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Synthesis, Characterization and Fungitoxicity of Complexes of *p*-Anisaldehydethiosemicarbazone with Mn(II), Fe(II), Co(II) and Ni(II)

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Abstract

The complexes of Mn(II), Fe(II), Co(II) and Ni(II) with *p*-anisaldehydethiosemicarbonzone (PAT) were synthesized. Charcterization of these complexes was carried out on the basis of elemental analysis, molar conductances, magnetic measurements and spectra studies. The fungicidal ability has also been evaluated against *Alternaria* sp., *Paecilomyces* sp. and *Pestalotia* sp.

Introduction

Thiosemicarbonzones have been demonstrated to show pharmacological activity against certain viruses and tumors [1]. It has also been demonstrated that the fungicidal activity of thiosemicarbazones is due basically to their capability to chelate the necessary metals which the fungus requires in its metabolism [2, 3]. On the basis of the chelation theory, the fungicidal behaviour of compounds containing the mercapter group SH adjacent to nitrogen has been explained [4]. *p*-Anisaldehydethiosemicarbazone (compound W) and abbreviated as PAT has been proposed as a selective and sensitive spectrophotometric reagent for Ni(II) [5], Cu(II) and Pt(II) [6] and also as a chelating agent for Cu(II), Zn(II), Hg(II) and Cd(II) [7]. We present in this paper the synthesis and characterization of Mn(II), Fe(II), Co(II) and Ni(II) with PAT and the fungitoxicity of the complexes on pathogenic fungi.

Experimental

The chelating ligand, *p*-anisaldehydethiosemicarbazone (compound W) was prepared by the standard method [8].

The synthesis of the complexes $M(PAT)_2(H_2O)_2X_2$ (M = Mn, Fe, Co, Ni; X = Br) followed the same procedure as in our previous paper [9].

Physical Measurements

For the magnetic measurements, the Guoy Balance was employed, with $Hg[Co(NCS)_4]$ used as the standard. The experimental magnetic susceptibilities were corrected for diamagnetism.

Mn, Fe, Co and Ni contents of the complexes were estimated using a Perkin-Elmer 603 Atomic Absorption Spectrophotometer. Carbon, hydrogen, nitrogen, sulphur and bromine were determined using a Perkin-Elmer Model 240G Elemental Analyser.

Conductance measurements were made on 10^{-3} M solutions of the complexes in nitromethane using a Toshniwal conductivity bridge.

Electronic absorption spectra of the complexes and the ligand were recorded on a Perkin-Elmer Model 402 Spectrophotometer in dimethylformamide (DMF).

Infrared spectra of the ligand and complexes were recorded on a Perkin-Elmer Model 983G Spectrophotometer in CsI pellets in the range 4000–180 cm^{-1}.

In the evaluation of the antifungal activity, the ligand and the complexes were incorporated in Czapecks medium against *Alternaria* sp., *Paecilomyces* sp. and *Pestalotia* sp. Dimethylsulphoxide (DMSO) was used as the solvent for preparing different concentrations (0.01% and 0.1%) of the ligand and metal complexes. The inhibition growth (%) was estimated on the basis of the average diameter of the fungal colony.

$$i.e.\ \%\ \text{Inhibition} = \frac{(C - T) \times 100}{C}$$

C = diameter of the fungus colony in the central plate, *T* = diameter of the fungus colony in the treated plate after 10 days. The values of % inhibition of the complexes are summarized in Table I.

Results and Discussion

The corrected magnetic moment data, Table II, confirm a high spin octahedral geometry for the complexes. They vary from 3.10 to 6.10 BM.

For the Ni(II) d^8 complex, the μ_{eff} of 3.10 BM is greater than $\mu_{s.o}$ of 2.83 BM for the two unpaired

TABLE I. Fungicidal Screening Data of Ligand and Complexes

Compound	Average percentage inhibition after 10 days					
	Alternaria sp.		*Paecilomyces* sp.		*Pestalogia* sp.	
	0.01%[a]	0.1%[a]	0.01%[a]	0.1%[a]	0.01%[a]	0.1%[a]
$Mn(PAT)_2(H_2O)_2Br_2$	52.3	68.2	55.6	70.4	55.6	70.3
$Fe(PAT)_2(H_2O)_2Br_2$	65.3	74.3	70.3	90.4	63.6	86.5
$Co(PAT)_2(H_2O)_2Br_2$	70.4	85.3	74.6	91.4	72.4	92.2
$Ni(PAT)_2(H_2O)_2Br_2$	75.5	93.6	80.4	97.8	90.4	96.7
PAT	46.4	48.6	48.8	50.2	51.3	53.6

[a] Ligand/complex concentration.

TABLE II. Analytical Data, Magnetic Moments and Conductance Data of the Complexes

Complex	Calc. (found) (%)						Ω	μ_{eff} (BM)
	C	H	N	S	Br	M		
$Mn(PAT)_2(H_2O)_2Br_2$	32.39 (32.27)	3.90 (3.82)	12.60 (12.56)	9.60 (9.57)	23.69 (23.71)	8.23 (8.18)	5.0	6.10
$Fe(PAT)_2(H_2O)_2Br_2$	32.35 (32.27)	3.90 (3.89)	12.58 (12.48)	9.58 (9.48)	23.66 (23.64)	8.36 (8.34)	6.5	5.12
$Co(PAT)_2(H_2O)_2Br_2$	32.20 (32.20)	3.88 (3.57)	12.52 (12.51)	9.54 (9.49)	23.55 (23.57)	8.78 (8.68)	7.6	4.85
$Ni(PAT)_2(H_2O)_2Br_2$	32.21 (32.31)	3.58 (3.87)	12.52 (12.48)	9.54 (9.47)	23.56 (23.54)	8.75 (8.68)	9.4	3.10

electrons. As it is A ground state, no orbital contribution to the magnetic moment is expected, but $\mu_{eff} > \mu_{s.o}$ as a result of mixing of the excited state with the ground state via spin-orbit coupling.

