

An Asymmetric Salen-type Bisoxime Ligand and Its Supramolecular Copper(II) Complex: Synthesis, Crystal Structure and Spectral Properties

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A supramolecular Cu(II) complex [CuL(H₂O)] with an asymmetric salen-type bisoxime ligand (H₂L = 4-nitro-6'-methoxy-2,2'-[ethylenediylldioxybis(nitrilomethylidyne)]diphenol) has been synthesized and characterized by elemental analysis, IR and UV/Vis spectroscopy, TG-DTA analysis, and molar conductance measurements. The crystal structure of the Cu(II) complex has been determined by single-crystal X-ray diffraction. The Cu(II) atom is penta-coordinated by N₂O₂ donor atoms from the asymmetric salen-type bisoxime L²⁻ unit and one oxygen atom from the coordinated water molecule, resulting in an almost regular square-pyramidal geometry. With the help of intermolecular O–H···O, C–H···O hydrogen bonding and $\pi\cdots\pi$ stacking interactions, a self-assembled 3D supramolecular structure is formed.

Key words: Asymmetric Salen-type Bisoxime Ligand, Cu(II) Complex, Synthesis, Crystal Structure

Introduction

Transition metal complexes with the *N,N'*-bis-(salicylaldehyde)ethylenediamine (salen) ligand or its analogs have been synthesized and characterized abundantly in the last few decades [1–3]; they played important roles in the development of catalysis, medical imaging, optical materials [4, 5] and others. Symmetric salen-type bisoxime ligands and their complexes have also attracted much attention for their novel structures and spectral characteristics [6, 7], especially for their excellent photoluminescence [8] and interesting magnetic [9] properties. Furthermore, salen-type Cu(II) complexes with symmetric bisoxime ligands have been studied for their fluorescence properties [10].

Compared with symmetric salen-type bisoxime ligands, the composition (R¹-CH=NO(CH₂)_nON=CH-R²) is rather unusual. A selective synthesis of asymmetrical salen-type bisoxime ligands is important because the electronic and steric effects of the ligands on salen-metal-assisted catalysis may be controlled by introduction of different substituents into the two benzene rings [11]. The asymmetric configuration would offer opportunities for a greater structural variation and infinite coordination polymers, which would be expected to lead to novel characteristics. Further, this change could create better ways to control polymer-

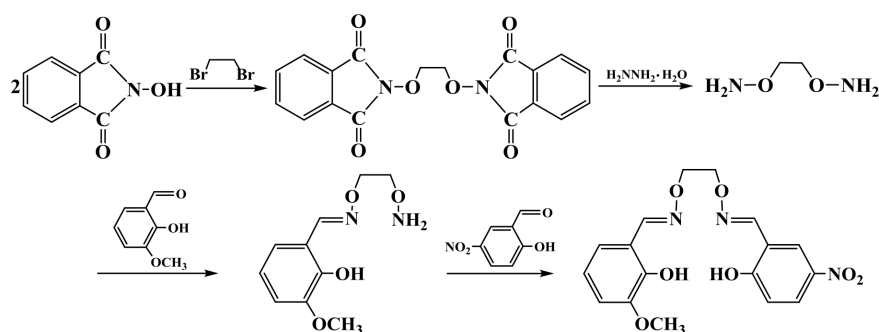
ization in the context of the infinite coordination polymer structures (different functionality allows to use different metals in the polymerization process) [12]. It has been reported that metal complexes derived from asymmetric salen ligands sometimes exhibit better enantioselectivities when compared with their symmetric counterparts [13]. In order to study the structural features and spectral characteristics of transition metal complexes with asymmetric salen-type bisoxime ligands, we herein report a supramolecular complex [CuL(H₂O)] with an asymmetric salen-type bisoxime ligand.

Experimental Section

Materials and physical measurements

2-Hydroxy-5-nitrobenzaldehyde and 2-hydroxy-3-methoxybenzaldehyde were purchased from Aldrich and used without further purification. The other reagents and solvents were of analytical grade from Tianjin Chemical Reagent Factory.

