

## BIOLOGICAL STUDIES OF ONS AND ONN DONAR SCHIFF BASES AND THEIR Cu(II), Ni(II), Zn(II), Co(II) AND Mn(II) COMPLEXES

R. K. PARASHAR, R. S. SHARMA\*, RAJESH NAGAR and R. C. SHARMA  
*Department of Chemistry, Agra University, Agra 282 004, India.*

\**Department of Pharmacy, G. S. V. M. Medical College, Kanpur 208 002, India.*

### ABSTRACT

Salicylidine-*o*-aminothiophenol (SATP) and salicylidine-*o*-aminopyridine (SAP) have been synthesized by the condensation of salicylaldehyde with 2-aminothiophenol and 2-aminopyridine respectively. The synthesized complexes of Cu(II), Ni(II), Zn(II), Co(II) and Mn(II) of these ligands have been assigned their geometry on the basis of molar conductance, infrared, and electronic spectral data and magnetic measurements. A comparative biocidal activity of the synthesized ligands and their metal chelates against gram +ve (*Staphylococcus aureus*), gram -ve (*Escherichia coli*) bacteria and *Aspergillus niger*, *Aspergillus nidulense* and *Candida albicans* fungi have been made by serial dilution method. In some cases, the biocidal activity of the organic ligands enhanced several times on complexation with suitable metal ion.

### INTRODUCTION

SCHIFF bases are well known for their biological activities<sup>1-4</sup>. It has also been reported in literature that the biological activity of organic ligands changes on coordination with metal ions<sup>5-7</sup>. This idea led us to synthesize the aforesaid schiff-bases and their metal chelates of the metal ions of biological importance to study the combined activity effect of the metal complexes as compared to that of the ligand molecule alone against some bacteria and fungi.

### MATERIALS AND METHODS

All the chemicals used were of AR grades. The ligands were prepared by condensing 1:1 molar amounts of salicylaldehyde with 2-aminothiophenol/2-aminopyridine in ethanol. Metal complexes of Cu(II), Ni(II), Zn(II), Co(II), Mn(II), were prepared by refluxing 1:1 mixture of metal acetates and the ligand in the case of SATP and 1:2-metal-ligand concentrations in the case of SAP. On concentrating and cooling the reaction mixture, the obtained coloured crystals were filtered under suction, washed first with water, ethanol and finally with ether and dried over P<sub>4</sub>O<sub>10</sub> in vacuum.

Metal contents in the complexes were estimated by standard methods<sup>8</sup>. C, H, N and S were estimated in RSIC, Bombay. The molar-conductance

was measured in dried DMF on a Toshniwal conductivity bridge. IR spectra were recorded in KBr using Perkin-Elmer-521 spectrophotometer. The electronic spectra of the complexes were recorded in DMF solution on a Cary-14 spectrophotometer. The magnetic measurements of the complexes were carried out at room temperature by Guoy's method using CuSO<sub>4</sub>.5H<sub>2</sub>O as a calibrant.

### RESULTS AND DISCUSSION

Elemental analyses data (table 1) indicate that one molecule of salicylidene-*o*-aminothiophenol (SATP) and two molecules of salicylidene-*o*-aminopyridine (SAP) are attached to a metal (II) ion, along with coordinated water molecules in some of the cases, depending upon the metal ion. The presence of coordinated water is confirmed by thermal dehydration, elemental and IR of the complexes. The low values (0.8-2.20 mhos) of the molar conductance suggest the neutral nature of the complexes.

#### IR studies

The free schiff bases show the characteristic azomethine and OH frequencies at 1650 and ~3500 cm<sup>-1</sup> respectively. The former shifts toward lower frequency region by 80-50 cm<sup>-1</sup> in the spectra of complexes due to the involvement of N of -C=N-group<sup>9</sup>, while the ν<sub>OH</sub> band disappears showing that it has been deprotonated. A weak band around 2570 cm<sup>-1</sup> probably due to ν<sub>SH</sub> group

\* For Correspondence.

