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Coordination modes of two flexidentate salicylaldimine ligands derived from *N*-(3-aminopropyl)morpholine toward zinc and copper

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Two flexidentate Schiff-base ligands condensed from salicylaldehyde or 5-chlorosalicylaldehyde with *N*-(3-aminopropyl)morpholine were prepared *in situ* and reacted with Zn(II) and Cu(II) salts. Upon complexation, the Schiff bases underwent deprotonation at hydroxyl to act as mono-anionic ligands. When a ligand : metal ratio of 2 : 1 was applied, the deprotonated Schiff bases coordinated metal ions through phenolate and imine in a square-planar or tetrahedral geometry. In contrast, 5-chlorosalicylaldimine reacted with the metal ions in a 1 : 1 ratio to form complexes wherein morpholine nitrogen also participates in an *N*,*N*,*O*-tridentate coordination mode. The structures of the complexes were characterized by spectroscopic methods and single-crystal X-ray diffraction.

Keywords: Salicylaldehyde; Schiff base; Coordination behavior; Divalent metal complexes; X-ray crystal structure

1. Introduction

Schiff bases formed by condensation of salicylaldehyde with a primary amine are capable of coordinating metal ions. Such complexes have numerous applications as anticancer [1], antimicrobial [2, 3], fungicide [4], and antiviral agents [5], as catalysts for chemical reactions [6] and also electrochemistry [7]. Various coordination modes of these compounds are useful models. Metal coordination modes in these complexes involve phenolate oxygen and imine nitrogen to form six-membered chelate rings. If the amine fragment contains other donors located for coordination to metal, the Schiff base can act as a polydentate ligand or, depending on flexibility of the amine fragment, may show ambidentate behavior. As an example, the Schiff base derived from salicylaldehyde and *N*-(2-aminoethyl)piperazine (**I**, figure 1) can be tetradentate or tridentate with nickel(II), depending on the piperazine ring conformation (chair or boat) [8]. The study also showed the profound influence of substitution in the aromatic ring on coordination behavior. Thus, while **I** showed both tridentate and tetradentate modes, the 5-nitro

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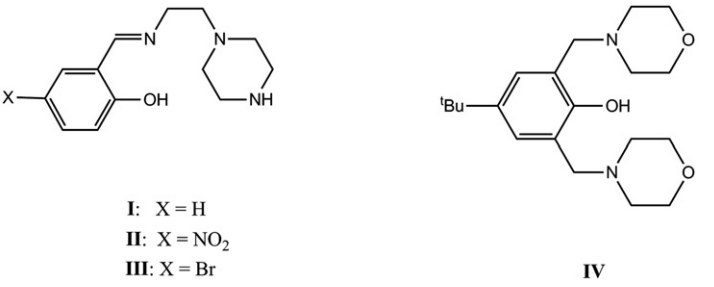
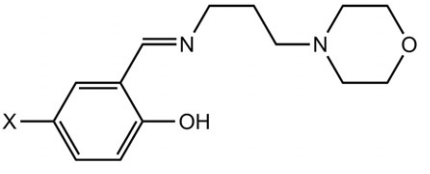


I: X = H
II: X = NO_2
III: X = Br
IV

Figure 1. Chemical diagram of ligands **I**, **II**, **III**, and **IV**.



L^1H: X = H
L^2H: X = Cl

Figure 2. Chemical diagram of L^1H and L^2H.

derivative, **II**, coordinated only in a tridentate, and the 5-bromo analog, **III**, only in a tetradentate fashion.

Similar to piperazine, a morpholine ring in a ligand can adopt both chair and boat conformations, thus coordinating in different manners. An example is ligand **IV** (figure 1) which has both chair and boat morpholine rings in its calcium complex [9].

We have recently reported the crystal structures of zinc(II) and manganese(III) complexes of the Schiff base derived from salicylaldehyde and *N*-(3-aminopropyl)morpholine (L^1H, figure 2) [10, 11]. In both structures, the Schiff base is a bidentate ligand using only the phenolate oxygen and imine nitrogen in metal coordination, while the N and O of the chair-like morpholine do not coordinate. Herein, we describe the complexation behavior of two flexidentate ligands, L^1H and its 5-chlorosalicylaldimine analog, L^2H, toward zinc(II) and copper(II) ions. The solid-state structures of the metal complexes are examined by X-ray diffraction analysis.

2. Experimental

2.1. *Materials and measurements*

All reagents were commercially available (Merck or Acros) and used as supplied. Ethanol was distilled prior to use. All chemicals were of analytical grades and used without purification. IR spectra were recorded on a Perkin-Elmer RX1 FT-IR spectrometer. NMR spectra were recorded on a Bruker AVN 400 MHz

FT-NMR spectrometer. Elemental analyses were recorded on a Perkin-Elmer 2400 Series II CHNS Analyzer. The electronic spectra were measured on a Shimadzu 1601 spectrophotometer from 200 to 1100 nm.

2.2. *Synthesis of the Schiff bases*

L^1H and L^2H were synthesized by refluxing a mixture of *N*-(3-aminopropyl)morpholine (0.35 g, 2.46 mmol) and salicylaldehyde (0.3 g, 2.46 mmol) or 5-chlorosalicylaldehyde (0.39 g, 2.46 mmol) in ethanol (15 mL) for 2 h. The solvent was then removed under reduced pressure to give yellow oil of the Schiff base.

2.2.1. L^1H. IR (NaCl cell, cm^{-1}): 3525 br; 2948m; 2853m; 2810m; 1630s ($\nu_{C=N}$); 1460 s; 1279s; 1118s; 759m. ^1H NMR (400 MHz, DMSO-d_6, δ ppm): 1.78 (quin, 2H, CH_2); 2.32 (m, 6H, CH_2); 3.56 (t, 4H, CH_2); 3.61 (t, 2H, CH_2); 6.90 (m, 2H, Ar–H); 7.32 (t, 1H, Ar–H); 7.42 (d, 1H, Ar–H); 8.55 (s, 1H, HC=N); 13.65 (s, 1H, OH). ^{13}C NMR (400 MHz, DMSO-d_6, δ ppm): 27.11, 53.29, 55.74, 56.20, 66.13 (CH_2); 116.49, 118.29, 118.51, 131.51, 132.18 (Ar); 160.91 (HC=N); 165.84 (C–OH).