Elemental analysis for Cu was carried out by an IRIS ER/S-WP-1 ICP atomic emission spectrometer, C, H and N analyses with a VarioEL V3.00 automatic elemental analyzer. IR spectra were recorded on a Vertex70 FT-IR spectrophotometer, with samples prepared as KBr (500–4000 cm⁻¹) and CsI (100–500 cm⁻¹) pellets. UV/Vis ab-



Scheme 1. The synthetic route to the asymmetric salen-type bisoxime ligand.

sorption spectra were recorded on a Shimadzu UV-2550 spectrometer. TG-DTA analyses were carried out at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ on a ZRY-1P thermoanalyzer. ^1H NMR spectra were recorded on a Mercury-400B spectrometer. The crystal structure was determined on a Rigaku Saturn CCD area detector. Melting points were measured by the use of a $\times 10$ microscopic melting point apparatus made by Beijing Taike Instrument Limited Company, and are uncorrected.

Preparation of $[\text{H}_2\text{L}]$

The synthetic route to the ligand is shown in Scheme 1.

1,2-Bis(phthalimidooxy)ethane was prepared by an analogous method reported earlier [10].

1,2-Bis(aminooxy)ethane was prepared by a similar method [14]. Yield: 77 %. Analysis for $\text{C}_2\text{H}_8\text{N}_2\text{O}_2$: calcd. C 26.08, H 8.76, N 30.42; found C 25.98, H 8.90, N 30.37.

3-Methoxysalicylaldehyde *O*-(1-ethyloxyamide)oxime

A solution of 1,2-bis(aminooxy)ethane (0.98 g, 10.6 mmol) in ethanol (10 mL) was added to a solution of 2-hydroxy-3-methoxybenzaldehyde (0.806 g, 5.3 mmol) in ethanol (20 mL), and the mixture was heated at $50\text{--}55\text{ }^{\circ}\text{C}$ for 5 h. The solution was concentrated *in vacuo*, and the residue was purified by column chromatography (SiO_2 , chloroform-ethyl acetate 50 : 3) to afford crystals of the monooxime compound. Yield 72 %. M. p. $96\text{--}97\text{ }^{\circ}\text{C}$. – ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 3.91 (s, 3H), 3.97 (t, $J = 4.4\text{ Hz}$, 2H), 4.37 (t, $J = 4.4\text{ Hz}$, 2H), 5.52 (brs, 2H), 6.81 (dd, $J = 7.7, 1.6\text{ Hz}$, 1H), 6.86 (t, $J = 7.7\text{ Hz}$, 1H), 6.91 (dd, $J = 7.7, 1.6\text{ Hz}$, 1H), 8.23 (s, 1H), 9.87 (s, 1H). – Analysis for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_4$ (226.23): calcd. C 53.09, H 6.24, N 12.38; found C 52.90, H 6.39, N 12.21.

4-Nitro-6'-methoxy-2,2'-(ethylenedioxybis(nitrilomethylidene))diphenol (H_2L)

A solution of 3-methoxysalicylaldehyde *O*-(1-ethyloxyamide)oxime (0.452 g, 2 mmol) in ethanol (20 mL) was added to a solution of 2-hydroxy-5-nitrobenzaldehyde