Table I Analytical, conductivity and magnetic data of Cu(II), Ni(II), Zn(II), Co(II) and Mn(II) complexes

Compound	Colour	m.p. d.p. (°C)	% Analysis found/(calcd.)					$\mu_{\text{eff}}$ (B.M.)	Molar conductance $\Omega^{-1} \text{cm}^2$ mol <sup>-1</sup> (in DMF)
			C	H	N	S	M		
SATP	Yellow	145	67.64 (68.09)	5.03 (4.83)	7.18 (6.10)	14.36 (13.98)	—	—	—
SAP	Yellow	68	73.43 (72.71)	6.07 (5.08)	13.78 (14.13)	—	—	—	—
Cu(II)-SATP.H <sub>2</sub> O	Green	248	51.08 (50.55)	4.18 (3.59)	4.06 (4.53)	9.68 (10.38)	22.06 (20.57)	2.01	0.94
Cu(II)-(SAP) <sub>2</sub>	Green	267	63.13 (62.94)	5.16 (4.40)	13.34 (12.23)	—	14.27 (13.87)	1.73	1.36
Ni(II)-SATP.H <sub>2</sub> O	Brown	310	51.96 (51.36)	4.07 (3.64)	5.18 (4.60)	11.34 (10.54)	20.42 (19.31)	Diam	0.80
Ni(II)-(SAP) <sub>2</sub>	Light green	257	61.43 (63.61)	5.16 (4.44)	13.18 (12.36)	—	13.16 (12.95)	3.14	1.73
Zn(II)-SATP.3H <sub>2</sub> O	Yellow	272	46.15 (45.03)	5.16 (4.36)	4.93 (4.03)	9.96 (9.24)	19.38 (18.85)	—	1.98
Zn(II)-(SAP) <sub>2</sub>	Yellow	246	61.64 (62.68)	4.96 (4.38)	13.06 (12.18)	—	15.08 (14.21)	—	2.10
Co(II)-SATP.3H <sub>2</sub> O	Black	293	46.13 (45.88)	4.90 (4.44)	5.08 (+ 11)	10.32 (9.42)	18.18 (17.31)	4.96	1.87
Co(II)-(SAP) <sub>2</sub>	Myrtle	307	62.36 (63.58)	4.24 (4.44)	13.30 (12.35)	—	11.54 (12.99)	4.88	2.20
Mn(II)-SATP.3H <sub>2</sub> O	Myrtle	287	46.40 (46.43)	5.04 (4.49)	4.96 (4.16)	10.03 (9.53)	17.12 (16.33)	5.80	0.86
Mn(II)-(SAP) <sub>2</sub>	Myrtle	245	65.36 (64.14)	4.02 (4.48)	13.26 (12.46)	—	11.96 (12.22)	5.63	1.16

in SATP, also disappeared in the spectra of its metal complexes showing its deprotonation during complexation. In the spectra of SAP, a band at  $1170 \text{ cm}^{-1}$  is probably due to pyridine ring which has shifted to  $\sim 1120 \text{ cm}^{-1}$  in the complexes indicating the involvement of pyridine nitrogen in complexation. The presence of coordinated water in the metal-SATP complexes is indicated by a sharp band around  $3450 \text{ cm}^{-1}$  and two more weaker bands around  $850$  and  $700 \text{ cm}^{-1}$  due to OH stretching, rocking and wagging vibrations respectively. The appearance of some new bands in the spectra of metal complexes around  $450$ ,  $370$  and  $310 \text{ cm}^{-1}$  is probably due to the formation of M-O, M-N, and M-S bands respectively through complexation<sup>10</sup>.

#### Magnetic and electronic spectral studies:

##### Copper(II)-complexes:

The  $\mu_{\text{eff}}$  values of Cu-SATP and Cu-SAP complexes are 2.01 and 1.73 which indicate a square-planar and octahedral geometry respectively. These

geometries are further confirmed by their electronic spectra. In the case of SATP complex, the band around 600 nm may be due to the combination of two transitions  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  and  ${}^2B_{1g} \rightarrow {}^2E_g$  confirming<sup>11,12</sup> the presence of a square-planar geometry whereas in the case of SAP complex, the band around 660 nm indicates a distorted octahedral configuration<sup>13,14</sup>.

##### Nickel(II)-complex:

The diamagnetic character of Ni-SATP complex probably indicates its square planar geometry, which is also supported by its electronic spectra having two bands around 525 and 415 nm probably due to  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  ( $\nu_3$ ) and  ${}^1A_{1g} \rightarrow {}^1B_{1g}$  ( $\nu_2$ ) transitions respectively. In the electronic spectrum of Ni(SAP)<sub>2</sub> complex, two absorption bands are noticed in the region of 900 nm and 600–500 nm which may be assigned to  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$  and  $\rightarrow {}^3T_{1g}(F)$  transitions respectively indicating<sup>10</sup> an octahedral geometry, as evidenced by its magnetic moment value (3.14 B.M.).