2.2.2. L^2H. IR (NaCl cell, cm^{-1}): 2950m; 2853m; 2810m; 1636s ($\nu_{C=N}$); 1483s; 1279s; 1118s; 822m; 644m. ^1H NMR (400 MHz, DMSO-d_6, δ ppm): 1.78 (quin, 2H, CH_2); 2.32 (m, 6H, CH_2); 3.56 (t, 4H, CH_2); 3.62 (t, 2H, CH_2); 6.88 (d, 1H, Ar–H); 7.33 (dd, 1H, Ar–H); 7.53 (d, 1H, Ar–H); 8.53 (s, 1H, HC=N), 13.75 (s, 1H, OH). ^{13}C NMR (400 MHz, DMSO-d_6, δ ppm): 26.90, 53.27, 55.65, 55.92, 66.12 (CH_2); 118.76, 119.39, 121.37, 130.43, 131.94 (Ar); 160.28 (HC=N); 164.77 (C–OH).

2.3. *Synthesis of the metal complexes*

For preparation of the metal complexes, L^1H and L^2H were synthesized *in situ* by refluxing solutions of *N*-(3-aminopropyl)morpholine (0.35 g, 2.46 mmol) and salicylaldehyde (0.3 g, 2.46 mmol) or 5-chlorosalicylaldehyde (0.39 g, 2.46 mmol) in ethanol or methanol (15 mL) for 2 h. The resulting solutions were then used for metal complexation.

2.3.1. $[Zn(L^1)_2]$. To a solution of the *in situ* prepared L^1H in ethanol, a few drops of triethylamine were added followed by addition of a solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.27 g, 1.23 mmol) (OAc stands for acetate) in ethanol. The mixture was refluxed for 1 h. The solvent was then removed under reduced pressure to give yellow oil which crystallized from methanol at room temperature. Yield: 0.58 g, 84.1%. Anal. Calcd for $C_{28}H_{38}N_4O_4Zn$ (%): C, 60.05; H, 6.84; N, 10.00. Found: C, 60.25; H, 7.05; N, 10.03. IR (KBr, cm^{-1}): 2938w; 2851 w; 1626s ($\nu_{C=N}$); 1463m; 1317m; 1118m; 759m. ^1H NMR (400 MHz, DMSO-d_6, δ ppm): 1.24 (s, 1H, CH_2); 1.67 (m, 2H, CH_2); 2.12 (m, 6H, CH_2); 2.20 (t, 2H, CH_2); 2.33 (m, 1H, CH_2); 3.60 (t, 2H, CH_2); 6.50 (s, 1H, Ar–H); 6.64 (d, 1H, Ar–H); 7.27 (m, 2H, Ar–H); 8.47 (s, 1H, HC=N). ^{13}CNMR (400 MHz, DMSO-d_6, δ ppm): 26.65, 52.90, 54.89, 57.87, 66.02, 113.96, 118.07, 122.27, 134.43, 135.97, 169.77, 171.90.

2.3.2. [Cu(L^1)$_2$]. A few drops of triethylamine were added to a solution of the *in situ* prepared L^1H in methanol at room temperature. A methanolic solution of $Cu(OAc)_2 \cdot H_2O$ (0.25 g, 1.23 mmol) was added and the mixture was stirred at room temperature for 2 h. It was then set aside for two weeks whereupon X-ray quality crystals of the copper complex were obtained. Yield: 0.60 g, 87.4%. Anal. Calcd for $C_{28}H_{38}N_4O_4Cu$ (%): C, 60.25; H, 6.86; N, 10.04. Found: C, 60.25; H, 7.05; N, 10.03. IR (KBr, cm^{-1}): 2954 w; 2851 w; 2801w; 1613s ($\nu_{C=N}$); 1445s; 1330s; 1115s; 760s; 574m. UV-Vis [λ_{max} (nm), THF (ε, $mol^{-1}\,dm^3\,cm^{-1}$)] 245 (37,185); 295 (7363); 307 (10,158); 363 (11,836); 619 (112).

2.3.3. [Zn(L^2)$_2$]·3H$_2$O. The compound was prepared following the same procedure as for preparation of [Zn(L^1)$_2$] except for using L^2H (0.39 g, 2.46 mmol) as the ligand. Yellow crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of an ethanol solution of the complex at room temperature. Yield: 0.57 g, 67.6%. Anal. Calcd for $C_{28}H_{42}Cl_2N_4O_7Zn$ (%): C, 49.24; H, 6.20; N, 8.20. Found: C, 49.24; H, 6.19; N, 8.20. IR (KBr, cm^{-1}): 3340 br (νH_2O); 2959w; 2852 w; 2822w; 1618s ($\nu_{C=N}$); 1461s; 1296s; 1114s; 832m; 716s. ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 1.24 (s, 1H, CH_2); 1.63 (m, 2H, CH_2); 2.12 (m, 6H, CH_2); 2.20 (t, 2H, CH_2); 2.33 (m, 1H, CH_2); 3.55 (m, 2H, CH_2); 6.66 (d, 1H, Ar–H); 7.25 (dd, 1H, Ar–H); 7.36 (d, 1H, Ar–H); 8.47 (s, 1H, HC=N). ^{13}C NMR (400 MHz, DMSO-d_6, δ ppm): 26.65, 52.65, 54.95, 58.10, 66.00, 116.60, 118.84, 124.20, 133.93, 134.04, 168.44, 170.96.