(0.334 g, 2 mmol) in ethanol (20 mL), and the mixture was heated at $50\text{--}55\text{ }^{\circ}\text{C}$ for 6 h. After cooling to r. t., a colorless precipitate was collected on a suction filter to give a colorless powder unlike the yellowish H_2salen analogs. Yield 80 %. M. p. $129.5\text{--}130.5\text{ }^{\circ}\text{C}$. – ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 3.92 (s, 3H), 4.30 (t, $J = 4.4\text{ Hz}$, 2H), 4.37 (t, $J = 4.4\text{ Hz}$, 2H), 6.80 (dd, $J = 7.7, 1.6\text{ Hz}$, 1H), 6.85 (t, $J = 7.6\text{ Hz}$, 1H), 6.92 (dd, $J = 7.6, 1.6\text{ Hz}$, 1H), 6.99 (d, $J = 7.6\text{ Hz}$, 1H), 7.17 (dd, $J = 7.6, 1.6\text{ Hz}$, 1H), 7.29 (t, $J = 7.6\text{ Hz}$, 1H), 8.24 (s, 2H), 9.88 (s, 2H). – Analysis for $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_7$ (375.33): calcd. C 54.40, H 4.57, N 11.20; found C 54.26, H 4.66, N 11.10.

Preparation of $[\text{CuL}(\text{H}_2\text{O})]$

A solution of Cu(II) acetate hydrate (0.0199 g, 0.1 mmol) in ethanol (10 mL) was added dropwise to a solution of H_2L (0.0375 mg, 0.1 mol) in methanol-MeCN (1 : 2) (15 mL) at r. t. The color of the solution turned to brown immediately. The mixture was filtered, and the filtrate was allowed to stand at r. t. for about three weeks. The solvent was partially evaporated, and several pale-brown needle-shaped single crystals suitable for X-ray crystallographic analysis were obtained. Yield 24 %. Analysis for $\text{C}_{17}\text{H}_{17}\text{CuN}_3\text{O}_8$ (454.88): calcd. C 44.89, H 3.77, N 9.24, Cu 13.97; found C 44.62, H 3.86, N 9.08, Cu 13.95.

X-Ray crystallography of $[\text{CuL}(\text{H}_2\text{O})]$

The crystal data and parameters pertinent to data collection and structure refinement for $[\text{CuL}(\text{H}_2\text{O})]$ are given in Table 1. The single crystal of $[\text{CuL}(\text{H}_2\text{O})]$ was placed on a Rigaku Saturn CCD area detector diffractometer. The reflections were collected using graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at $143(2)\text{ K}$. The structure was solved using the program SHELXS and difference Fourier techniques, and refined by full-matrix least-squares methods on F^2 using SHELXL. All hydrogen atoms were added in calculated positions.

CCDC 832647 contains the supplementary crystallographic data for this paper. These data can be obtained free

Table 1. Crystal data and structure refinement for [CuL(H₂O)].

Molecular formula	C ₁₇ H ₁₇ CuN ₃ O ₈
Molecular weight, g mol ⁻¹	454.88
Color, habit	pale-brown, needle-like
Crystal size, mm ³	0.32 × 0.08 × 0.06
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	13.094(3)
<i>b</i> , Å	7.5888(15)
<i>c</i> , Å	18.410(4)
β, deg	99.82(3)
<i>V</i> , Å ³	1802.4(6)
<i>Z</i>	4
<i>T</i> , K	143(2)
<i>D</i> _{calcd} , g cm ⁻³	1.68
μ(MoKα), mm ⁻¹	1.3
<i>F</i> (000), e	932
<i>hkl</i> range	±17, ±9, ±24
θ range for data collection, deg	2.52–27.89
Reflections collected / unique / <i>R</i> _{int}	21053 / 4283 / 0.0524
Data / restraints / parameters	4283 / 2 / 272
Final <i>R</i> ₁ / <i>wR</i> ₂ indices [<i>I</i> ≥ 2σ(<i>I</i>)] ^{a,b}	0.0574 / 0.1424
<i>R</i> ₁ / <i>wR</i> ₂ indices (all data) ^{a,b}	0.0659 / 0.1482
Goodness-of-fit (<i>F</i> ²) ^c	1.096
Largest diff. peak / hole, e Å ⁻³	0.96 / -1.09

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$; ^c $GoF = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

Table 2. Selected bond lengths (Å) and bond angles (deg) for [CuL(H₂O)] with estimated standard deviations in parentheses.

