Studies on Some Antifungal Transition Metal Chelates of 2–(2'–5'–Dihydroxy Acetophenonelidene) Aminobenzimidazole

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Abstract:
Some new complexes of the type M (C15H12N3O2)₂. x H₂O {where M= Mn(II), Co(II) ,Ni (II) and Cu (II } and M ($C_{15}H_{12}N_3O_2$)₃ [M = Cr(III) and Fe(III] have been prepared and characterized on the basis of their element analysis, IR spectra, electronic spectra, and magnetic moments. All the metal chelates have significant fungitoxicity at 1000 ppm, but their toxicity decreased marketedly on dilution (viz at 100 and 10 ppm). The metal chelates were more potent against both the fungi, viz A. niger and R. nigracans than the parent compound and its sodium salt.

*Key words: Transition metal chelates, spectral studies, fungi*

1. Introduction

The benzimidazole nucleus appears to be especially toxic to fungi. Recently, a large number of benzimidazole derivaties have been developed and patented as fungicides.[1–5] 2–(Benzylthiomethyl)benzimidazoles have been found to be carcinostatic and fungicidal[6]. Methyl–1–butyl carbamoyl–2–benzimidazole carbamate is a novel fungicide which has been successfully used to control losse smut of wheat and barley [7]. Benzimidazole carbamates possess fungicidal, acaricidal and nematocidal properties. [8] However, very little is known about metal chelates of 2–(2'–5'–Dihydroxy acetophenonelidene) aminobenzimidazole. Recently it has been observed that the metal complexes are more fungitoxic than the parent compounds [9]. This prompted us to synthesise and characterize it and evaluate the fungitoxic properties of some of its complexes with transition metal ions.

2. Experimental

All the chemicals used were of AR grade or equivalent quality. 2–Aminobenzimidazole was prepared by the method of Phillips [10]. Its Schiff base with 2; 5–Dihydroxyacetophenone was prepared by the usual condensation method. The metal complexes were prepared by the following method.

The requisite metal salt and sodium salt of ligand were refluxed in 1:2 molar ratio in 50% aq. Ethanol (v/v) for 5–6 hrs. The compounds which precipitated on cooling were washed several times with cold water followed by 50% aq. Ethanol (v/v) and dried in vacuo.
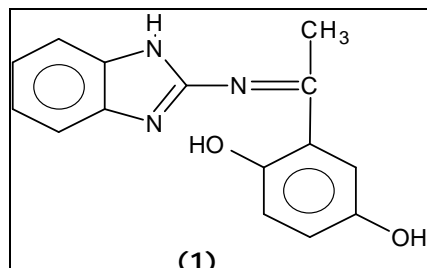
Figure 1

The complexes were analysed for their metal contents employing standard literature procedures after destroying the organic residue with a mixture of concentrated hydrochloric and nitric acids. The analytical results are given in Table 1.

Physical measurements were carried out by the methods reported earlier; fungicidal activity was also studied by the reported method [9]. The water content of the complexes were determined by heating them in the range of 150–300°C and determining the loss in weight.

3. Results and Discussion

The elemental analysis (Table 1) indicate that the stoichiometry of the complexes is M(benzimidazole)$_2$.xH$_2$O except for the Cr(III) and Fe(III) complexes. These complexes show stoichiometry of M (benzimidazole)$_3$. The low conductance values ($\sim$ 2 mho cm^2 $\times$ 1 mol^{-1}) showed their non–electrolytic nature in dioxane.

The infrared spectrum of the ligand shows two absorption bands, one at 1640cm^{-1} due to stretching mode of acyclic N=C group and the other at 1610 cm^{-1} due to –N=C of the heterocyclic ring. A band appearing at 3440 cm^{-1} can be attributed to νN–H mode. The band in the region 3640–3480 cm^{-1} in the spectra of the complexes is attributed to νOH of the water molecule. The ligand (I) with four potential donors can interact with metals in a number of ways. However, there is a positive shift of 10–20 cm^{-1} on complexation in the νNH and νC=N (heterocyclic ring) modes. This rules out the possibility of coordination through the nitrogens of these groups as well as its behaviour as monodentate ligand.[11] A negative shift of ~40 cm^{-1} in the acyclic–N=C band and disappearance of –OH band in the IR spectra of the complexes indicate bonding through the nitrogen of acyclic –N=C group and oxygen of hydroxyl group. Thus, the ligand behaves as a bidentate ligand bonding through only one nitrogen. In addition the complexes exhibited two bands (rocking and wagging) in the region 650–880 cm^{-1} assignable to the coordinated water which is absent in the chelating agent[12]. The loss of water at relatively high temperature (160–210°C) indicated that these are coordinated.