2.3.4. [Zn(L^2)(OAc)]. An ethanolic solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.54 g, 2.46 mmol) was added to an *in situ* prepared ligand (L^2H) solution in ethanol (15 mL). The mixture was refluxed for 2 h and then left undisturbed at room temperature for two days whereupon X-ray quality crystals of the complex were obtained. Yield: 0.54 g, 58.7%. Anal. Calcd for $C_{16}H_{23}N_2O_4Zn$ (%): C, 47.19; H, 5.45; N, 6.88. Found: C, 47.43; H, 5.05; N, 6.85. IR (KBr, cm^{-1}): 2928w; 2847 w; 1646 s ($\nu_{C=N}$); 1577s; 1461s; 1314s; 1114s; 850s; 703s. ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 1.22 (s, 1H); 1.84 (m, 6H); 2.13 (m, 2H); 2.71 (br, 2H); 3.66 (m, 6H); 6.63 (d, 1H, Ar–H); 7.16 (d, 1H, Ar–H); 7.25 (s, 1H, Ar–H); 8.29 (s, 1H, HC=N).

2.3.5. [Cu(L^2)$_2$]. To a methanolic solution (15 mL) of *in situ* prepared L^2H, a few drops of triethylamine were added followed by addition of a methanolic solution of $Cu(OAc)_2 \cdot H_2O$ (0.25 g, 1.23 mmol) at ambient temperature. During the addition, dark green precipitate was formed. The precipitate was filtered off and the filtrate was left undisturbed at room temperature. After one week, X-ray quality crystals were collected by filtration, washed with cold methanol, and air dried. Yield: 0.52 g, 68.1%. Anal. Calcd for $C_{28}H_{36}Cl_2N_4O_4Cu$ (%): C, 53.63; H, 5.79; N, 8.93. Found: C, 53.56; H, 5.82; N, 8.91. IR (KBr, cm^{-1}): 2951 w; 2858w; 2808 w; 1624s ($\nu_{C=N}$); 1455s; 1333m; 1114s; 834s; 720s. UV-Vis [λ_{max} (nm), THF (ε, $mol^{-1}\,dm^3\,cm^{-1}$)] 246 (38735); 295 (8313); 307 (9157); 374 (9819); 597 (115).

2.3.6. [Cu(L^2)Cl]·CH$_3$OH. A methanolic solution of $CuCl_2 \cdot 2H_2O$ (0.42 g, 2.46 mmol) was added to an *in situ* prepared L^2H in methanol (15 mL) at room temperature. The mixture was stirred for 1 h and then left undisturbed at

Table 1. Crystal data and refinement parameters for L^1 complexes.

	$[Zn(L^1)_2]$	$[Cu(L^1)_2]$
Empirical formula	$C_{28}H_{38}N_4O_4Zn$	$C_{28}H_{38}CuN_4O_4$
Crystal system	Orthorhombic	Monoclinic
Space group	*Fdd*2	*P*21/*n*
Unit cell dimensions (Å, °)		
a	19.7143(12)	9.6854(3)
b	48.358(3)	7.9100(3)
c	5.5790(4)	17.6325(2)
β		90.067(3)
Volume (Å^3), *Z*	5318.7(6), 8	1350.85(3), 2
Calculated density (g cm^{-3})	1.399	1.372
Crystal size (mm^3)	0.26 × 0.11 × 0.05	0.26 × 0.19 × 0.11
θ range for data collection (°)	2.23–26.76	2.31–27.00
Reflections collected	11,709	9091
Independent reflections	2816 [R(int) = 0.0407]	2932 [R(int) = 0.0262]
Completeness to $\theta = 26.77$ (%)	99.9	99.4
Data/restraints/parameters	2816/1/168	2932/0/169
Goodness-of-fit on F^2	1.040	1.035
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0268$, $wR_2 = 0.0579$	$R_1 = 0.0304$, $wR_2 = 0.0757$
R indices (all data)	$R_1 = 0.0303$, $wR_2 = 0.0592$	$R_1 = 0.0367$, $wR_2 = 0.0787$

room temperature. Crystals suitable for crystallographic analysis were obtained after one week. Yield: 0.71 g, 70.1%. Anal. Calcd for $C_{15}H_{22}Cl_2N_2O_3Cu$ (%): C, 43.64; H, 5.37; N, 6.79. Found: C, 43.30; H, 4.69; N, 7.23. IR (KBr, cm^{-1}): 3440s (ν_{OH}); 2942 w; 2872w; 1625s ($\nu_{C=N}$); 1460m; 1316m; 1119m; 1024s; 850m; 703s. UV-Vis [λ_{max} (nm), THF (ε, mol^{-1} dm^3 cm^{-1})] 247 (22413); 295 (4932); 353 (6165); 377sh; 772 (116).

2.4. *Crystallography*

Diffraction data were measured with a Bruker SMART Apex II CCD area-detector diffractometer (graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å). The orientation matrix, unit-cell refinement, and data reduction were all handled by Apex2 software (SAINT integration, SADABS absorption correction [12]). The structures were solved using direct or Patterson methods in SHELXS-97 and were refined by full matrix least squares on F^2 with SHELXL-97 [13]. All non-hydrogen atoms were refined anisotropically and all the C-bound hydrogen atoms were placed at calculated positions and refined isotropically. O-bound hydrogen atoms were located in difference Fourier maps and refined with distance restraints of O–$H_{methanol}$ 0.84(2) and O–H_{water} 0.88(2) Å. Drawings of the molecules were produced with XSEED [14]. Crystal data and refinement are summarized in tables 1 and 2.

3. Results and discussion

3.1. *General characterization of the ligands and complexes*

The Schiff bases can be prepared *via* condensation of *N*-(3-aminopropyl)morpholine with salicylaldehyde (for L^1H) or 5-chlorosalicylaldehyde (for L^2H). IR spectra of the

Table 2. Crystal data and refinement parameters for L^2 complexes.

