

# Synthesis, Spectral, Thermal, and Magnetic Studies of Cobalt(II), Nickel(II), Copper(II), Zinc(II), and Cadmium(II) Complexes with N<sub>2</sub>O<sub>2</sub> Donor Groups<sup>1</sup>

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**Abstract**—A new Schiff base ligand was prepared by condensation of 2-hydroxy-4-methoxybenzaldehyde with 1,2-propanediamine. The ligand and its metal complexes were characterized by elemental analysis, FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR, magnetic moment, molar conductance, UV-Vis, SEM and thermal analysis (TGA). The molar conductance measurements indicated that all the metal complexes were non-electrolytes. IR spectra showed that ligand (L) behaves as a neutral tetradentate ligand and binds to the metal ions by the two azomethine nitrogen atoms and two phenolic oxygen atoms. The electronic absorption spectra and magnetic susceptibility measurements indicated square planar geometry for the Ni(II) and Cu(II) complexes while other metal complexes showed tetrahedral geometry. Also the surface morphology of the complexes was studied by SEM.

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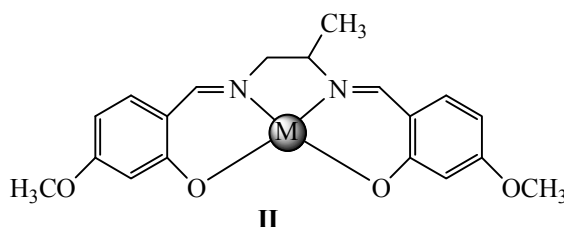
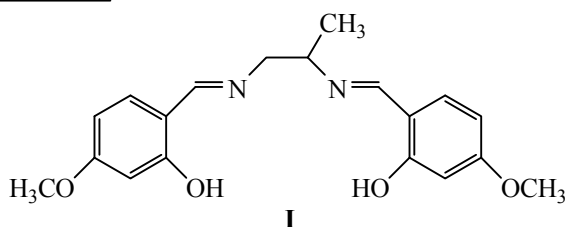
## INTRODUCTION

The Schiff base ligands are one of the most widely used ligands due to the ease of formation and remarkable versatility, and therefore they have played an important role in the development of coordination chemistry because they readily form stable complexes with various transition metals. The research field dealing with Schiff base metal complexes is very broad due to their potential interest for a number of interdisciplinary studies in bioinorganic chemistry, catalysis, and magnetochemistry [1–5].

Tetradentate salen type Schiff base ligands derived from salicylaldehyde and diamines form complexes with transition metal ions, which were investigated using different chemical techniques. The composition of complexes was 1 : 1 [M : L] when the Schiff base

ligands were coordinated to the metal ion in a tetradentate manner with N<sub>2</sub>O<sub>2</sub> donor sites of the two *O*-phenol and two *N*-azomethine [5, 6]. Schiff base transition metal complexes have been extensively studied because of their potential use as catalysts in a wide range of oxidation reactions [7–8].

In recent years many cobalt, copper, nickel and zinc complexes of Schiff bases were prepared and characterized by several techniques [9–11]. Some transition metals such as Cu, Co, and Cd are both vital and toxic for many biological systems [12–14]. In the present study the synthesis of a new Schiff base ligand **I** and its metal complexes **II** with Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) as well as their investigation by thermal, magnetic and spectroscopic techniques is reported.



<sup>1</sup> The text was submitted by the author in English.