Cu1–O2	1.926(2)	Cu1–O5	1.961(2)
Cu1–N2	1.990(3)	Cu1–N1	2.006(3)
Cu1–O8	2.260(2)		
O5–Cu1–N1	168.40(10)	O2–Cu1–N2	169.30(9)
O5–Cu1–N2	87.65(10)	O2–Cu1–N1	89.52(10)
O2–Cu1–O5	83.35(9)	N2–Cu1–N1	98.40(11)
O2–Cu1–O8	93.92(9)	O5–Cu1–O8	96.48(9)
N2–Cu1–O8	92.83(10)	N1–Cu1–O8	93.11(10)

of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

The ligand H₂L is remarkably soluble in polar aprotic solvents such as DMF, DMSO and MeCN, and also soluble in ethanol, methanol, THF, CH₂Cl₂ and CHCl₃, but insoluble in Et₂O, *n*-hexane, water, and petroleum ether. The Cu(II) complex is only soluble in DMF and DMSO, but insoluble in the other solvents mentioned above. The molar conductivities in DMF solution indicate that H₂L and the Cu(II) complex are non-electrolytes [15].

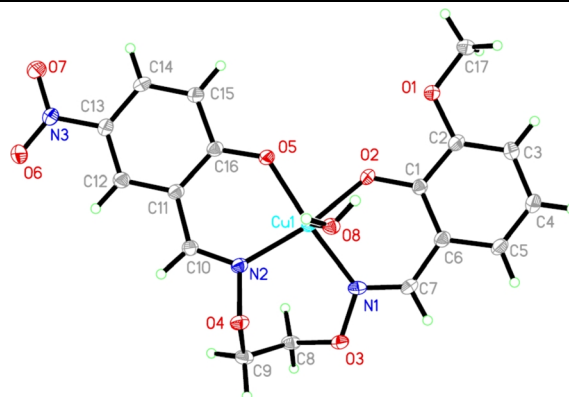


Fig. 1 (color online). ORTEP drawing of the Cu(II) complex with the atom numbering. Displacement ellipsoids for non-H atoms are drawn at the 30 % probability level.

The crystal structure of [CuL(H₂O)]

The crystal structure and atom numbering of the Cu(II) complex [CuL(H₂O)] is shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 2. The Cu(II) complex crystallizes in the monoclinic space group *P*2₁/*c* with *Z* = 4. The molecular structure of the Cu(II) complex consists of one Cu(II) atom, one L²⁻ unit, and one coordinated water molecule. The value of $\tau = 0.015$ [16] clearly indicates that the environment of the Cu(II) atom could be best described as a square-pyramidal topology with the metal atom being penta-coordinated. The two phenolic oxygen atoms (O2 and O5) and the two oxime nitrogen atoms (N1 and N2) of the L²⁻ unit constitute the basal plane (Cu1–O2, 1.926(2); Cu1–O5, 1.961(2); Cu1–N1, 2.006(3) and Cu1–N2, 1.990(3) Å), and one O atom (O8) of the coordinated water molecule is occupying the axial position (Cu1–O8, 2.260(4) Å). It is obvious that the axial bond length Cu1–O8 is longer than all of the others which form the basal plane. The bond lengths of Cu–N and Cu–O are similar as those of analogous Cu(II) complexes with symmetric salen-type bisoxime ligands [6, 17].

The four coordinated atoms in the basal plane deviate slightly from the mean plane, with O2 and N2 above on average by 0.029(2) and 0.025(2) Å, and O5 and N1 below on average by 0.029(2) and 0.025(2) Å, respectively. These deviations indicate a very minor distortion of the basal plane toward a tetrahedron. The Cu(II) atom is displaced by 0.138(3) Å from the mean plane. The dihedral angle between the planes O2–Cu1–N1 and O5–Cu1–N2 is 11.38°. Although the molecule of the ligand H₂L contains two different

