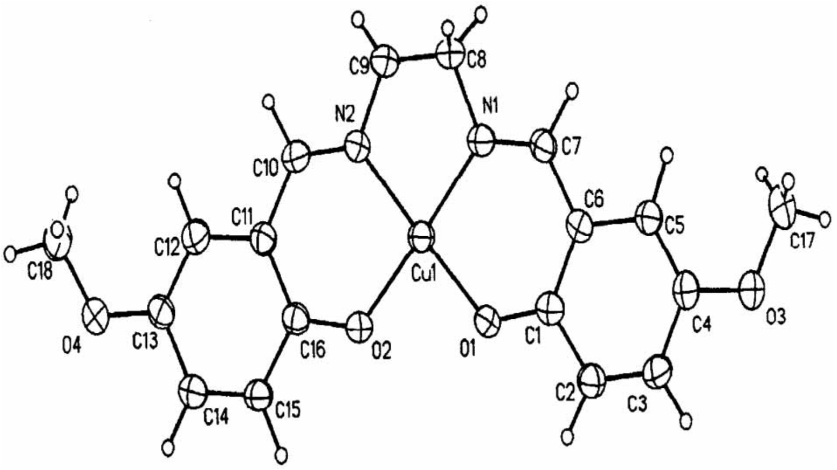

Figure 2. Structure and atom labeling scheme for **2**.

and the two aromatic planes make a dihedral angle of 34.5°. The water molecule is hydrogen bonded to one of the coordinated O atoms of a neighboring molecule: $O1 \cdots O2' = 2.739$ Å.

In complex **2**, the Cu(II) atom is four-coordinated by an N_2O_2 donor set from the imine-phenol with the two phenol O atoms being deprotonated. The shortest intermolecular distance involving the Cu(II) atom is 3.350 Å to C6′, so the possibility of dimerization is excluded. The mononuclear complex is different to the five-coordinate dimer of an analog, Cu-(5-MeO-salen), reported in the literature for the same ligand [28]. Hydrogen bonding to a ligand oxygen in **2** seems to decrease the ability of the copper atom to accommodate a fifth ligand as in Cu-salen [29]. The displacement

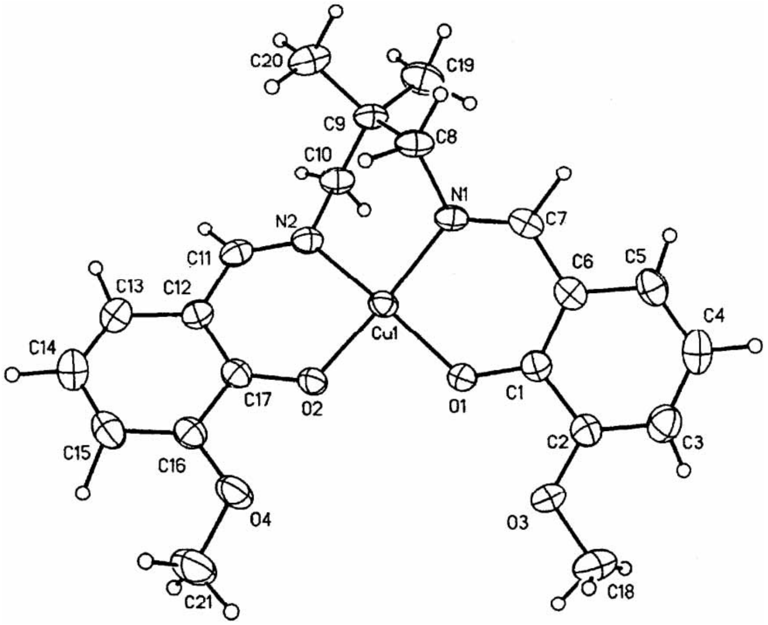

Figure 3. Structure and atom labeling scheme for **3**.

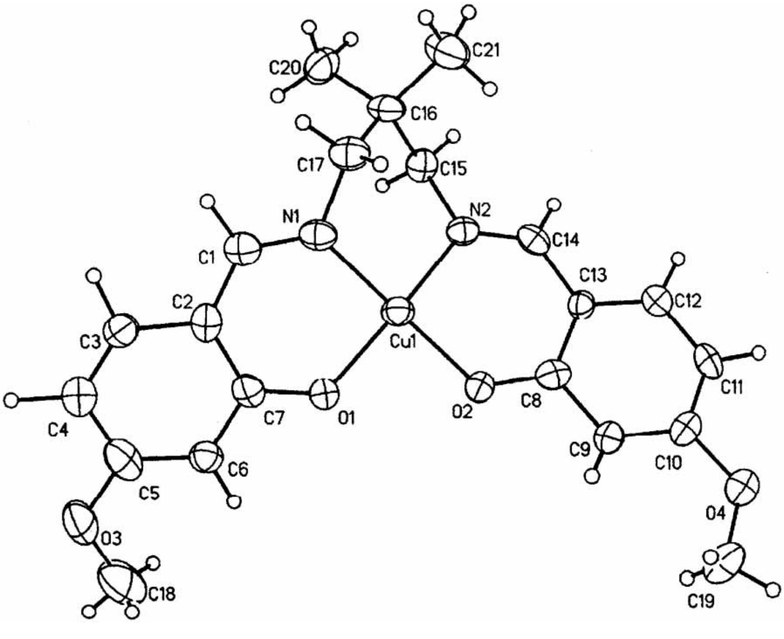

Figure 4. Structure and atom labeling scheme for **4**.