**Table 1.** Analytical and physical data of the ligand and their complexes

Compound	mp	$\mu_{\text{eff}}$ , BM	Colour	Analysis found (calculated), %				$\Lambda_m$ , $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$
				C	H	N	M	
<b>I</b>	122		Yellow	66.54 (66.65)	6.43 (6.48)	8.30 (8.18)		
Co(I)	234	2.97	Black brown	57.31 (57.15)	5.12 (5.05)	6.94 (7.02)	14.60 (14.76)	4.7
Ni(I)	271	Dia.	Brown	57.05 (57.18)	5.15 (5.05)	6.97 (7.02)	14.66 (14.71)	4.3
Cu(I)	267	1.81	Dark brown	56.39 (56.50)	4.80 (4.99)	7.09 (6.94)	15.65 (15.73)	4.9
Zn(I)	240	Dia.	Orange	55.96 (56.24)	4.90 (4.97)	7.04 (6.90)	16.07 (16.12)	4.1
Cd(I)	121	Dia.	Light yellow	50.24 (50.40)	4.35 (4.45)	6.37 (6.19)	24.94 (24.83)	4.2

## RESULTS AND DISCUSSION

The analytical and physical data of ligand **I** and its complexes are listed in Table 1. The Schiff base is soluble in EtOH, MeOH, dichloromethane, and diethyl ether. All the metal complexes are insoluble in EtOH, acetone or chloroform, but soluble in DMF and DMSO. The elemental analysis data are consistent with the calculated empirical formulae for each compound.

**Infrared spectra.** The FTIR spectral data of ligand **I** and its metal complexes are given in Table 2. The spectrum of the free ligand exhibited a band at  $1630 \text{ cm}^{-1}$  belonging to the  $\nu(\text{C}=\text{N})$  vibrations. This band is shifted to lower frequencies in the complexes, indicating that the nitrogen atom of the azomethine group is coordinated to the metal ion [15]. The  $\nu(\text{OH})$  band in the free ligand at  $3300 \text{ cm}^{-1}$  disappears in the complexes due to deprotonation of the donor and involvement of oxygen in bonding with the metal ion. In the complexes, weak bands in the 470–510 and

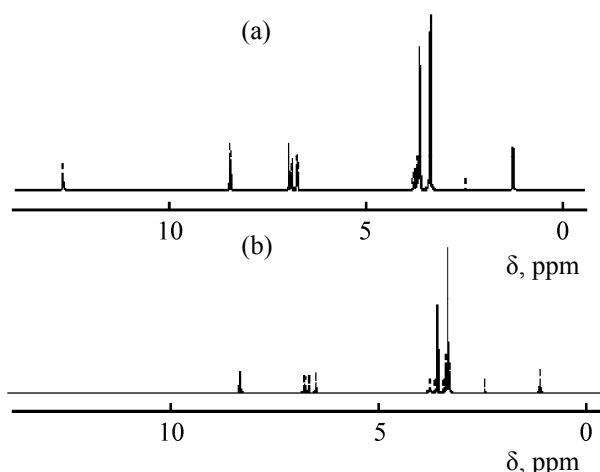
$420\text{--}455 \text{ cm}^{-1}$  range can be attributed to M–N and M–O respectively [16, 17].

**NMR spectra.**  $^1\text{H}$  NMR spectra of ligand **I** and its Zn(II) are shown in Fig. 1. The OH singlet in **I** appears at  $\delta$  12.75 and is lacking in the complex (Fig. 1a, cf. [18, 19]). All signals of the complex are slightly shifted upfield due to coordination of the N and O atoms of **I** with metal ion.

**Conductance measurements.** The complexes were dissolved in DMF and the molar conductivities of  $10^{-3} \text{ M}$  of their solutions at  $25 \pm 2^\circ\text{C}$  were measured (Table 1). The values of molar conductance fall in the range of  $4.1\text{--}4.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  indicating that these complexes are non-electrolytes.

**Magnetic susceptibility and electronic spectra measurements.** The UV-Vis spectra of the ligand and the complexes were recorded in DMF solution in the wavelength range from 200 to 800 nm. The spectra showed a sharp and intense band at 270 nm which is attributed to  $\pi\text{--}\pi^*$  transition within the benzene ring of the ligand molecule. The two bands observed at 291 and 346 nm in the free ligand are reasonably accounted for  $\pi\text{--}\pi^*$  and  $n\text{--}\pi^*$  transitions for the phenolic-OH and azomethine moieties, respectively [20].