D–H...A	D–H	H...A	D...A	D–H...A	Symmetry code
O8–H8A...O5	0.81	2.00	2.784(3)	165	$-x+2, -y+2, -z$
O8–H8B...O1	0.81	2.09	2.853(3)	158	$-x+2, -y+2, -z$
O8–H8B...O2	0.81	2.54	3.016(3)	119	$-x+2, -y+2, -z$
C10–H10...O6	0.95	2.36	3.238(3)	154	$-x+1, -y+1, -z$
C12–H12...O6	0.95	2.47	3.326(3)	150	$-x+1, -y+1, -z$
C17–H17C...O7	0.98	2.68	3.644(3)	169	$x, -y+3/2, z-1/2$
C8–H8D...O2	0.99	2.51	3.518(3)	158	$-x+2, -y+1, -z$
C8–H8D...O5	0.99	2.71	3.460(3)	133	$-x+2, -y+1, -z$
C9–H9A...O1	0.99	2.70	3.525(3)	141	$-x+2, y+1/2, -z+1/2$
C5–H5...O7	0.95	2.36	3.216(3)	150	$x+1, -y+3/2, z+1/2$
C8–H8C...O4	0.99	2.71	3.528(3)	140	$-x+2, -y+1, -z$
C9–H9B...O8	0.99	2.60	3.523(3)	156	$-x+2, y+1/2, -z+1/2$
C17–H17B...O3	0.98	2.60	3.509(3)	155	$x, -y+3/2, z-1/2$

Table 3. Hydrogen bonding distances (Å) and angles (deg).

units of salicylaldehyde [sal(1) and sal(2)], they have a similar degree of distortion. The mean plane (N₂O₂) and sal(1) (N1–C7–C6–C1–O2) have a dihedral angle of 15.48°, and the dihedral angle of sal(2) (N2–C10–C11–C16–O5) and the mean plane is 16.56°. In addition, the ethylenedioxiime carbon atoms (C8 and C9) in the Cu(II) complex are buckled asymmetrically from the Cu1–N1–N2 plane.

Supramolecular structure of [CuL(H₂O)]

The introduction of a coordinated water molecule in the Cu(II) complex leads to the assembly of the [CuL(H₂O)] units by intermolecular hydrogen bonds. As illustrated in Fig. 2, three pairs of intermolecular hydrogen bonds, O8–H8A...O5, O8–H8B...O1 and O8–H8B...O2 are formed. One of the protons (–O8H8A) of the coordinated water molecule is hydrogen-bonded to one of the μ -phenoxo oxygen atoms (O5) of the L^{2–} unit. The other one (–O8H8B) is hydrogen-bonded to the other μ -phenoxo oxygen atom (O2) and the methoxy oxygen atom (O1) of the L^{2–} unit, respectively (Table 3). Consequently, these hydrogen bonding interactions have stabilized a pair of

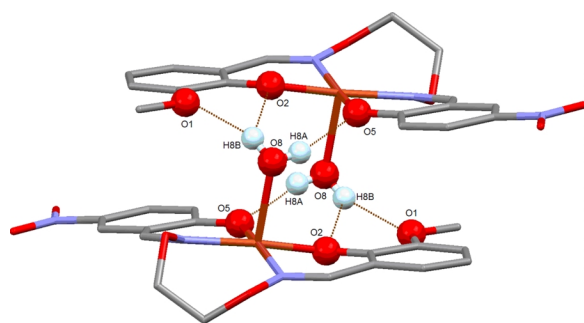


Fig. 2 (color online). A dimeric unit of the Cu(II) complex formed by intermolecular hydrogen bonds.

the Cu(II) complex molecules to form a dimer with the nearest Cu...Cu distance of 4.948(4) Å [18].

Moreover, every dimer is further interlinked with four other adjacent dimers into an infinite 2D supramolecular structure in the crystallographic *ab* plane by intermolecular C10–H10...O6, C12–H12...O6 and C17–H17C...O7 hydrogen bonds between the –C10H10 units of the oxime groups, the –C12H12 units of the benzene rings and the –C17H17C units of the methoxy groups and the nitro oxygen atoms (O6 and O7) of the L^{2–} unit, respectively (Fig. 3) [19, 20].