of the Cu(II) atom from the N_2O_2 plane is 0.030 Å and the N_2O_2 donor atoms deviate by ±0.072 Å from the plane. Ethylenediamine carbons C8 and C9 are displaced by 0.205 and 0.258 Å, respectively, in opposite directions from the CuNN′ plane. Both dihedral angles between the two CuON planes and between the two aromatic

Table 2. Selected bond lengths (Å) and angles (°).

1			
Cu1–O1	1.943(3)	Cu1–O2	2.294(4)
Cu1–N1	1.957(4)	Cu1–O1a	1.943(3)
Cu1–N1a	1.957(4)	O1–C8	1.299(5)
O3–C6	1.361(6)	O3–C9	1.428(6)
N1–C1	1.473(8)	N1–C2	1.271(7)
C1–C1a	1.331(15)		
O1–Cu1–O2	94.1(1)	O1–Cu1–N1	91.3(1)
O2–Cu1–N1	97.1(1)	O1–Cu1–O1a	91.5(2)
O2–Cu1–O1a	94.1(1)	N1–Cu1–O1a	168.3(2)
O1–Cu1–N1a	168.3(2)	O2–Cu1–N1a	97.1(1)
N1–Cu1–N1a	83.7(3)	O1a–Cu1–N1a	91.3(1)
Cu1–O1–C8	127.9(3)	Cu1–N1–C1	111.1(4)
Cu1–N1–C2	127.2(3)		
2			
Cu1–O1	1.906(2)	Cu1–O2	1.907(2)
Cu1–N1	1.936(3)	Cu1–N2	1.940(3)
O1–C1	1.325(5)	O2–C16	1.323(5)
O3–C4	1.389(5)	O3–C17	1.435(4)
O4–C13	1.390(5)	O4–C18	1.421(4)
N1–C7	1.290(5)	N1–C8	1.480(4)
N2–C9	1.479(4)	N2–C10	1.287(5)
O1–Cu1–O2	88.9(1)	O1–Cu1–N1	93.3(1)
O2–Cu1–N1	176.7(1)	O1–Cu1–N2	173.4(1)
O2–Cu1–N2	93.7(1)	N1–Cu1–N2	84.3(1)
Cu1–O1–C1	127.1(2)	Cu1–O2–C16	126.9(2)
C4–O3–C17	116.6(3)	C13–O4–C18	117.4(3)
Cu1–N1–C7	126.9(2)	Cu1–N1–C8	113.8(2)
C7–N1–C8	119.2(3)	Cu1–N2–C9	113.7(2)
Cu1–N2–C10	126.7(2)	C9–N2–C10	119.4(3)
3			
Cu1–O1	1.899(4)	Cu1–O2	1.905(3)
Cu1–N1	1.947(4)	Cu1–N2	1.938(4)
O1–C1	1.315(7)	O2–C17	1.319(7)
O3–C2	1.364(7)	O3–C18	1.426(8)
O4–C16	1.359(6)	O4–C21	1.425(7)
N1–C7	1.295(8)	N1–C8	1.461(7)
N2–C10	1.473(6)	N2–C11	1.289(8)
O1–Cu1–O2	90.1(1)	O1–Cu1–N1	94.4(2)
O2–Cu1–N1	155.4(2)	O1–Cu1–N2	156.6(2)
O2–Cu1–N2	93.5(2)	N1–Cu1–N2	91.9(2)
Cu1–O1–C1	127.0(3)	Cu1–O2–C17	126.0(3)
C2–O3–C18	116.4(6)	C16–O4–C21	117.8(5)
Cu1–N1–C7	124.6(3)	Cu1–N1–C8	115.6(4)
C7–N1–C8	119.0(4)	Cu1–N2–C10	113.8(4)
Cu1–N2–C11	126.0(3)	C10–N2–C11	119.9(4)
4			
Cu1–O1	1.904(7)	Cu1–O2	1.896(6)
Cu1–N1	1.948(8)	Cu1–N2	1.931(8)
O1–C7	1.293(13)	O2–C8	1.306(12)
O3–C5	1.369(16)	O3–C18	1.419(18)
O4–C10	1.363(13)	O4–C19	1.410(17)
O5–C22	1.564(28)	N1–C1	1.278(14)
N1–C17	1.485(14)	N2–C14	1.300(13)
N2–C15	1.468(13)		
O1–Cu1–O2	90.1(3)	O1–Cu1–N1	93.8(3)
O2–Cu1–N1	155.4(3)	O1–Cu1–N2	153.3(3)
O2–Cu1–N2	94.9(3)	N1–Cu1–N2	92.5(3)

(continued)

Table 2. Continued.

