

# Complexes of 2-(2'-Hydroxy-1'-naphthalidene)imino-5-p-anisyl-1,3,4-thiadiazole with a few Metal(II) Ions

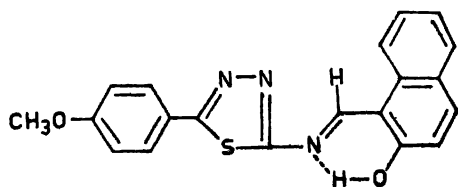
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Two series of complexes of the type  $[M(SB)_2(H_2O)_2]$  and  $[M'(SB)_2]$ , where  $M = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}$ ; and  $M' = Zn^{II}, Cd^{II}, Hg^{II}, Pb^{II}$ ; and  $SB =$  deprotonated 2-(2'-hydroxy-1'-naphthalidene)imino-5-p-anisyl-1,3,4-thiadiazole, have been prepared. The Schiff base acts as a monoprotic bidentate ligand coordinating to the metal ions through the azomethine nitrogen and the phenolic oxygen atoms. The stereochemistry around  $M(II)$  and  $M'(II)$  ions have been discussed. Crystal field parameters calculated for  $Co^{II}$  and  $Ni^{II}$  ions are in agreement with the proposed stereochemistry. Non-electrolytic nature of the complexes is evident from the molar conductance values.

**B**IOLGICAL importance of heterocyclic compounds such as 2,5-disubstituted oxadiazole and thiadiazoles are well known<sup>1,2</sup>. Schiff bases of various heterocyclic amines and related compounds are reported to be anticonvulsant, insecticidal, antibacterial and antifungal agents. It is further reported that heterocyclic organic compounds exhibit enhanced biological activity when administered in the form of metal complexes<sup>3-5</sup>. In view of this, in recent years, considerable attention has been paid to the metal complexes containing oxadiazole and thiadiazole moieties<sup>6-9</sup>. As a part of our study in search of some new Schiff base complexes with possible biological activities we further report in the present communication the preparation and characterisation of some bivalent metal complexes with 2-(2'-hydroxy-1'-naphthalidene)imino-5-p-anisyl-1,3,4-thiadiazole.



## Experimental

The amine, 2-amino-5-(p-anisyl)-1,3,4-thiadiazole was prepared by literature methods<sup>10,11</sup>. The Schiff base 2-(2'-hydroxy-1'-naphthalidene)imino-5-p-anisyl-1,3,4-thiadiazole was prepared by condensation of the amine in ethanol with 2-hydroxy-1-naphthaldehyde and recrystallisation from petroleum ether-acetone, (85%), yellow, m.p. 98°,  $C_{20}H_{15}O_2N_3S$ ;  $\lambda_{max}$  245 and 310 nm;  $\delta(CDCl_3)$  3.17 (3H, s,  $OCH_3$ ), 7.15 (1H, s,  $N=CH$ ), 6.7 (1H, s, phenolic OH) and 7.4-7.86 (10H, m, unsym. Ar)

The complexes were prepared by refluxing the Schiff base and the hydrated metal chlorides in 2 : 1

molar ratio in ethanol. The complexes are quite stable at room temperature, and insoluble in common organic solvents. However, freshly prepared complexes are sparingly soluble in dioxane, DMF and acetone. Most of the complexes melt above 250 and a few decompose before melting. The molecular formulae of the complexes are computed basing on elemental analysis (Table 1) and physical measurements by the methods as reported earlier<sup>12,13</sup>.

## Results and Discussion

The electronic spectrum of the ligand 2-(2'-hydroxy-1'-naphthalidene)imino-5-(p-anisyl)-1,3,4-thiadiazole shows an intense band at  $\sim 245$  nm ( $40\,820\text{ cm}^{-1}$ ) with a weak shoulder at 252 nm ( $36\,680\text{ cm}^{-1}$ ) followed by a strong intense band at  $\sim 310$  nm ( $32\,260\text{ cm}^{-1}$ ). The former two bands may be due to  $n-\sigma^*$  transition in a heterocyclic thiadiazole moiety, whereas the latter band indicates a  $\pi-\pi^*$  transition in an extended conjugated system which arises due to greater delocalisation of the  $\pi$ -electron resulting in a bathochromic shift<sup>14,15</sup>. A strong and broad band appearing in the ir spectrum of the ligand at  $\sim 3\,000-2\,800\text{ cm}^{-1}$  is attributed to stretching vibration of the phenolic OH engaged in intra-molecular hydrogen bonding<sup>16,17</sup>. The disappearance of  $\nu_{OH}$  band in the complexes indicates the coordination of the ligand through deprotonated phenolic oxygen. A strong and sharp band in the spectrum of the ligand at  $\sim 1\,260\text{ cm}^{-1}$  is assigned to the combination mode of phenolic  $\nu_{C-O}$  and  $\delta_{O-H}$  vibrations. Another band at  $\sim 1\,180\text{ cm}^{-1}$  is characteristic of phenolic  $\nu_{C-O}$ <sup>18,19</sup>. The hypsochromic shift of both these bands on complexation suggests coordination through oxygen.