As shown in Fig. 4, the dimers are interlinked by C8–H8D...O2, C8–H8D...O5 and C9–H9A...O1 hydrogen bonding interactions into a 1D structure along the *b* axis. This linkage is further stabilized by the π ... π stacking interactions of the two benzene rings (C1–C6 and C11–C16) of neighboring dimers with a centroid-centroid distance of 3.989(4) Å. In addition, the adjacent chains along the *b* axis are held together to form an infinite 2D supramolecular structure by C5–H5...O7 hydrogen bonding interactions (Fig. 5). The dimers are further interlinked by six pairs of C8–H8C...O4, C9–H9B...O8 and C17–H17B...O3 hydrogen bonding interactions to form another 2D structure (Fig. 6) [21].

To sum up, with the help of intermolecular O–H...O and weak C–H...O hydrogen-bonding and π ... π stacking interactions, the crystal structure shows a self-assembled 3D supramolecular aggregate.

IR spectra of [H₂L] and [CuL(H₂O)]

The IR spectra of the free ligand H₂L and its corresponding Cu(II) complex exhibit various vibration bands in the 100–4000 cm^{–1} region (Table 4). The free ligand H₂L shows a broad characteristic band of

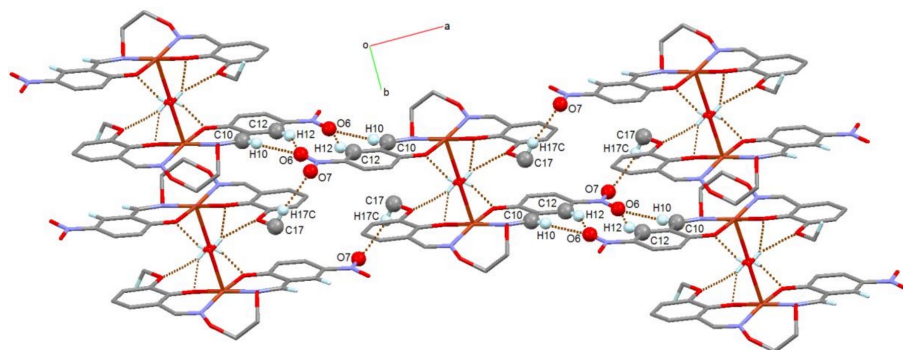


Fig. 3 (color online). Projection of the infinite 2D supramolecular network of the Cu(II) complexes onto the *ab* plane (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

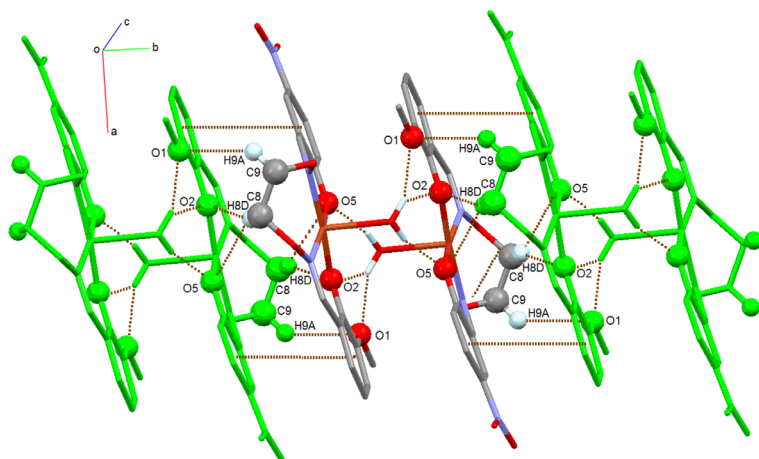


Fig. 4 (color online). View of the infinite chain motif of the Cu(II) complexes along the *b* axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