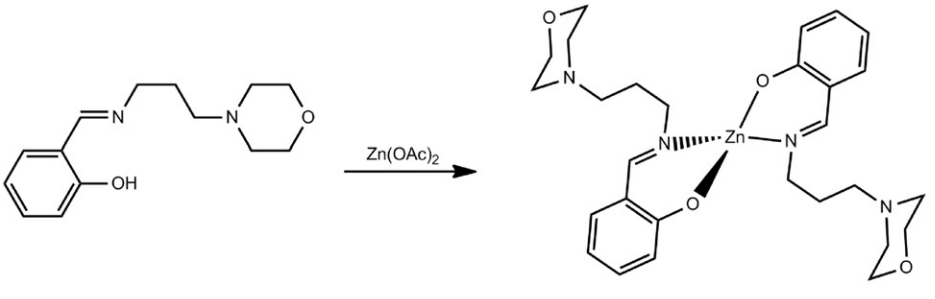
	$[Zn(L^2)_2]\cdot 3H_2O$	$[Zn(L^2)(OAc)]$	$[Cu(L^2)_2]$	$[Cu(L^2)Cl]\cdot CH_3OH$
Empirical formula	$C_{28}H_{42}Cl_2N_4O_7Zn$	$C_{16}H_{21}ClN_2O_4Zn$	$C_{28}H_{36}Cl_2CuN_4O_4$	$C_{15}H_{22}Cl_2CuN_2O_3$
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P21/c$	$Pca21$	$P\bar{1}$	$P21/c$
Unit cell dimensions (Å, °)				
a	14.6066(14)	13.0216(2)	6.4917(14)	8.8556(3)
b	11.7494(11)	10.2210(2)	8.5461(18)	13.8205(2)
c	18.4867(18)	25.8385(4)	13.199(3)	14.0612(2)
α			88.348(3)	
β	101.488(3)		81.750(4)	99.964(3)
γ			70.792(3)	
Volume (Å^3), Z	3109.1(5), 4	3438.94(10), 8	684.2(3), 1	1694.98(4), 4
Calculated density (g cm^{-3})	1.459	1.569	1.522	1.618
Crystal size (mm^3)	$0.31\times0.19\times0.06$	$0.32\times0.22\times0.20$	$0.18\times0.13\times0.12$	$0.51\times0.41\times0.30$
θ range for data collection (°)	2.07–27.00	1.99–27.00	2.52–25.48	2.08–27.50
Reflections collected	16,987	29,957	4784	12,966
Independent reflections	6729 [R(int) = 0.0357]	7401 [R(int) = 0.0352]	2511 [R(int) = 0.0758]	3894 [R(int) = 0.0179]
Completeness to $\theta = 26.77$ (%)	99.4	100.0	98.7	99.9
Data/restraints/parameters	6729/6/397	7401/1/435	2511/0/178	3894/1/212
Goodness-of-fit on F^2	1.033	1.048	1.055	1.041
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0344$, $wR_2 = 0.0728$	$R_1 = 0.0254$, $wR_2 = 0.0574$	$R_1 = 0.0574$, $wR_2 = 0.1497$	$R_1 = 0.0212$, $wR_2 = 0.0533$
R indices (all data)	$R_1 = 0.0493$, $wR_2 = 0.0781$	$R_1 = 0.0300$, $wR_2 = 0.0592$	$R_1 = 0.0649$, $wR_2 = 0.1591$	$R_1 = 0.0235$, $wR_2 = 0.0543$

oily products exhibit the characteristic absorptions of azomethine at 1631 and 1636 cm^{-1}. ^1H NMR spectra display the imine HC=N peaks at 8.55 and 8.53 ppm and the phenol hydrogen atoms at 13.65 and 13.75 ppm. ^{13}C NMR spectra of L^1H and L^2H show the imine HC=N resonances at 160.9 and 160.3 ppm and the aromatic carbons attached to the hydroxyls at 164.8 and 165.8 ppm, respectively. Although the ligands can be isolated and then used for metal complexation, it was more convenient to prepare them *in situ*. Treatment of the *in situ* prepared ligands with the appropriate divalent zinc or copper salts, in 1 : 1 or 2 : 1 ratio, led to the corresponding Schiff-base metal complexes. Complexation is accompanied by shifts of ν(C=N) bands to lower or higher frequencies, implying involvement of the azomethine in coordination. This is supported by upfield shifts of the imine HC=N signals in ^1H NMR spectra of the zinc complexes when compared to those of free ligands. ^{13}C NMR spectra display downfield shifts of the ligand HC=N resonances upon complexation with Zn(II). Loss of phenolic hydrogen atoms in ^1H NMR spectra and downfield shifts of C–O resonances in ^{13}C NMR spectra of the zinc complexes suggest participation of phenolate in metal coordination. Electronic absorption spectra of the three copper complexes were measured in THF and showed d–d transitions as broad bands at 619, 597, and 772 nm for $[Cu(L^1)_2]$, $[Cu(L^2)_2]$, and $[Cu(L^2)Cl]$, respectively.

3.2. *X-ray crystallographic analysis*

3.2.1. Crystal structure of $[Zn(L^1)_2]$. Crystals of $[Zn(L^1)_2]$ were obtained through the reaction of L^1H with zinc(II) acetate in a 2 : 1 ratio (scheme 1). As depicted in figure 3, the deprotonated Schiff base, L^1, chelates Zn(II) *via* phenolate oxygen and imine nitrogen. The metal is on a crystallographic two-fold rotational axis of symmetry and is four-coordinate by two mono-anionic ligands to form two six-membered chelating rings. The dihedral angle between the two rings is 79.61(7)° and the coordination geometry can be best described as a distorted tetrahedron. Table 3 lists selected bond lengths and angles for the structure. The Zn–O and Zn–N distances of 1.9221(14) and 1.9916(16) Å are comparable with values reported for similar structures [15–17].

3.2.2. Crystal structure of $[Cu(L^1)_2]$. The reaction of L^1H with copper(II) acetate in a 2 : 1 ratio led to the formation of $[Cu(L^1)_2]$ (scheme 2). As shown in figure 4, the copper



Scheme 1. Synthesis of $[Zn(L^1)_2]$.