The electronic spectra of Co(II) complexes show peaks at 403–430 nm, which can be tentatively assigned to  $^4A_2(F) \rightarrow ^4T_1(P)$  transition for the tetrahedral geometry [21]. The Ni(II) complex shows a band at 534 nm that may be assigned to the  $^1A_{1g} \rightarrow ^1A_{2g}$  transition, indicating a square-planar environment around the metal ion which is confirmed by the diamagnetic properties of the complex [21, 22]. The spectrum of the Cu(II) complex shows  $d\text{--}d$  bands at 570 and 498 nm, assignable to  $^2B_{1g} \rightarrow ^2A_{1g}$  and  $^2B_{1g} \rightarrow ^2E_{1g}$  transitions, respectively, characteristic of a square-planar geometry of the complex [23, 24]. The Cd(II) and Zn(II) complexes do not exhibit any  $d\text{--}d$



**Fig. 1.** (a)  $^1\text{H}$  NMR spectrum of Schiff Base ligand and (b) Zn(II) complex.

**Table 2.** IR spectral data of the Schiff base ligand **I** and its complexes

Compounds	$\nu(\text{O}-\text{H})$	$\nu(\text{C}-\text{H})$	$\nu(\text{C}-\text{H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
Ligand	3300 s	3030 w	2960 w	1630 s	1195 w		
$\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{Co}$		3045 w	2860 w	1622 s	1160 w	510 w	455 w
$\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{Ni}$		3020 w	2930 w	1620 s	1160 w	510 w	455 w
$\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{Cu}$		3010 w	2925 w	1618 s	1130 m	505 w	440 w
$\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{Zn}$		3015 w	2915 w	1610 s	1155 w	480 w	420 w
$\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{Cd}$		3050 w	2865 w	1615 s	925 m	470 w	420 w

**Table 3.** Thermogravimetric data of Schiff base metal complexes

Compounds	Molecular weight	TG range, °C	DTG <sub>max</sub> , °C	$n^a$	Weight loss, % found (calculated)	Assignment	Metallic residue, %: found (calculated)
$\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{Co}$	399.312	50–200	40, 173	2	5.61 (5.53)	Loss of $\text{NH}_2$ , $3\text{H}_2$	CoO 18.48 (18.76)
		200–250	204	1	7.12 (7.02)	Loss of CO	
		250–400	316	1	10.85 (10.78)	Loss of $\text{C}_2\text{H}_3\text{O}$	
		400–550	512	1	14.58 (14.54)	Loss of $\text{C}_2\text{H}_4\text{NO}$	
		550–900		1	43.37 (43.36)	Loss of $\text{C}_{14}\text{H}_5$	
$\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{Ni}$	399.072	50–200	56	1	4.56 (4.52)	Loss of $\text{NH}_2$ , $\text{H}_2$	NiO 18.75 (18.72)
		200–450	385	1	32.25 (32.11)	Loss of $\text{C}_6\text{H}_{10}\text{NO}_2$	
		400–900	457	1	44.43 (44.65)	Loss of $\text{C}_{13}\text{H}_6\text{O}$	
$\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{Cu}$	403.925	50–400	313	1	55.53 (55.52)	Loss of $\text{C}_{15}\text{H}_{12}\text{O}_2$	CuO 19.74 (19.69)
		400–900			24.73 (24.79)	Loss of $\text{C}_4\text{H}_8\text{N}_2\text{O}$	
$\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{Zn}$	405.77	50–200	181	1	4.34 (4.45)	Loss of $\text{NH}_2$ , $\text{H}_2$	ZnO 20.09 (20.06)
		200–350	321	1	7.32 (7.40)	Loss of NO	
		350–900	390, 563	2	68.26 (68.12)	Loss of $\text{C}_{19}\text{H}_{16}\text{O}_2$	
$\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{Cd}$	452.790	50–350	305	1	6.30 (6.63)	Loss of CO, $\text{H}_2$	CdO 28.58 (28.36)
		350–900			65.16 (65.00)	Loss of $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2$	

<sup>a</sup>( $n$ ) number of decomposition step.

transitions due to the completely filled  $d^{10}$  electronic configuration, however, often exhibit charge transfer spectra [25].