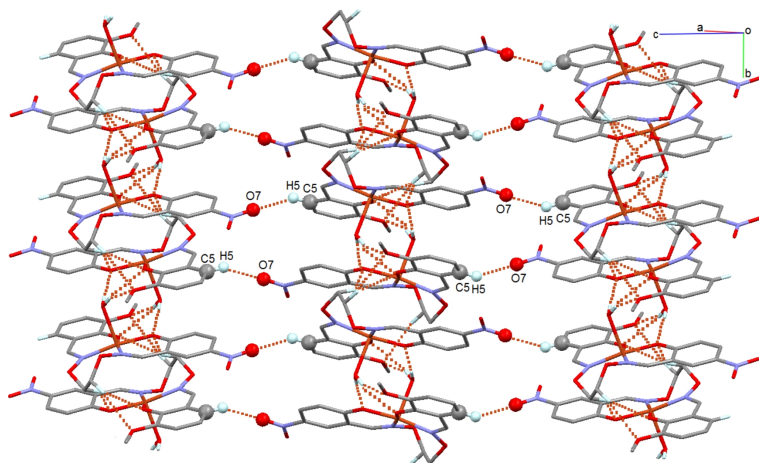


Fig. 5 (color online). View of the infinite 2D supramolecular network of the Cu(II) complexes on the *bc* plane (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

the OH group at 3466 cm^{-1} . The disappearance of this band in the FT-IR spectrum of the Cu(II) complex is indicative of the fact that the phenolic OH group of the tetradentate ligand H_2L has been deprotonized and coordinated to the Cu(II) atoms [17]. The Ar–O stretching frequency appears as a strong band within the

$1263\text{--}1213\text{ cm}^{-1}$ range as reported for similar salen-type ligands [22–24]. This band occurs at 1269 cm^{-1} for H_2L , and at 1231 cm^{-1} for the Cu(II) complex. The Ar–O stretching band is shifted to lower frequency, indicating that Cu–O bonds are formed between the Cu(II) atom and the oxygen atoms of the phenolic

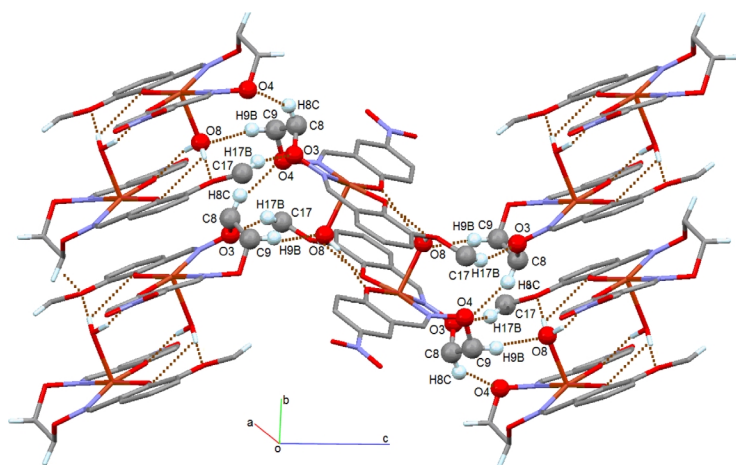


Fig. 6 (color online). Projection of the infinite 2D supramolecular network of the Cu(II) complexes onto the *bc* plane (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

Table 4. Selected FT-IR bands for the ligand and its Cu(II) complex (cm^{-1}).

Compound	$\nu(\text{PhO}-\text{H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{Ar}-\text{O})$	$\nu(\text{Cu}-\text{N})$	$\nu(\text{Cu}-\text{O})$
H_2L	3466	1612	1269	—	—
Complex	—	1608	1231	467	412

groups. The free ligand H_2L exhibits a characteristic $\text{C}=\text{N}$ stretching band at 1608 cm^{-1} , which is shifted in the Cu(II) complex to 1612 cm^{-1} indicating a weak π -acceptor ability of the deprotonated ligand [25].