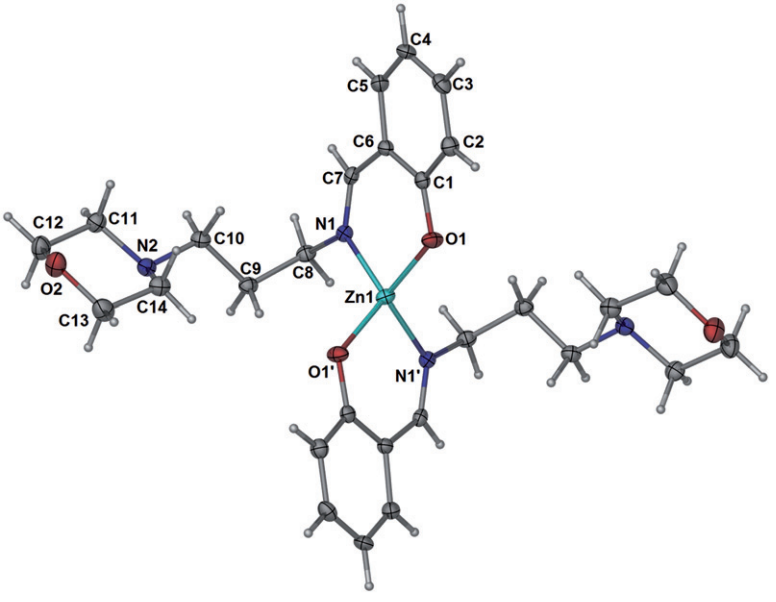
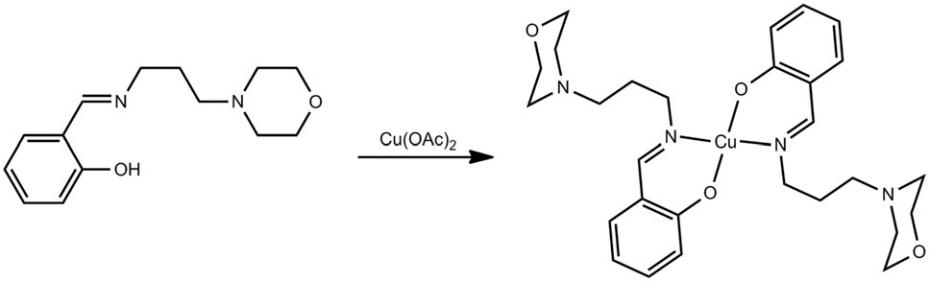


Figure 3. The crystal structure and atom-labeling scheme of $[Zn(L^1)_2]$ (50% probability ellipsoids). The two-fold rotation axis is perpendicular to the plane of the paper.

Table 3. Selected bond lengths (Å) and angles (°) for L^1 complexes.

$[Zn(L^1)_2]$		$[Cu(L^1)_2]$	
Zn(1)–O(1)	1.9221(14)	Cu(1)–O(1)	1.8908(12)
Zn(1)–N(1)	1.9916(16)	Cu(1)–N(1)	2.0029(14)
O(1)–C(1)	1.319(2)	O(1)–C(1)	1.308(2)
N(1)–C(7)	1.285(2)	N(1)–C(7)	1.294(2)
O(1)–Zn(1)–O(1)#1	113.70(9)	O(1)#2–Cu(1)–O(1)	180.0
O(1)–Zn(1)–N(1)	96.18(6)	O(1)–Cu(1)–N(1)#2	88.50(5)
O(1)–Zn(1)–N(1)#1	120.66(6)	O(1)–Cu(1)–N(1)	91.50(5)
N(1)–Zn(1)–N(1)#1	111.23(9)	N(1)#2–Cu(1)–N(1)	180.0

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+2, z$; #2 $-x+1, -y+2, -z$.



Scheme 2. Synthesis of $[Cu(L^1)_2]$.

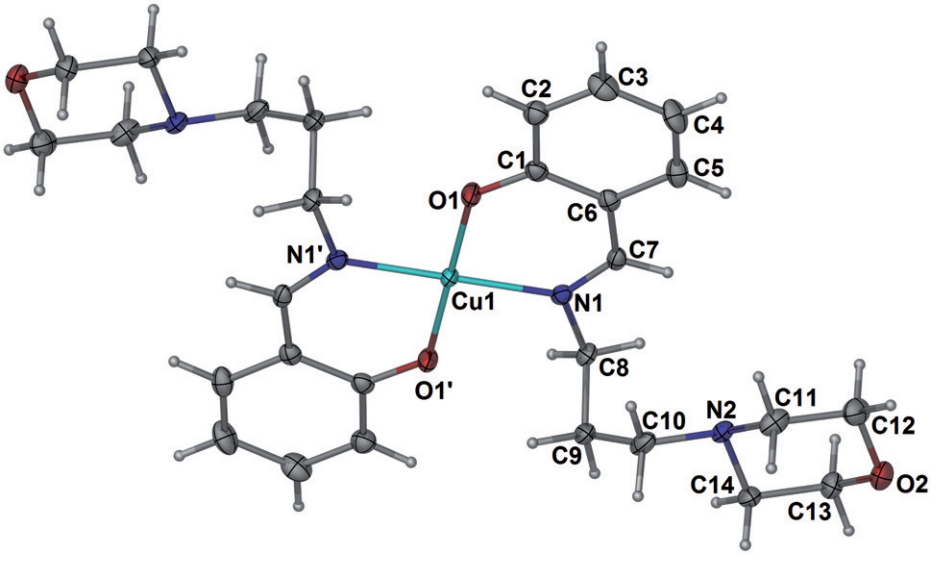
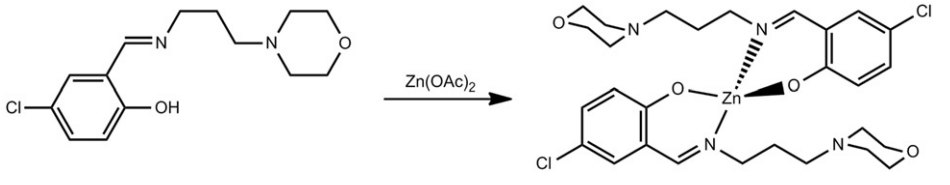


Figure 4. The crystal structure and atom-labeling scheme of $[Cu(L^1)_2]$ (50% probability ellipsoids).



