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## Schiff Bases of Terephthalaldehyde with 2-Aminophenol and 2-Aminothiophenol and Their Metal Complexes

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### ABSTRACT

Terephthalaldehyde on reaction with 2-aminophenol and 2-aminothiophenol yielded a new series of polydentate Schiff's base ligands ( $H_2L^a$  and  $H_2L^b$ ). Dibasic tetradentate coordination of the compounds in their  $[M_2L_2]$  complexes [ $M = Ni(II), Cu(II)$  and  $Zn(II)$ ] has been established on the basis of analytical and spectral data.

**Keywords:** Terephthalaldehyde, Schiff base, imine, metal complexes.

### INTRODUCTION

There has been a steady growth of interest in the synthesis, structure, and reactivity of Schiff bases due to their potential applications in biological modeling, catalysis, design of molecular magnets [1-3] and in the synthesis of important drugs, such as antibiotic, antiallergic, anticancer and antitumor [4,5]. Intramolecular hydrogen bonding between OH hydrogen and C=N nitrogen atoms of Schiff bases determines the properties of various molecular systems and plays a significant role in many biochemical mechanisms [6]. Schiff bases have been extensively used as ligands in coordination chemistry because of their excellent donor abilities [7-11]. Schiff base metal complexes have many industrial uses, especially in catalysis [12], dyeing [13] and analytical chemistry [14]. Although the coordination compounds of Schiff bases of terephthalaldehyde have been extensively studied [15-18], reports are scanty on Schiff bases derived from terephthalaldehyde and *ortho* substituted aromatic amines. Presence of such metallizable groups at suitable position markedly influences their coordination characteristics [19]. As part of our investigation on Schiff bases and their metal complexes [9-11,19-21], we report herein the synthesis and characterization of a new series of Schiff bases produced from terephthalaldehyde with 2-aminophenol and 2-aminothiophenol. Typical metal complexes of these ligand systems were also studied.

### MATERIALS AND METHODS

Carbon, hydrogen and nitrogen contents were determined by microanalyses (Heraeus Elemental analyzer) and metal contents of complexes by AAS (Perkin Elmer 2380). The UV spectra of the compounds in methanol ( $10^{-6}$  M) were recorded on a JASCO V-550 UV-Visible spectrophotometer, IR spectra (KBr discs) on a JASCO FT/IR 4100 instrument, <sup>1</sup>H NMR spectra (CDCl<sub>3</sub> or DMSO-d<sub>6</sub>) on a JEOL JMS 60011 NMR spectrometer and mass spectra on a JEOL-JMS 600H, FAB mass spectrometer. Molar conductance of the complexes was determined in DMF ( $\sim 10^{-3}$  mol/L) at  $28 \pm 1^\circ\text{C}$ . Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance at room temperature ( $28 \pm 1^\circ\text{C}$ ) using Hg[Co(NCS)<sub>4</sub>] as standard. All the chemicals and solvents were of reagent grade (Merck, Fluka and Sigma-Aldrich) and were used without further purification.

**Synthesis of H<sub>2</sub>L<sup>a</sup>**

An ethanolic solution of 2-aminophenol (2.18 g, 0.02 mol, 20 mL) was mixed with an ethanolic solution of terephthalaldehyde (1.34 g, 0.01 mol, 20 mL) and refluxed for ~5 h and kept overnight. The resulting solution was then poured into hot water. The precipitate formed was filtered and recrystallised from hot methanol to get chromatographically (TLC) pure compound.

**Synthesis of H<sub>2</sub>L<sup>b</sup>**

A methanolic solution of terephthalaldehyde (1.34 g, 0.01 mol, 20 mL) was added to a methanolic solution of 2-aminothiophenol (2.50 g, 0.02 mol, 20 mL) and stirred for ~ 9 h in a closed flask maintaining the temperature at ~60°C. The precipitate formed was filtered and recrystallised from hot benzene to get chromatographically (TLC) pure compound.

**Synthesis of metal complexes of H<sub>2</sub>L<sup>a</sup>**

A concentrated aqueous solution of metal(II)acetate (0.01 mol) was added to a methanolic solution of the ligand (3.16 g, 0.01 mol, 25mL) and the mixture was refluxed for ~4 h. The precipitated complex on cooling to room temperature was filtered, washed with water, then with methanol and dried in vacuum.