The infrared spectrum of the Cu(II) complex shows the expected absorption bands at *ca.* 3422 , 1630 and 537 cm^{-1} , assigned to the effect of the coordinated water molecule, as is substantiated by the crystal structure [17].

The far-infrared spectrum of the Cu(II) complex was obtained in the region $500\text{--}100\text{ cm}^{-1}$ in order to identify frequencies due to the Cu–O and Cu–N bonds. The spectrum shows $\nu(\text{Cu}-\text{N})$ and $\nu(\text{Cu}-\text{O})$ vibration frequencies at 467 and 412 cm^{-1} [25]. As pointed out by Percy and Thornton [26], the metal-oxygen and metal-nitrogen frequency assignments are at times very difficult.

UV/Vis spectra of H_2L and $[\text{CuL}(\text{H}_2\text{O})]$

The UV/Vis absorption spectra of H_2L and its Cu(II) complex $[\text{CuL}(\text{H}_2\text{O})]$ were determined in $5.0 \times 10^{-5}\text{ mol L}^{-1}$ DMF solution (Fig. 7). The spectrum of the salen-type bisoxime ligand H_2L consists of two relatively intense bands centered at 273 and 316 nm , assigned to the $\pi-\pi^*$ transitions of the benzene ring of the salicylaldehyde and oxime groups [27]. Upon coordination of the ligand, the absorption band at

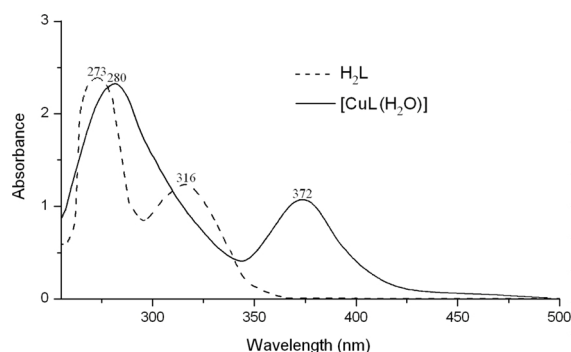


Fig. 7. UV/Vis absorption spectra of H_2L and the Cu(II) complex in dilute DMF solution at room temperature ($c = 5 \times 10^{-5}\text{ mol L}^{-1}$).

about 316 nm disappears, which indicates that the oxime nitrogen atom is involved in coordination to the Cu(II) atom [28]. The intraligand $\pi-\pi^*$ transition of the benzene ring of salicylaldehyde is slightly shifted in the Cu(II) complex and appears at 280 nm . The new band observed at 372 nm for the Cu(II) complex is assigned to an $\text{L} \rightarrow \text{M}$ charge-transfer transition which is characteristic of a transition metal complex with N_2O_2 coordination sphere [29].

Thermal properties

The thermal decomposition of the Cu(II) complex can mainly be divided into two stages. First, the initial weight loss occurs in the range of 128.0 to $145.4\text{ }^\circ\text{C}$, corresponding to an endothermic peak, and the TG curve shows that the weight loss corresponding to this temperature range is 4.3% that roughly coincides with the value of 4.0% , calculated for the loss of one co-

ordinated water molecule; The Cu(II) complex has no melting point. The Cu(II) complex is thermally more stable than its ligand H₂L. Its second weight loss starts at around 278.2 °C. Subsequently, continuous mass loss was observed up to 650 °C. At this temperature, CuO is formed. The total mass loss found (80.6 %) was approximately consistent with that calculated (82.5 %).

Conclusion

We have reported the synthesis and structural characterization of a supramolecular Cu(II) complex with an asymmetric salen-type bisoxime ligand H₂L. The

Cu(II) atom in the complex is penta-coordinated by one bisoxime L²⁻ unit and one water molecule. The new complex contains two different salicylaldehyde molecules which could be helpful for the development of new metal-organic complexes and be worth to study their potential value of applications.

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