Cu1–O1–C7	127.2(7)	Cu1–O2–C8	126.5(6)
C5–O3–C18	117.9(10)	C10–O4–C19	117.6(9)
Cu1–N1–C1	126.1(8)	Cu1–N1–C17	115.5(6)
C1–N1–C17	118.1(9)	Cu1–N2–C14	124.8(7)
Cu1–N2–C15	114.4(6)	C14–N2–C15	119.5(8)

Table 3. Absorption, IR and magnetic moment data.

		IR/cm^{-1}			
Complex	λ_{max}/nm (ε/$M^{-1} cm^{-1}$)	$\nu_{(C–N)}$	$\nu_{(C=N)}$	$\nu_{(O–H)}$	μ_{eff}/BM
1	218 (8799), 270 (11 324) 356 (9888), 570 (328)	1391	1640	3440[a]	1.58
2	218 (6482), 266 (7035) 386 (5628), 560 (200)	1384	1632	3280[b]	1.62
3	216 (5412), 268 (5347) 386 (4999), 566 (332)	1391	1618	3300[b]	1.63
4	215 (5638), 268 (6422) 382 (5118), 560 (268)	1386	1636	3350[c]	1.81

[a]Coordinated water, [b]Water of crystallization, [c]C_2H_5OH.

planes are 6.5°. A water molecule is hydrogen bonded to a coordinated O atom as well as a methoxyl O atom ($O5 \cdots O1 = 2.767$ Å, $O5 \cdots O4 = 2.898$ Å), rather than being associated with the Cu(II) atom as in complex **1**.

In **3**, the Cu(II) atom is four-coordinated with two *cis* O and two *cis* N atoms to form a distorted square plane. The shortest intermolecular distance involving the Cu(II) atom is 3.592 Å to C7′. The displacement of the Cu(II) atom from the N_2O_2 plane is 0.011 Å. O1 and N2 are 0.41 and 0.39 Å below the N_2O_2 plane while O2 and N1 are 0.41 and 0.39 Å above the plane, respectively, and the dihedral angle between the two CuON planes is 33.0°. The two aromatic planes make a dihedral angle of 40.9°. The water molecule is hydrogen bonded to one of the coordinated O atoms as well as two other water molecules: $O5 \cdots O2 = 2.895$ Å, $O5 \cdots O6 = 2.909$ Å, $O5 \cdots O7 = 3.038$ Å.

In **4**, the Cu(II) atom is coordinated through two phenol O and two imine N atoms to form a distorted square plane. The shortest intermolecular distance involving the Cu(II) atom is 3.416 Å to C1′. Cu1 is displaced by 0.017 Å from the N_2O_2 plane. O1 and N2 are 0.44 and 0.41 Å below the N_2O_2 plane while O2 and N1 are 0.44 and 0.42 Å above the plane, respectively. The dihedral angle between the two CuON planes is 35.3°. The two aromatic planes make a dihedral angle of 43.4°. Ethanol is hydrogen bonded to one of the coordinated O atoms: $O5 \cdots O1 = 2.857$ Å.

3.2. *Spectroscopy*

Electronic absorption data for the complexes in MeOH are given in table 3. Intense bands at higher energies can be attributed to benzene ring $\pi \rightarrow \pi^*$ transitions (216–270 nm) and charge transfer $n \rightarrow \pi^*$ bands (350–390 nm) [20]. The band in the region 560–570 nm can be assigned to d–d transitions.

Table 4. Values of the d–d transition (max) of complex **1** in different solvents.

Solvent	Color of solution	λ_{max}/nm
$CHCl_3$	Violet	560
CH_3CN	Violet	560
MeOH	Bluish violet	570
DMF	Bluish violet	574
THF	Light blue	578
DMSO	Blue	581
Pyridine	Blue	587

IR spectra of the complexes and the ligands were recorded and characteristic bands of the complexes are listed in table 3. The band assignable to $\nu_{(C–N)}$ shows a shift of 10–20 cm^{-1} towards lower frequency in the complexes. The strong band around 1618–1640 cm^{-1} in the complexes is characteristic of $\nu_{(C=N)}$, which is red shifted upon coordination. The band centered at 3440 cm^{-1} in **1** indicates the presence of coordinated water, whereas the bands at 3280 and 3330 cm^{-1} for **2** and **3**, respectively, are due to water of crystallization. The band at 3350 cm^{-1} indicates the presence of ethanol in complex **4**.

3.3. *Color isomerism of complex 1*

Complex **1** shows color isomerism in the solid state. It exists as a green solid when obtained from ethanol and DMSO, while brown and blue solids were obtained from methanol in the presence and absence of water, respectively. The color of the solution of the green complex **1** is different depending on the solvent, changing from violet to blue as the σ donor capacity of the solvent increases (table 4), but no green color was noted for organic solvents. This is due to the coordination of solvent molecules to the metal ion, substituting the coordinated water molecule, as confirmed by elemental analysis of the blue complex obtained from MeOH.

Supplementary material

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 236229, 236230, 236231 and 236232 for **4**, **3**, **1** and **2**, respectively. Copies of this information are available free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.ac.uk or http://www.ccdc.cam.ac.uk).

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