**Synthesis of metal complexes of H<sub>2</sub>L<sup>b</sup>**

A concentrated methanolic solution of metal(II)acetate (0.01 mol) was added to the ligand in benzene (3.50g, 0.01 mol, 20 mL) and the mixture was refluxed for ~2 h. The precipitated complex on cooling to room temperature was filtered, washed with water, then with hot benzene and dried in vacuum.

**RESULTS AND DISCUSSION**

Elemental analytical data (Table 1) of the Schiff bases suggest that the condensation between terephthalaldehyde and 2-aminophenol/2-aminothiophenol has occurred in the 1:2 ratio as in figure 1. The compounds are crystalline in nature and are soluble in common organic solvents. They formed well defined and crystalline complexes with Ni(II), Cu(II) and Zn(II) ions. The analytical data (Table 1) together with non-electrolytic nature in DMF (specific conductance  $<10\Omega^{-1}\text{cm}^{-1}$ ;  $10^{-3}$  M solution) suggest [M<sub>2</sub>L<sub>2</sub>] stoichiometry of the complexes. The Ni(II) and Zn(II) chelates are diamagnetic while Cu(II) complexes showed normal paramagnetic moment. The observed IR, <sup>1</sup>H NMR and mass spectral data of the complexes are fully consistent with figure 2.

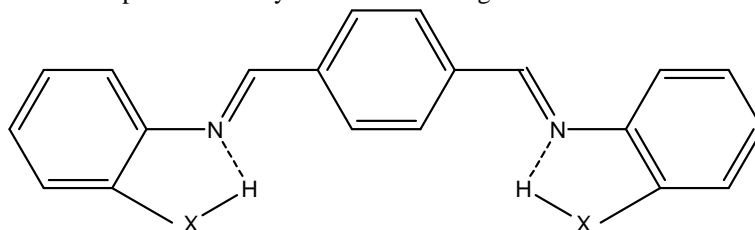
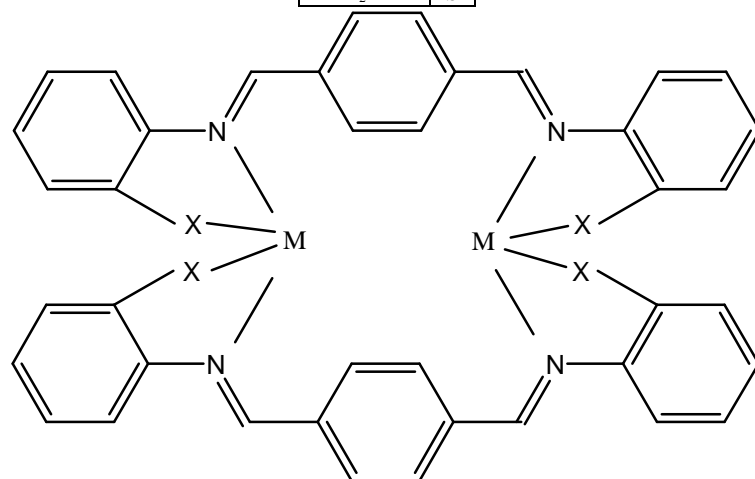


Figure 1. Structure of the Schiff bases

Compound	X
H <sub>2</sub> L <sup>a</sup>	O
H <sub>2</sub> L <sup>b</sup>	S



M = Ni(II), Cu(II) and Zn(II)

Figure 2. Structure of the metal complexes of Schiff bases

Table:- 1 Physical and analytical data of H<sub>2</sub>L<sup>a</sup>, H<sub>2</sub>L<sup>b</sup> and their metal complexes