Magnetic susceptibility measurements carried out at 25°C provide sufficient data to characterize the structure of the metal complexes. The magnetic moment value of Co(II) complex is 2.97 BM suggesting the tetrahedral geometry. Ni(II) complex is diamagnetic showing square planar geometry. The Cu(II) complex magnetic moment of 1.81 BM is indicative of square planar geometry around the metal ion. The Zn(II) and Cd(II) complexes are diamagnetic as expected for  $d^{10}$  systems. A tetrahedral structure is suggested for these complexes.

**Thermal analyses.** Thermal data of the complexes are given in Table 3. The weight losses for each

chelate were calculated within the corresponding temperature ranges (Fig. 2).

The thermogram of Co(II) complex shows five decomposition steps in the temperature range 50–900°C. The first step is the loss of  $\text{NH}_2$  and three  $\text{H}_2$  molecules with weight loss of 5.61% (calculated 5.53%). The second steps of decomposition occurs at 200–250°C correspond to the loss of CO molecules with a weight loss of 7.12% (calculated 7.02%). The third stages found in the range 250–400°C with a weight loss of 10.85% (calculated 10.78%), was assigned to removal of  $\text{C}_2\text{H}_3\text{O}$  molecule. The subsequent (fourth and fifth) stages involve the loss of  $\text{C}_2\text{H}_4\text{NO}$  and  $\text{C}_{14}\text{H}_5$  molecules with a weight loss of 14.58% (calculated 14.54%) and 43.37% (calculated 43.36%) for Co(II) complexes. Above 900°C the substance exists in the form of the metal oxide.