The ir spectra of the complexes  $[M(SB)_2(H_2O)_2]$  display strong and broad bands at  $\sim 3\,400-3\,200\text{ cm}^{-1}$  which may be assigned to  $\nu_{O-H}$  of coordinated water molecules. This is supported by

TABLE I—ANALYTICAL DATA

Compd.	Colour	M.p. °C	Analysis % : Found/(Calcd.)				
			C	H	N	S	M
HSB	Yellow	98	66.89 (66.48)	4.09 (4.15)	11.52 (11.63)	8.79 (8.86)	—
[Mn(SB) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Brown	>250	69.20 (59.19)	3.89 (3.96)	10.21 (10.36)	7.99 (7.89)	6.55 (6.78)
[Co(SB) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Greenish blue	200	58.90 (58.89)	3.89 (3.93)	10.25 (10.30)	7.78 (7.85)	7.36 (7.28)
[Ni(SB) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Yellow	>250	58.81 (58.91)	3.88 (3.93)	10.19 (10.31)	7.89 (7.86)	7.15 (7.20)
[Cu(SB) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Yellowish green	240d	58.44 (58.56)	3.81 (3.90)	10.31 (10.25)	7.77 (7.81)	7.68 (7.75)
[Zn(SB) <sub>2</sub> ]	Orange yellow	>250	60.93 (61.13)	3.66 (3.57)	10.59 (10.70)	8.01 (8.15)	8.19 (8.28)
[Cd(SB) <sub>2</sub> ]	Pale yellow	250	57.58 (57.66)	3.29 (3.36)	10.13 (10.09)	7.73 (7.69)	13.36 (13.52)
[Hg(SB) <sub>2</sub> ]	Yellowish brown	120	52.03 (52.14)	3.11 (3.04)	9.02 (9.18)	6.93 (6.89)	21.70 (21.78)
[Pb(SB) <sub>2</sub> ]	Yellow	175	51.93 (51.77)	3.09 (3.02)	9.11 (9.06)	6.88 (6.90)	22.28 (22.33)

SB = Deprotonated 2-(2'-hydroxy-naphthalidene)-imino-5-p-anisyl-1,3,4-thiadiazole.

appearance of bands at  $\sim 1580$  and  $840\text{ cm}^{-1}$  characteristic of  $\delta_{\text{HOH}}$  and  $\text{H}_2\text{O}$  rocking and wagging modes of vibrations, respectively<sup>20-22</sup>. However, in the ir spectra of the complexes of  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ ,  $\text{Hg}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$ , these bands were found to be absent.

Bands at  $\sim 1650$  and  $1410\text{ cm}^{-1}$  in the spectrum of the Schiff base may be due to  $\nu_{\text{C}=\text{N}}$  mode of azomethine linkage and  $\nu_{\text{C}-\text{N}}$ , respectively. The bathochromic shift of both these vibrations by  $10\text{-}15\text{ cm}^{-1}$  in the spectra of the complexes indicates the coordination of the azomethine nitrogen to the metal ion<sup>23,24</sup>. The bands at  $\sim 1620$ ,  $910$  and  $660\text{ cm}^{-1}$  appearing in the spectrum of the ligand are assigned to  $\nu_{\text{C}=\text{N}-\text{N}=\text{C}}$ ,  $\nu_{\text{N}-\text{N}}$  and  $\nu_{\text{C}-\text{S}-\text{C}}$ , respectively<sup>25-27</sup>. These bands remain unaltered in the spectra of the complexes indicating that the hetero atoms in the thiadiazole moiety do not take part in coordination. The molar conductance values of the complexes in the range  $0.5\text{--}10\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$  in acetone ( $10^{-3}\text{ M}$ ) suggest the non-electrolytic nature of the complexes.