Scheme 3. Synthesis of $[Zn(L^2)_2]$.

is placed on a center of inversion and is four-coordinate by two deprotonated Schiff bases, L^1, in a square-planar environment. The ligand uses phenolate oxygen and imine nitrogen to chelate. The morpholine ring adopts a chair conformation and its nitrogen and oxygen atoms stay away from coordination. Selected bond lengths and angles are given in table 3. Deviations from ideal square-planar geometry are reflected in the O1–Cu1–N1 bite angle of 91.50(5)°. For four-coordinate Cu(II) complexes, bis-chelated by salicylaldimine ligands, both tetrahedral [18, 19] and square-planar [20, 21] geometries have been observed. There is an example wherein the unit cell of the structure of a salicylaldimine Cu(II) complex contains both square-planar and flattened tetrahedral structures [22].

3.2.3. Crystal structure of $[Zn(L^2)_2]\cdot H_2O$. The complex was obtained *via* reaction of L^2H with zinc(II) acetate in a 2 : 1 ratio (scheme 3). The asymmetric unit of the crystal structure contains one metal complex molecule, co-crystallized with three molecules of water. Figure 5 shows the molecular structure of the metal complex. Zn, located in a general position, is four-coordinate by two deprotonated L^2 ligands through their phenolate O and azomethine N. The geometry of the coordination sphere can be

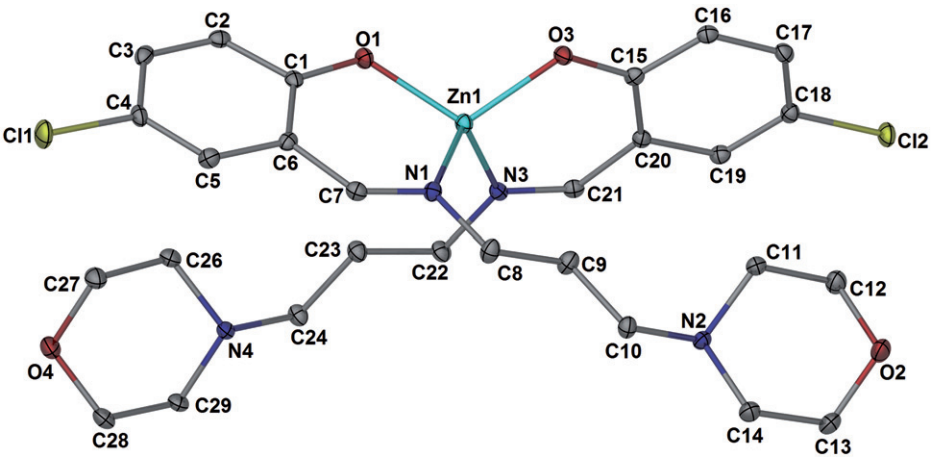


Figure 5. The crystal structure of $[Zn(L^2)_2]\cdot 3H_2O$ with 30% thermal ellipsoids. Water molecules and hydrogen atoms have been omitted for clarity.

described as a distorted tetrahedron from the dihedral angle of 86.80(7)° formed between the two six-membered chelating rings. Dissimilar to the structure of $[Zn(L^1)_2]$, the three methylene groups of the spacer in each L^2 adopt an all-*trans* conformation. Selected bond lengths and angles for the structure are given in table 4. The geometrical parameters pertaining to the coordination spheres are within normal ranges [15–17].

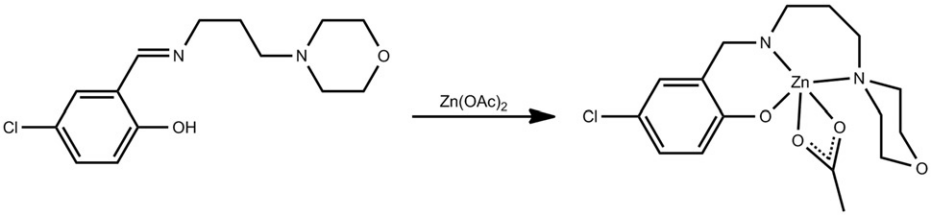
3.2.4. Crystal structure of $[Zn(L^2)(OAc)]$. The reaction of L^2H with $Zn(OAc)_2$ in a 1 : 1 ratio gave $[Zn(L^2)(OAc)]$ (scheme 4). The asymmetric unit of the crystal structure consists of two crystallographically independent molecules with slightly different geometries. The weighted root mean square (rms) fit for the superposition of the non-H atoms in both molecules is 0.0412 Å. Figure 6 displays the molecular structure of one molecule. In contrast with the former structures, in this complex, the deprotonated Schiff base, L^2, coordinates through not only the phenolate O and imine N, but also its morpholine nitrogen. Each ligand forms two six-membered chelate rings with zinc, one of which (Zn1/O1/C1/C6/C7/N1) is planar whereas the other (Zn1/N1/C8/C9/C10/N2) adopts a chair conformation. The zinc is five-coordinate by tridentate L^2 and a bidentate acetate. The coordination geometry is distorted square-pyramidal as determined by Addison τ index of 0.11 [23]. Table 4 provides selected bond lengths and angles for $[Zn(L^2)(OAc)]$. The $Zn–O_{phenolate}$ distance of 1.9392(18) Å is within the normal range as are the Zn–N distances of 2.005(2) and 2.140(2) Å [24, 25].

3.2.5. Crystal structure of $[Cu(L^2)_2]$. Reaction of Cu(II) with two equivalents of H^2L generated $[Cu(L^2)_2]$ (scheme 5). The crystal structure is represented in figure 7 and selected bond lengths and angles are given in table 4. The copper, located on a center of inversion, is four-coordinate in a distorted square plane defined by two *N,O*-bidentate mono-anionic L^2. Distortion from ideal geometry is evident from *cisoid*-angles of 87.44(10)° and 92.56(10)°. The morpholine nitrogen and oxygen are not involved in coordination. The coordination geometrical parameters are comparable to values observed in similar structures [18, 19].