For the Co(II) d^7 configuration μ_{eff} 4.85 BM > $\mu_{s.o}$ 3.87 BM. The complex is orbitally triply degenerate and therefore an orbital contribution to the magnetic moment is expected.

The Fe(II) complex is orbitally triply degenerate and hence $\mu_{eff} > \mu_{s.o}$.

For the Mn(II) d^5 complex, it is orbitally singly degenerate and hence no orbital contribution to the magnetic moment is expected. However as $\mu_{eff} < \mu_{s.o}$ some of the magnetic moment must have been quenched by the field of the ligand.

Electronic Spectra

The Ni(II) complex exhibits three spin allowed transitions (cm^{-1}) namely $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ 11035; $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ 18 800 and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 31 000. These transitions are indicative of an octahedral arrangement around Ni(II).

The Co(II) complex shows two spectral bands centred at 10 000 and 19 300 cm^{-1} with the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ respectively. These data seem like those for other Co(II) complexes and are in conformity with the assignment of a distorted 6-coordinate geometry. The spectrum of the Fe(II) complex consists of an absorption peak at 11 010 cm^{-1} due to the $^5T_{2g} \rightarrow {}^5E_g$ transition and is characteristic of a high spin octahedral configuration around Fe(II).

The absorption spectrum of the Mn(II) complex gives rise to three peaks at 1700, 25 060 and 35 100 cm^{-1} in agreement with an octahedral geometry of the Mn(II) complexes.

Vibraitional Spectra

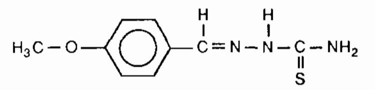
The spectra data of the free ligand PAT and a representative IR spectra of compound $Ni(PAT)_2(H_2O)_2Br_2$ are summarized in Table III.

For our convenience we discuss selective infrared absorption bands. The highest absorption band of PAT centred at 3425 cm^{-1} is assigned to the asymmetric ν(N–H) stretching vibration of the terminal NH_2 group [9]. The other bands at 3250 and 3140 cm^{-1} may be due to the vibration of the imino group and the symmetric ν(N–H) vibration of the amino group. The C=N and C=C frequency bands are partially overlapping and the strong band at 1620 cm^{-1} (doublet) is assigned to them [9]. The absorption band at 1580 cm^{-1} is assigned to δ(N–H) vibration of the NH_2 group [10]. The band at 782 cm^{-1} may be assigned to ν(C=S) vibration.

TABLE III. Infrared Data of PAT and Ni(PAT)$_2$(H$_2$O)$_2$Br$_2$

PAT	Ni(PAT)$_2$(H$_2$O)$_2$Br$_2$	Assignments
3425vs	3425	asy ν(N–H)
3250		sym ν(N–H)
3140	–	ν(N–H) of NH$_2$
1620	1640	ν(C=N) + (C=C)
1580	1580	δ(N–H) of NH$_2$
782	–	ν(C=S)
–	670	coordinated water
	510	ν(Ni–N)
	390	ν(Ni–S)

One significant band at 3140 cm^{-1} in the free ligand has completely disappeared due to enolization of the C=S on complex formation [9]. There is a remarkable shift from 1620 (doublet) to 1640 (doublet) cm^{-1} in the absorption frequencies of C=N and C=C due to the involvement of the C=N group in complex formation. The δ(N–H) frequency of the NH$_2$ moiety is not shifted at all because it is not involved in bonding. The ν(C=S) vibration of the NH$_2$ group in the uncomplexed ligand disappears in all the complexes with the implication that the enolized form of C=S is involved in the metal–ligand bonding. Thus the new bands that have emerged in the spectra of the complexes in the ranges 510–480 and 390–340 cm^{-1} have been ascribed to ν(M–N) and ν(M–S) respectively. In addition to these frequency bands the complexes also exhibited bands in the range 890–670 cm^{-1} attributable to coordinated water molecules, which are not present in the uncomplexed ligand. On the basis of this evidence, we conclude that PAT is a bidentate ligand and hence Fig. 1 is the proposed structure.



Compound W

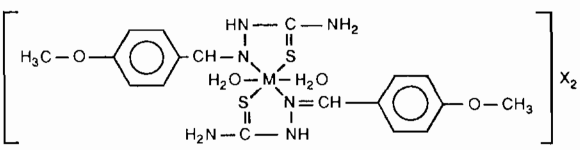


Fig. 1. Proposed structure.

Fungitoxicity

Alternaria (sp.), *Paecilomyces* (sp.) and *Pestalotia* (sp.) were used to check the antifungal behaviour of the ligand and the metal complexes. From the screening data presented in Table I, it was obvious that the metal chelates were more fungitoxic than the chelating ligand. Also as the radius of the metal ion decreases, the toxicity of the metal chelate increases.

On the premise of the chelation theory, a probable mode of toxicity may be envisaged. On chelation, the polarity of the metal ion is greatly reduced due to the sharing of its positive charge with the donor group and consequent π-electron delocalization over the entire chelate ring manifold. Thus the lipophilic attitude of the metal chelate increases and promotes its permeation through lipoid layers of the fungus membranes. Involvement of hydrogen bond via the –N=C group may be another explanation of the mode of action of the compounds.

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