

TABLE I. Analytical Data, Melting Point, Magnetic Moment and Conductance Data of the Complexes.

Complex	M.P. (°C)	C% Calc. (found)	H% Calc. (found)	N% Calc. (found)	S% Calc. (found)	M% Calc. (found)	Ω	μ_{eff} (BM) (27 °C)
Mn(PAT) ₂ (H ₂ O) ₂ Cl ₂	260	37.25 (37.18)	4.48 (4.45)	14.48 (14.43)	11.04 (11.09)	9.47 (9.49)	4.0	5.90
Fe(PAT) ₂ (H ₂ O) ₂ Cl ₂	360	37.18 (37.09)	4.48 (4.46)	14.46 (14.39)	11.02 (11.00)	9.62 (9.60)	5.6	4.90
Co(PAT) ₂ (H ₂ O) ₂ Cl ₂	170	36.99 (36.72)	4.45 (4.39)	14.38 (14.39)	10.96 (10.70)	10.09 (10.20)	6.8	4.80
Ni(PAT) ₂ (H ₂ O) ₂ Cl ₂	210	37.00 (37.10)	4.45 (4.49)	14.39 (14.29)	10.96 (10.88)	10.06 (10.02)	8.0	3.05

TABLE II. Fungicidal Screening Data of Complexes and Ligand.

Compound	Average percentage inhibition after 8 days					
	Organism <i>Alternaria Sp.</i> Conen used		Organism <i>Paecilomyces Sp.</i> Conen used		Organism <i>Pestalotia Sp.</i> Conen used	
	0.01%	0.1%	0.01%	0.1%	0.01%	0.1%
Mn(PAT) ₂ (H ₂ O) ₂ Cl ₂	43.2	58.3	45.3	60.4	45.4	65.3
Fe(PAT) ₂ (H ₂ O) ₂ Cl ₂	55.1	64.7	50.2	79.7	52.4	78.9
Co(PAT) ₂ (H ₂ O) ₂ Cl ₂	60.4	75.8	60.4	80.9	64.2	86.8
Ni(PAT) ₂ (H ₂ O) ₂ Cl ₂	65.6	89.8	70.8	95.9	85.1	98.2
PAT	36.2	40.7	38.7	42.2	43.1	44.5

The electronic spectra of the complexes and the chelating agent were recorded on a Varian Cary, Model 219, spectrophotometer.

Infrared spectra of the ligand and complexes were recorded on a Perkin-Elmer model 983 G spectrophotometer in CsI pellets in the range 4000–180 cm⁻¹.

In the evaluation of antifungal activity, the ligand and the metal complexes were incorporated in Czapeck's medium against *Alternaria* (Sp.), *Paecilomyces* (Sp.) and *Pestalotia* (Sp.). Dimethyl sulphoxide was used as a solvent for preparing different concentrations (0.01% and 0.1%) of the chelating agent and metal complexes. The growth inhibition percentage was calculated on the basis of the average diameter of the fungal colony.

$$\text{Percentage Inhibition} = \frac{(C - T) \times 100}{C}$$

C = diameter of the fungus colony in the control plates after 8 days, T = diameter of the fungus colony in the treated plates after 8 days. The values of percentage inhibition of various compounds are recorded in Table II.

Results and Discussion

The stoichiometries of the complexes are confirmed by the elemental analyses reported in Table I. All the complexes are soluble in acetone, methanol, nitromethane, DMF, DMSO, acetonitrile and chloroform. The molar conductivities range 4–8 cm² Ω⁻¹ mol⁻¹ which clearly indicates that all the complexes behave as non-electrolytes.

Magnetic Moments

The corrected magnetic moment data (Table I) indicate high spin octahedral geometry for the Mn(II), Fe(II), Co(II) and Ni(II) complexes.

Electronic Spectra

The electronic spectrum of the Mn(II) complex gives three peaks of 16000, 25050 and 35100 cm⁻¹ which are compatible with the octahedral geometry of Mn(II) complexes.

The spectrum of the Fe(II) complex shows a weak absorption band at 11000 cm⁻¹ which is due to the ⁵T_{2g} → ⁵E_g transition and is characteristic of a high spin octahedral configuration around Fe(II).

The spectrum of the Co(II) complex exhibits two absorption bands at 9250 and 18300 cm^{-1} with the transitions ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ respectively. These data are very much like those reported for other Co(II) complexes and are consistent with the assignment of distorted 6-coordinate geometry.

The Ni(II) complex exhibits three spin-allowed transitions (cm^{-1}) 11025, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$; 17900, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and 30100, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$. These data suggest an octahedral configuration around Ni(II).

Infrared Spectra

The infrared spectra of the complexes and the ligand were recorded in the range 4000 to 180 cm^{-1} and we will only discuss the selective infrared bands. The highest frequency band of PAT at 3425 cm^{-1} can be assigned to the asymmetric $\nu(\text{N-H})$ vibration of the terminal NH_2 group. The other bands at 3250 and 3100 cm^{-1} may be due to the vibration of the imino group and the symmetric $\nu(\text{N-H})$ vibration of the amino group. The C=N and C=C stretching vibrations are partially overlapping and the band at 1611 cm^{-1} (doublet) is assigned to them. The band at 1589 cm^{-1} can be assigned to $\delta(\text{N-H})$ vibration of the NH_2 group. The C=N and C=C stretching vibrations are shifted from 1611 cm^{-1} (doublet) to 1620 cm^{-1} (doublet) on complex formation. This shift of 10 cm^{-1} is possibly due to the involvement of the C=N group in the complex formation. The $\delta(\text{N-H})$ vibration of the NH_2 group is not shifted at all because it is not involved in bonding. The $\nu(\text{C=S})$ vibration of the NH_2 group is not shifted at all downwards by about 40 cm^{-1} in the spectra of the complexes suggesting the coordination of thio-carbonyl sulphur to the metal ion. The new bands which appeared in the spectra of the complexes in the regions 505–475 cm^{-1} , and 385–335 cm^{-1} have been assigned to $\nu(\text{M-N})$ and $\nu(\text{M-S})$ respectively. In addition to these absorption bands, the complexes exhibited bands in the region 880–650 cm^{-1} assignable to the coordinated water, which is absent in the free ligand. On the basis of this evidence, it is concluded that PAT is bidentate in nature.

Fungitoxicity

Alternaria (Sp.), *Paecilomyces* (Sp.), and *Pestalotia* (Sp.) were employed to check the antifungal activity of the ligand and its complexes. It is clear from the fungicidal screening data (Table II) that the metal

chelates were found to be more fungitoxic than the chelating agent itself. Further, it was noted that the toxicity of the metal chelates increases as the radius of the metal ion decreases.

A possible mode of toxicity may be speculated in the light of chelation theory. Chelation reduces considerably the polarity of the metal ion mainly because of partial sharing of its positive charge with the donor groups and possible π -electron delocalisation over the whole chelate ring. This increases the lipophilic character of the metal chelate which favours its permeation through lipid layers of fungus membranes. Furthermore, the mode of action of the compounds may involve the formation of hydrogen bond through the $-\text{N}=\text{C}$ -group and/or hydroxyl group with the active centers of the cell constituents resulting in the interference with the normal cell process.

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