Table 2 Minimum inhibitory concentration (MIC) in  $\mu\text{g/ml}$ 

Substance	S.a.	E.c.	A.ni.	A.nid.	C.a.
SATP/SAP	100/75	75/>100	100/>100	75/75	50/>100
Cu(II)SATP/(SAP) <sub>2</sub>	50/12.5	12.5/50	25/50	6.25/12.5	50/75
Ni(II)SATP/(SAP) <sub>2</sub>	25/6.25	100/50	6.25/25	12.5/50	25/50
Zn(II)SATP/(SAP) <sub>2</sub>	25/12.5	12.5/6.25	6.25/50	6.25/25	25/25
Co(II)SATP/(SAP) <sub>2</sub>	50/12.5	50/25	25/6.25	50/75	6.25/12.5
Mn(II)SATP/(SAP) <sub>2</sub>	6.25/12.5	75/100	50/25	25/12.5	50/75
Temperature (Time)	37°C (24 hr)	37°C (24 hr)	28°C (48 hr)	28°C (48 hr)	28°C (48 hr)

**Cobalt(II)-complex:**

These complexes appear to be in their hexacoordinated state with  $\mu_{\text{eff}}$  values of 4.96 and 4.88 for SATP and SAP complexes respectively. The octahedral geometry of these complexes is further evidenced by two main bands around 575 and 900 nm which corresponds to  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$  ( $\nu_3$ ) and  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$  ( $\nu_2$ ) transition respectively<sup>16</sup>

**Manganese(II)-complexes:**

The magnetic moment values 5.8 and 5.63 B.M for SATP and SAP complexes respectively indicate the presence of five unpaired electrons. Since the analytical data of the complex indicate the coordination of only two-ligand molecules in the case of SAP and one-ligand with three coordinated water molecules in the case of SATP around the manganese ion; an octahedral geometry of the complex has been assumed.

**Zinc(II)-complexes:**

On the basis of analytical conductance, and IR spectral data, the Zn(II) complexes may be assigned an octahedral configuration (table 1).

**Biological activity:**

All the synthesized compounds were tested *in vitro* for their antibacterial activity against *Staphylococcus aureus* (S.a), *Escherichia coli* (E.c.) and antifungal activity against *Aspergillus niger* (A.ni.), *A. nidulense* (A.nid.), *Candida albicans* (C.a.) by serial dilution method<sup>17</sup> (table 2). A comparative study of the minimum inhibitory concentration (MIC) values indicates that most of the metal chelates exhibit an increased antimicrobial activity than that of the involved free-ligand molecule alone.

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## ANNOUNCEMENTS

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### NATIONAL SYMPOSIUM ON CROP PLANTS

Food and Agriculture Committee of the Board of Research in Nuclear Sciences, Department of Atomic Energy is organizing a National Symposium on "Micronutrients Stresses in Crop Plants — Physiological and genetic approach to control them" at

Mahatma Phule Agricultural University, Rahuri from December 16 to 18, 1987.

Further details may be had from: Dr S. Kanna, Nuclear Agriculture Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085.

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### WORLD CONFERENCE ON HAZARDOUS WASTE

Budapest, October 25-31, 1987

Sponsored and organized by International Association of Medicine and Biology of the Environment, and National Hungarian Committee with co-sponsorship of UNEP, UNIDO, WHO, CEC, IUTA, WPCF etc. The conference will focus attention on: a) Identification and classification of hazardous wastes, b) Present status and trends in legislative and regulatory apparatus affecting hazardous wastes, c) Data collection, analysis and control systems, d) Ecological impacts of hazardous wastes. e) Management of hazardous wastes.

The Conference would include extensive plenary sessions, panel discussions, sectorial reports, pre-

sentation of contributed papers, exhibitions, and excursions. Registration fees: US \$ 350 (after June 30 it will be \$ 400).

Deadline for submission of 250-300 word abstract: June 30

For further details please contact: Dr S.A. Abbasi, Convenor of the Indian National Committee, Head-in-charge, Water Quality & Environment Division Centre for Water Resources Development & Management, Kozhikode 673 571, India or Dr Richard Abbou, General Chairman, 115, Rue de la Pompe, 75116 Paris, France.