Compound/ Molecular formula	Yield %	M.P. °C	$\mu_{\text{eff}}$ BM	Elemental Analysis: Found (Calculated)%			
				C	H	N	M
H <sub>2</sub> L <sup>a</sup> C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	70	202	-	75.70 (75.95)	5.10 (5.06)	8.82 (8.86)	-
H <sub>2</sub> L <sup>b</sup> C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> S <sub>2</sub>	50	80	-	68.78 (68.97)	4.50 (4.60)	8.02 (8.05)	-
[Ni <sub>2</sub> (L <sup>a</sup> ) <sub>2</sub> ] C <sub>40</sub> H <sub>28</sub> N <sub>4</sub> Ni <sub>2</sub> O <sub>4</sub>	55	>300	-	64.22 (64.39)	3.74 (3.76)	7.49 (7.51)	15.52 (15.75)
[Ni <sub>2</sub> (L <sup>b</sup> ) <sub>2</sub> ] C <sub>40</sub> H <sub>28</sub> N <sub>4</sub> Ni <sub>2</sub> S <sub>4</sub>	50	>300	-	59.18 (59.30)	3.44 (3.46)	6.82 (6.92)	14.42 (14.51)
[Cu <sub>2</sub> (L <sup>a</sup> ) <sub>2</sub> ] C <sub>40</sub> H <sub>28</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>4</sub>	50	>300	1.76	63.44 (63.57)	3.72 (3.71)	7.32 (7.42)	16.74 (16.83)
[Cu <sub>2</sub> (L <sup>b</sup> ) <sub>2</sub> ] C <sub>40</sub> H <sub>28</sub> Cu <sub>2</sub> N <sub>4</sub> S <sub>4</sub>	60	>300	1.74	58.51 (58.60)	3.41 (3.42)	6.75 (6.84)	15.48 (15.51)
[Zn <sub>2</sub> (L <sup>a</sup> ) <sub>2</sub> ] C <sub>40</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> Zn <sub>2</sub>	50	>300	-	63.36 (63.26)	3.61 (3.69)	7.32 (7.38)	17.11 (17.23)
[Zn <sub>2</sub> (L <sup>b</sup> ) <sub>2</sub> ] C <sub>40</sub> H <sub>28</sub> N <sub>4</sub> S <sub>4</sub> Zn <sub>2</sub>	60	>300	-	58.28 (58.34)	3.42 (3.40)	6.70 (6.80)	15.74 (15.89)

### Infrared spectra

The IR spectra of the Schiff bases in the 1600-1800 cm<sup>-1</sup> region showed a strong band at ~1620 cm<sup>-1</sup> due to C=N stretching vibration [9,22] and no other band is observed in this region indicating the involvement of both aldehydic groups of terephthalaldehyde in Schiff base formation. The comparatively low value of  $\nu_{\text{C=N}}$  suggest that apart from conjugation intramolecular hydrogen bond is also involved between azomethine nitrogen and OH/SH group at *ortho* position. Several medium intensity bands are appeared in the 1580-1600 cm<sup>-1</sup> region of the spectra due to the stretching of various C=C vibrations. That the compounds exist in the intramolecularly hydrogen bonded form [22] as in figure 1 is clearly evident from the broad band appeared in the region 2300-3500 cm<sup>-1</sup>.

In the IR spectra of all the complexes the strong band at ~1620 cm<sup>-1</sup> due to conjugated free azomethine group of the ligand disappeared and instead a new strong band appeared at ~1580 cm<sup>-1</sup> due to metal bonded C=N function [9,23]. The broad band in the region 2300-3500 cm<sup>-1</sup> of the ligand cleared up in the spectra of all the complexes confirming the replacement of the hydrogen bonded OH/SH proton by metal ion during complexation. Spectra of all the complexes show additional medium intensity bands in the 420-480 and 520-570 cm<sup>-1</sup> region presumably due to  $\nu_{\text{M-O}}$  and  $\nu_{\text{M-N}}$  vibrations [23]. Thus the observed IR spectral data strongly suggest that the phenolic oxygen/ thiol sulphur and the imino nitrogen are involved in coordination with the metal ion. Important bands that appeared in the spectra are given in Table 2.

Table:- 2 Characteristic IR stretching frequencies (cm<sup>-1</sup>) of H<sub>2</sub>L<sup>a</sup>, H<sub>2</sub>L<sup>b</sup> and their metal complexes

Compound	C=N	M-N	M-O
H <sub>2</sub> L <sup>a</sup>	1622	-	-
H <sub>2</sub> L <sup>b</sup>	1618	-	-
[Ni <sub>2</sub> (L <sup>a</sup> ) <sub>2</sub> ]	1580	550, 520	450, 428
[Ni <sub>2</sub> (L <sup>b</sup> ) <sub>2</sub> ]	1584	565, 536	475, 436
[Cu <sub>2</sub> (L <sup>a</sup> ) <sub>2</sub> ]	1589	568, 522	478, 432
[Cu <sub>2</sub> (L <sup>b</sup> ) <sub>2</sub> ]	1583	578, 530	468, 422
[Zn <sub>2</sub> (L <sup>a</sup> ) <sub>2</sub> ]	1586	546, 524	462, 422
[Zn <sub>2</sub> (L <sup>b</sup> ) <sub>2</sub> ]	1582	570, 542	472, 426