Table 4. Selected bond lengths (Å) and angles (°) for L^2 complexes.

$[Zn(L^2)_2]\cdot 3H_2O$		$[Zn(L^2)(OAc)]$		$[Cu(L^2)_2]$		$[Cu(L^2)Cl]\cdot CH_3OH$	
Zn(1)–O(1)	1.9122(15)	Zn(1)–O(1)	1.9392(18)	Cu(1)–O(1)	1.892(2)	Cu(1)–O(1)	1.8883(10)
Zn(1)–O(3)	1.9277(14)	Zn(1)–N(1)	2.005(2)	Cu(1)–N(1)	2.013(3)	Cu(1)–N(1)	1.9507(12)
Zn(1)–N(3)	2.0116(17)	Zn(1)–N(2)	2.140(2)	O(1)–C(1)	1.306(4)	Cu(1)–N(2)	2.0473(12)
Zn(1)–N(1)	2.0164(17)	Zn(1)–O(3)	2.435(2)	N(1)–C(7)	1.284(4)	Cu(1)–Cl(2)	2.2496(4)
O(1)–C(1)	1.315(2)	Zn(1)–O(4)	2.0027(18)			O(1)–C(1)	1.3121(17)
O(3)–C(15)	1.323(2)	O(1)–C(1)	1.316(3)			N(1)–C(7)	1.2877(18)
N(1)–C(7)	1.287(3)	N(1)–C(7)	1.273(4)				
N(3)–C(21)	1.288(3)						
O(1)–Zn(1)–O(3)	112.51(6)	O(1)–Zn(1)–O(4)	104.25(7)	O(1)–Cu(1)–O(1)#1	180.00	O(1)–Cu(1)–N(1)	94.72(5)
O(1)–Zn(1)–N(3)	119.48(7)	O(1)–Zn(1)–N(1)	95.03(9)	O(1)–Cu(1)–N(1)	92.56(10)	O(1)–Cu(1)–N(2)	141.79(5)
O(3)–Zn(1)–N(3)	95.83(6)	O(4)–Zn(1)–N(1)	145.12(9)	O(1)–Cu(1)–N(1)#1	87.44(10)	N(1)–Cu(1)–N(2)	94.36(5)
O(1)–Zn(1)–N(1)	97.02(6)	O(1)–Zn(1)–N(2)	121.30(9)	N(1)–Cu(1)–N(1)#1	180.00	O(1)–Cu(1)–Cl(2)	95.98(3)
O(3)–Zn(1)–N(1)	119.24(7)	O(4)–Zn(1)–N(2)	103.38(8)			N(1)–Cu(1)–Cl(2)	141.51(4)
N(3)–Zn(1)–N(1)	114.35(7)	N(1)–Zn(1)–N(2)	90.46(8)			N(2)–Cu(1)–Cl(2)	99.60(3)
		O(1)–Zn(1)–O(3)	138.32(8)				
		O(4)–Zn(1)–O(3)	58.45(7)				
		N(1)–Zn(1)–O(3)	87.89(8)				

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+2, -z+1$.



Scheme 4. Synthesis of $[Zn(L^2)(OAc)]$.

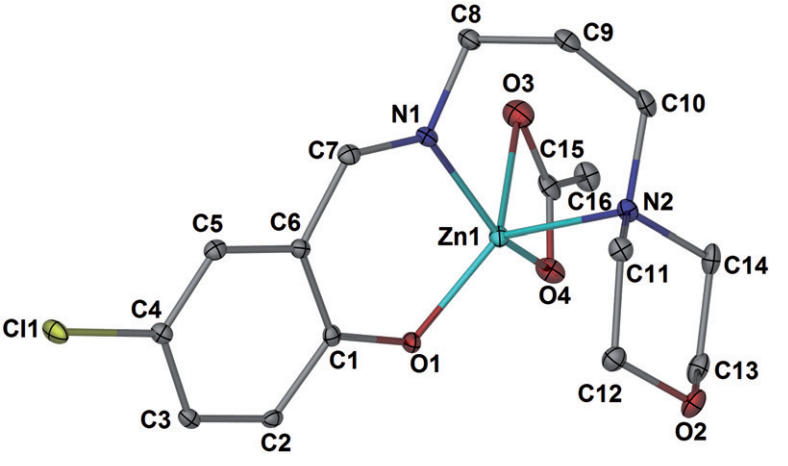
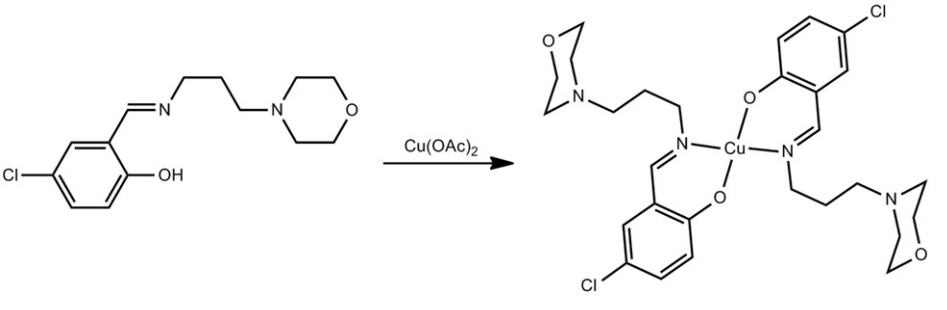


Figure 6. The molecular structure of $[Zn(L^2)(OAc)]$ with 40% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.



Scheme 5. Synthesis of $[Cu(L^2)_2]$.