**Thermal analysis:** The general scheme of the thermal decomposition of the complexes  $[\text{M}(\text{SB})_2(\text{H}_2\text{O})_2]$  is same. The TGA curve displays no mass loss upto  $150^\circ$  indicating absence of lattice water. Around  $150^\circ$ , a rapid loss in weight corresponding to two molecules of water is observed in the thermogram, accompanied by a sharp endothermic peak at the same temperature in the DTA curve. This suggests the presence of two molecules of water coordinated to the metal ion in the complex. The abrupt change in weight loss around  $270^\circ$ , with an exothermic peak at the same temperature in the DTA curve indicates the commencement of decomposition of the organic ligand. In case of the complexes of  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$ , the loss in weight starts at  $200\text{-}400^\circ$  and the decomposition continues without any abrupt change in the weight-loss. The TGA curves of all the complexes attain stability around  $600^\circ$  and the weights of the residues corres-

pond to the formation of the metal oxide. The thermal stability of the complexes is found to be in the order,  $\text{Zn} > \text{Mn} > \text{Ni} > \text{Cd} > \text{Cu} > \text{Co} > \text{Pb}$ .

**Electronic spectra and magnetic properties:** The  $\text{Mn}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  complexes are paramagnetic with observed magnetic moments 5.9, 4.8, 3.25 and 2.03 B.M., respectively. The electronic spectrum (Fig. 1) of  $\text{Mn}^{\text{II}}$  complex displays bands at  $18180$ ,  $21980$ ,  $25000$  and  $28570\text{ cm}^{-1}$  which

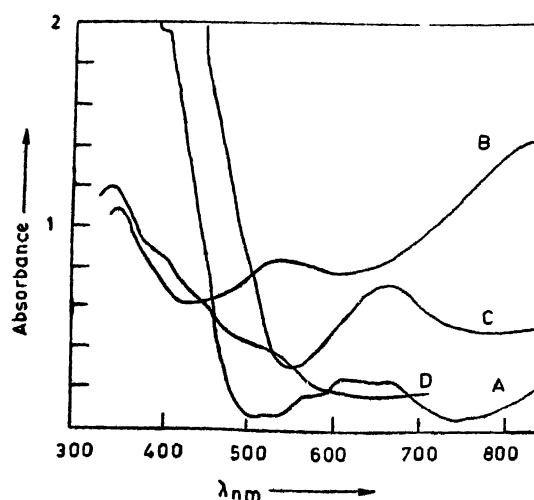


Fig. 1

may be assigned to the transitions  ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{1g}(\text{G})$ ,  $\rightarrow {}^4\text{T}_{2g}(\text{G})$ ,  $\rightarrow {}^4\text{A}_{1g}$ ,  ${}^4\text{E}_g(\text{G})$  and  $\rightarrow {}^4\text{T}_{2g}(\text{D})$ , respectively. The  $\text{Co}^{\text{II}}$  complex shows ligand field bands at  $\sim 15040$  and  $17390\text{ cm}^{-1}$  assignable to  ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})$  and  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$  transitions, respectively. A charge transfer band is also observed at  $\sim 24390\text{ cm}^{-1}$ . The  $\text{Ni}^{\text{II}}$  complex yield three bands at  $\sim 11900$ ,  $18180$  and  $29410\text{ cm}^{-1}$ . In an octahedral field, these bands can be assigned to

${}^3A_{2g} \rightarrow {}^3T_{2g}$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  transitions, respectively. The electronic spectrum of  $\text{Cu}^{\text{II}}$  complex shows a broad asymmetric ligand field band in the region  $13000\text{--}16000\text{ cm}^{-1}$  with maxima at  $\sim 14390\text{ cm}^{-1}$  corresponding to  ${}^3E_g \rightarrow {}^3T_{2g}$  transition in a nearly octahedral arrangement.

Various ligand field parameters, such as  $\nu_3/\nu_2$ ,  $10D_q$ ,  $\beta$ ,  $B$ ,  $C$ ,  $F_2$  and  $F_4$  have also been calculated for  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  from the electronic spectral data (Table 2). The nephelauxetic ratio ( $\beta$ ) for  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  complexes were calculated to be 0.78 and 0.87, respectively which are less than unity indicating partial covalence in the metal-ligand bond. The

TABLE 2—CRYSTAL FIELD AND NEPHELAUXETIC PARAMETERS ( $\text{cm}^{-1}$ ) FOR  $[\text{Co}(\text{SB})_2(\text{H}_2\text{O})_2]$  AND  $[\text{Ni}(\text{SB})_2(\text{H}_2\text{O})_2]$

Compd.	$D_q$	$B$	$C$	$F_2$	$F_4$
$[\text{Co}(\text{SB})_2(\text{H}_2\text{O})_2]$	831.8	756.1	3503	1256.6	100.1
$[\text{Ni}(\text{SB})_2(\text{H}_2\text{O})_2]$	1180	904.6	4260	1513	121.7

magnetic moment values together with the position of the ligand field absorption bands and the spectral data suggest octahedral stereochemistry for  $\text{Mn}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  complexes and distorted octahedral geometry around the  $\text{Cu}^{\text{II}}$  ion<sup>28-31</sup>.

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