### <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectra of H<sub>2</sub>L<sup>a</sup> and H<sub>2</sub>L<sup>b</sup> displayed two proton signals at  $\delta$  12.50 and  $\delta$  5.60 ppm respectively due to intramolecularly hydrogen bonded phenolic and thiol protons [21]. The two proton signals at  $\sim\delta$  6 ppm are due to methine protons [24]. The aryl proton signals are observed in the range  $\delta$  6.80-7.80 ppm as a complex multiplet. The integrated intensities of all the signals agree well with the figure 1 of the compounds.

In the <sup>1</sup>H NMR spectra of the diamagnetic Ni(II) complexes the signals due to the OH/SH protons disappeared indicating their replacement by the metal ion during complexation [21]. The methine proton signal shifted slightly to low field indicating the complexation through azomethine nitrogen. The integrated intensities of all the signals agree well with the figure 2 of the complexes. The assignments of various proton signals observed are assembled in Table 3.

Table:- 3 <sup>1</sup>H NMR spectral data (δ, ppm) of H<sub>2</sub>L<sup>a</sup>, H<sub>2</sub>L<sup>b</sup> and their Ni(II) complexes

Compound	OH/SH	Methine	Aryl
H <sub>2</sub> L <sup>a</sup>	12.50 (2H)	6.02 (2H)	6.88-7.78 (12H)
H <sub>2</sub> L <sup>b</sup>	5.60 (2H)	6.08 (2H)	6.80-7.72 (12H)
[Ni <sub>2</sub> (L <sup>a</sup> ) <sub>2</sub> ]	-	6.22 (4H)	6.92-7.68 (24H)
[Ni <sub>2</sub> (L <sup>b</sup> ) <sub>2</sub> ]	-	6.28 (4H)	6.88-7.70 (24H)

### Mass spectra

The mass spectrum of H<sub>2</sub>L<sup>a</sup> shows intense (P+1) peak at m/z 317 corresponding to its formulation [25]. Peaks due to the elimination of OH, phenyl rings, PhN, PhN=CH *etc* are observed in the spectrum. The FAB mass spectrum of the Cu(II) complex of H<sub>2</sub>L<sup>a</sup> shows molecular ion peak of appreciable intensity corresponding to [Cu<sub>2</sub>L<sub>2</sub>] stoichiometry. Peaks correspond to L<sup>+</sup> and fragments of L<sup>+</sup> are also present in the spectrum [26]. The spectrum of the chelate contains a number of fragments containing copper in the natural isotopic abundance. Important fragments appeared in the spectra are given in Table 4.

Table:- 4 Mass spectral data of H<sub>2</sub>L<sup>a</sup> and its Cu(II) complex

Compound	Mass spectral data (m/z)
H <sub>2</sub> L <sup>a</sup>	317, 299, 282, 209, 196, 120, 102
[Cu <sub>2</sub> (L <sup>a</sup> ) <sub>2</sub> ]	760, 758, 756, 754, 481, 479, 587, 585, 455, 453, 317, 299, 120

### UV spectra

The UV spectra of the Schiff bases show two broad bands with maxima at ~360 and ~260 nm due to the various n→π\* and π→π\* transitions. The absorption maxima of the metal chelates bear close resemblance with the free ligand which indicates that no structural alteration of the ligand has occurred during complexation. However the values shifted slightly to longer wavelength indicating the involvement of the azomethine groups in metal complexation [19].

## CONCLUSION

Two new Schiff base ligands have been prepared by the condensation of terephthalaldehyde with 2-aminophenol and 2-aminothiophenol. Analytical, IR, <sup>1</sup>H NMR and mass spectral data revealed a 1:2 product in which both the carbonyl groups of terephthalaldehyde are involved in Schiff base formation. Analytical, physical and spectral data of the [M<sub>2</sub>L<sub>2</sub>] complexes of Ni(II), Cu(II) and Zn(II) showed the dibasic tetradentate coordination involving the imino nitrogens and phenolic oxygens/ thiol sulphur where the intramolecularly hydrogen bonded phenol/thiol protons are replaced by metal cations.

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