3.2.6. Crystal structure of $[Cu(L^2)Cl]\cdot CH_3OH$. The complex was obtained through reaction of H^2L with an equimolar amount of copper(II) chloride (scheme 6). The crystal structure contains one methanol co-crystallized with each Cu(II) complex. Figure 8 demonstrates the molecular structure of the copper(II) complex. Similar to the structure of $[Zn(L^2)(OAc)]$, the morpholine nitrogen of the deprotonated Schiff base,

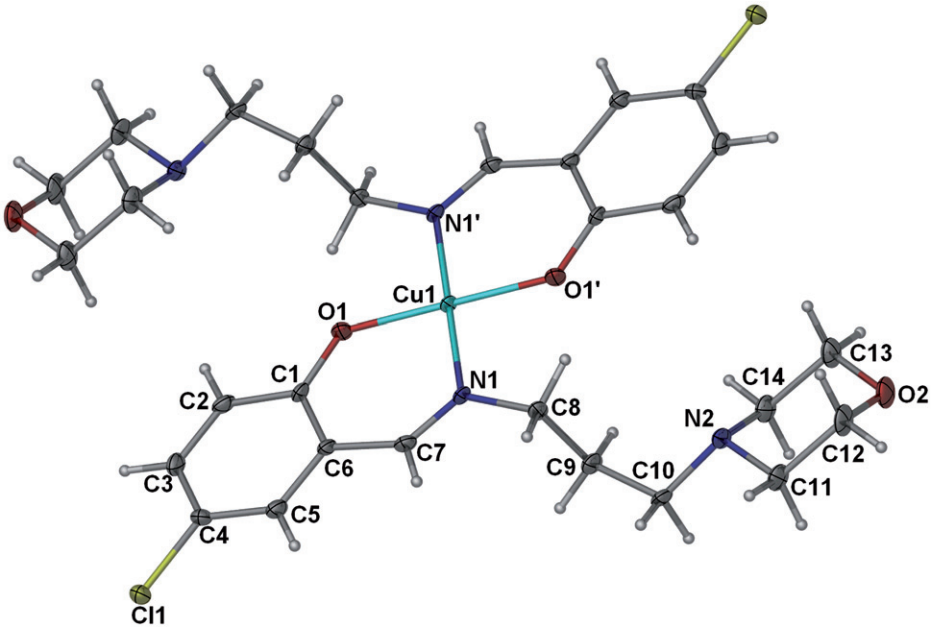
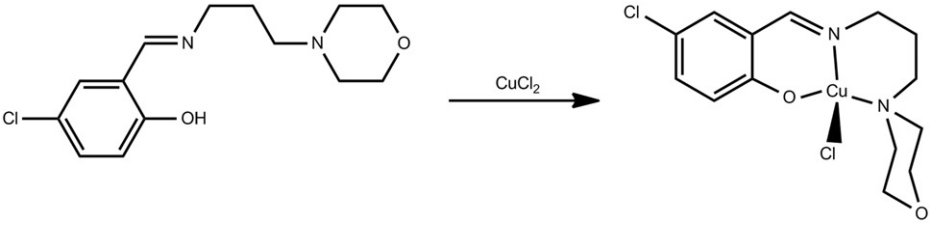


Figure 7. The crystal structure and atom-labeling scheme of $[Cu(L^2)_2]$ (50% probability ellipsoids).



Scheme 6. Synthesis of $[Cu(L^2)Cl]$.

L^2, is involved in metal coordination. Thus, the ligand is a mono-anionic *N*,*N*,*O*-tridentate chelate to form one planar and one chair-like six-membered ring with copper. The four-coordinate copper is completed by Cl^-. The rms deviation from the least-squares plane involving Cu1/Cl2/O1/N1/N2 is 0.0182(4) Å and copper atom is 0.0228(5) Å out of the coordination plane, Cl2/O1/N1/N2. Table 4 gathers selected bond lengths and angles for $[Cu(L^2)Cl] \cdot CH_3OH$. The coordination geometrical parameters are in agreement with the values observed in similar structures [26–28].

4. Conclusion

L^1H and L^2H may show ambidentate behavior in coordination to metal ions. Upon reactions of the Schiff bases with metal salts in a 2 : 1 ratio (ligand : metal), the ligands

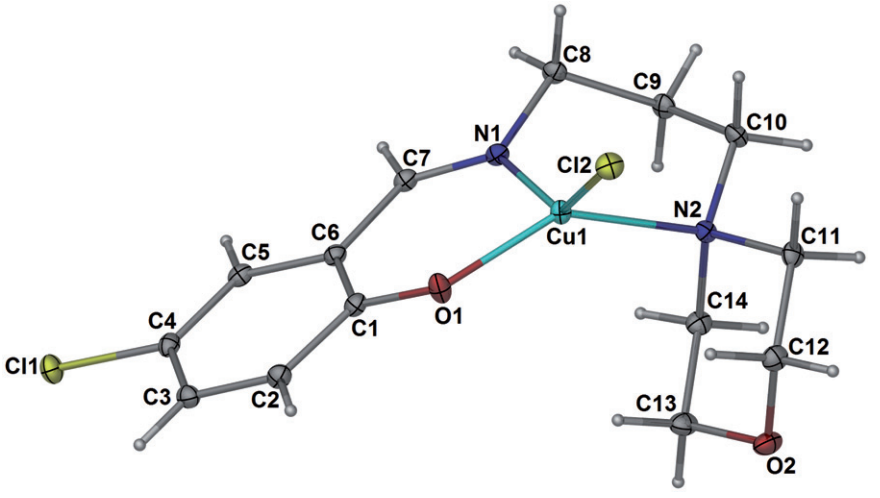


Figure 8. The crystal structure of $[Cu(L^2)Cl]\cdot CH_3OH$ with 40% thermal ellipsoids. The methanol and hydrogen atoms have been omitted for clarity.

deprotonate and chelate through phenolate and imine to form the di-ligated metal complexes. In these complexes, morpholine nitrogen and oxygen stay away from the coordination spheres. Structures of the products obtained from reactions of L^2H with metal salts in a 1 : 1 ratio show involvement of the morpholine nitrogen in coordination. In the latter complexes, L^2 is tridentate, forming two chelate rings with the metal centers. Coordination environments of the metal complexes vary from square-planar to tetrahedral to square-pyramidal.

Supplementary material

CCDC nos 874169–874174 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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