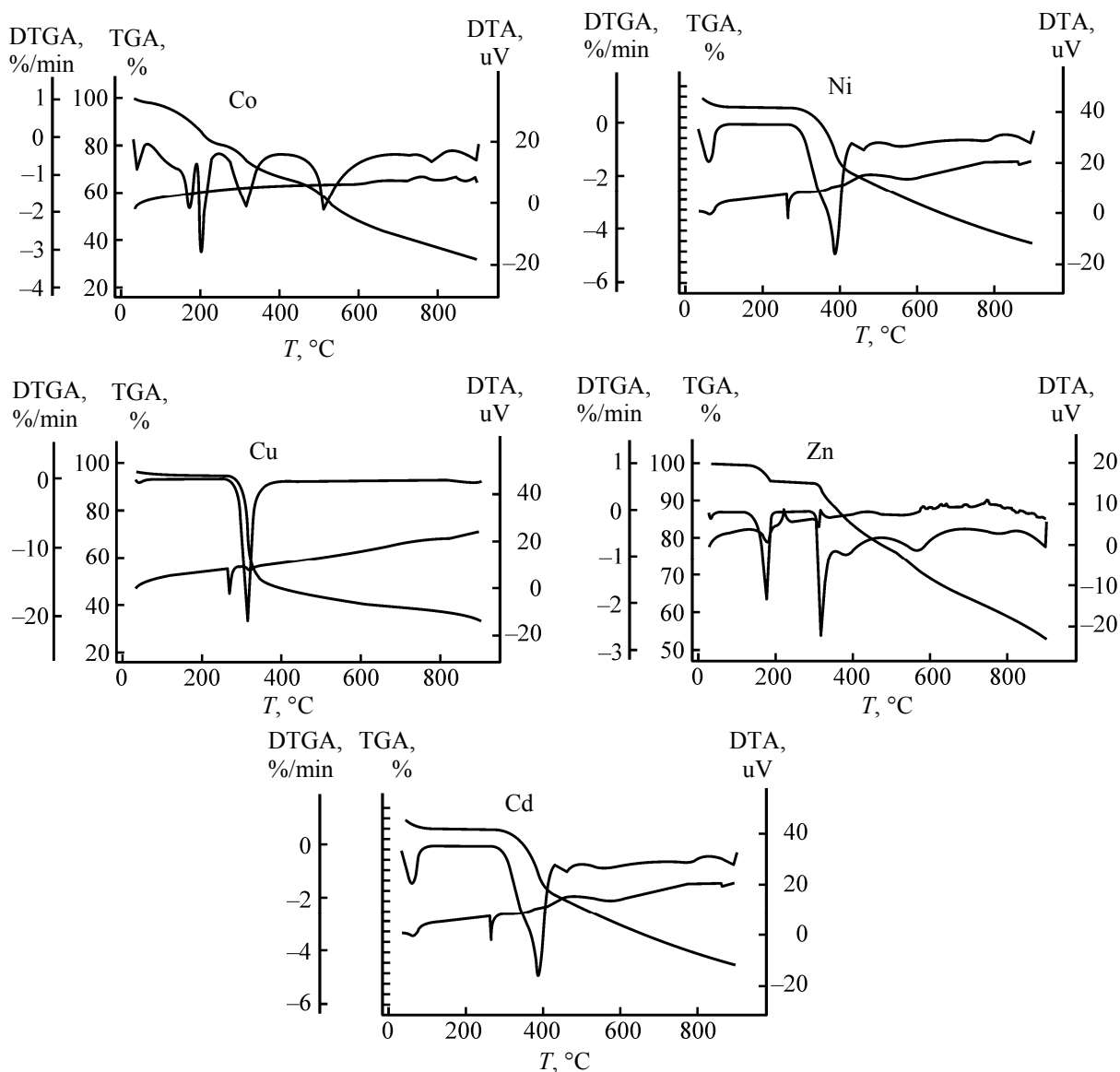


Fig. 2. TGA-DTA curves Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes.

The TGA curve of the Ni(II) complex shows three steps of decomposition in the same temperature range. The first step in the 50–200°C corresponds to the loss of  $\text{NH}_2$  and  $\text{H}_2$  molecule with estimated weight loss 4.56% (calculated 4.52%). The second step observed in the range 50–450°C with weight loss of 32.25% (calculated 32.11%), was assigned to the partial decomposition of  $\text{C}_6\text{H}_{12}\text{NO}_2$  molecule. The final step found in the range 400–900°C was assigned to the removal of the Schiff base moiety leaving NiO as residue.

Cu(II) complex decomposed in two main steps. The first step observed in the range 50–400°C with a weight loss of 55.53%, was assigned to the partial

decomposition of the Schiff base moiety as  $\text{C}_{15}\text{H}_{12}\text{O}_2$  molecule. The final step is represented by the removal of complete organic ligand moiety in the 400–900°C ranges with the formation of CuO as the final product.

The thermogram of Zn(II) complex shows three decomposition steps in the temperature range 50–900°C. The first step occurring in the range 50–200°C shows a weight loss 4.34% corresponding to loss of  $\text{NH}_2$  and  $\text{H}_2$  molecule. The second step found in the range 200–350°C, with a weight loss of 7.32%, was assigned to the removal of NO molecule. The final decomposition step is represented by the removal of complete organic ligand moiety in the 350–900°C ranges with the formation of metal oxide as the final product.

Cd(II) complex decomposed in two main steps. The first step of decomposition in the temperature range 50–350°C shows that a weight loss 6.30% corresponds to loss of CO and H<sub>2</sub> molecule. The final decomposition step is represented by the removal of complete organic ligand moiety in the 350–900°C ranges with the formation of metal oxide as the final product.

**Scanning electron microscope.** In the SEM result of ligand and its transition metal complexes, the original morphology of the Schiff base ligand disappeared and aggregates of amorphous pieces of irregular size appeared. Overall, the SEM results indicated that a complex formation between ligand **I** and metal cations such as Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) was occurred.

### EXPERIMENTAL

**Materials and measurements.** Commercial chemicals and solvents of analytical grade from Merck and Sigma-Aldrich were used. Elemental analysis was performed on a Carlo Erba 1106 elemental analyzer. Magnetic susceptibilities of metal complexes were determined using a Sheerwood Scientific MX Gouy magnetic susceptibility apparatus, and magnetic measurements were carried out using the Gouy method with Hg[Co(SCN)<sub>4</sub>] as calibrant. The FTIR spectra were recorded on a Perkin Elmer Spectrum BX-II spectrophotometer (ATR sampling accessory) in the range 4000–400 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectra in CDCl<sub>3</sub>, DMSO-*d*<sub>6</sub> were obtained on a Bruker 200 MHz spectrometer. Electronic spectral studies were conducted on a Shimadzu 160 UV Visible spectrophotometer in the wavelength region 200–800 nm. Molar conductivity was measured with a WTW LF model 330 conductivity meters, using solutions in DMF. Thermal gravimetric analysis was carried out on a TGA SHIMADZU model 50 thermal gravimetric analyzer.

**Preparation of Schiff base ligand.** A solution of salicylaldehyde (0.608 g, 4 mmol) was dissolved in anhydrous ethanol (30 mL), one drop of glacial acetic acid (catalytic amount, not necessary) and 1,2-propanediamine (0.148 g, 2 mmol) were added. The reaction mixture was refluxed for 4 h under a CaCl<sub>2</sub> drying tube. The resulting yellow solution was cooled to room temperature and evaporated to dryness. The obtained solid was crystallized from dichloromethane/methanol and dried in vacuo. Yield: 1.121 g (82%); mp: 122°C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>), δ, ppm: 12.75 s (1H, OH), 8.50 s (1H, CH=N), 6.99–6.78 m (3H, aromatic), 3.68 s (3H, OMe), 3.81–3.74 m (1H, CH), 3.72–3.71 d

(2H, CH<sub>2</sub>, *J* = 4.38 Hz), 1.30–1.28 d (3H, Me, *J* = 5.68 Hz). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>), δ, ppm: 167.43–165.34 (CH=N), 155.07–115.59 (aromatic), 65.50 (CH), 64.68 (CH<sub>2</sub>), 55.80 (OCH<sub>3</sub>), 20.68 (CH<sub>3</sub>).

**Preparation of Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) Schiff base complexes.** A solution of ligand (1 mmol) in methanol (20 mL) was added to a solution of metal(II) acetate (1 mmol) in methanol (20 mL). The reaction mixture was stirred and then refluxed for 3 h at 70°C. The precipitate was filtered, washed several times with cold ethanol, ether and then dried in vacuo over anhydrous CaCl<sub>2</sub>.

### CONCLUSIONS

As a conclusion, a new Schiff base ligand and its Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) complexes were synthesized and characterized using various spectral techniques. The NMR and IR spectra showed that the ligand coordinated with metal ion through two phenolic oxygen atoms and two azomethine nitrogen atoms. The physical properties, elemental analysis and magnetic susceptibility of the complexes were investigated. The magnetic data indicated that Ni(II), Zn(II), and Cd(II) complexes were diamagnetic, Co(II), and Cu(II) complexes were paramagnetic. Thermal stability of complexes were investigated and evaluated individually by using TGA/DTA. Based on these findings, tetradentate Schiff base ligand **I** containing N<sub>2</sub>O<sub>2</sub> binding site would be useful for the design of chemical sensors, solid-state sensors and phase-transfer catalysis.

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