Analytical data and magnetic moments of the chelates are recorded in Table 1.

S. No.	Complex (m.p. °C)	Found (Calcd.), %				
		C	H	Metal	Nitrogen	μ_{eff} (BM)
1.	Cr(C$_{15}$H$_{12}$N$_3$O$_2$)$_3$ (>250 d)	63.40 (63.52)	4.10 (4.25)	6.00 (6.11)	14.70 (14.87)	3.70
2.	Mn(C$_{15}$H$_{12}$N$_3$O$_2$)$_2$(H$_2$O$_2$) (>250 d)	57.62 (57.78)	4.35 (4.49)	8.70 (8.87)	13.35 (13.48)	6.0
3.	Fe(C$_{15}$H$_{12}$N$_3$O$_2$)$_3$ (>250 d)	42.0 (42.16)	4.04 (4.21)	6.40 (6.53)	14.60 (14.75)	5.82
4.	Co(C$_{15}$H$_{12}$N$_3$O$_2$)$_2$(H$_2$O$_2$) (>250 d)	57.33 (57.42)	4.30 (4.45)	9.00 (9.40)	13.45 (13.79)	4.42
5.	Ni(C$_{15}$H$_{12}$N$_3$O$_2$)$_2$(H$_2$O$_2$) (>250 d)	57.30 (57.44)	4.30 (4.46)	9.20 (9.36)	13.34 (13.44)	3.20
6.	Cu(C$_{15}$H$_{12}$N$_3$O$_2$)$_2$(H$_2$O$_2$) (>250 d)	60.30 (60.44)	4.0 (4.02)	10.50 (10.66)	14.0 (14.10)	1.82

Table 1: Analytical data, melting points and magnetic moments of the complexes
L = (C$_{15}$H$_{13}$N$_3$O$_2$)
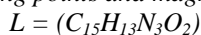
S. No.	Complex	Average percentage inhibition after 96 hrs					
		A. niger conc. used (ppm)			R. nigraicans conc. used (ppm)		
		1000	100	10	1000	100	10
1.	(C$_{15}$H$_{13}$N$_3$O$_2$)	61.6	42.0	28.6	62.2	40.6	26.8
2.	Cr(C$_{15}$H$_{12}$N$_3$O$_2$)$_3$	68.5	48.6	32.8	70.0	46.5	30.6
3.	Mn(C$_{15}$H$_{12}$N$_3$O$_2$)$_2$(H$_2$O$_2$)	97.0	80.8	70.0	95.5	78.0	68.5
4.	Fe(C$_{15}$H$_{12}$N$_3$O$_2$)$_3$	96.5	81.7	72.8	90.6	72.5	62.6
5.	Co(C$_{15}$H$_{12}$N$_3$O$_2$)$_2$(H$_2$O$_2$)	65.0	50.2	30.0	63.2	42.2	28.6
6.	Ni(C$_{15}$H$_{12}$N$_3$O$_2$)$_2$(H$_2$O$_2$)	66.6	48.2	28.8	64.2	42.8	30.7
7.	Cu(C$_{15}$H$_{12}$N$_3$O$_2$)$_2$(H$_2$O$_2$)	98.0	82.5	69.5	88.6	80.0	70.5
	Dithane M–45 (A commercial fungicide)	100.0	88.2	72.6	98.0	86.8	75.0

Table 2: Fungicidal Screening data

From the assignment of the electronic spectral bands, their positions and spectral parameters, it is clear that all the complexes are octahedral except Cu (II) complex which shows planar environment around the Cu (II) ion. The values of Dq, and B$^|$ have been calculated from ν$_2$ and ν$_3$ bands using the matrices of Tanabe and Sugano [13].

Cr (III) has $3d^3$ electronic configuration with $^4A_{2g}$ ground state. Three bands observed at 18000, 25000 and 36000 cm^{-1} for Cr(III) complexes are assigned to the transitions:
$^4A_{2g} \to {}^4T_{2g}$ (F), $^4A_{2g} \to {}^4T_{1g}$ (F) and $^4A_{2g} \to {}^4T_{1g}$ (P) respectively.

For Mn(II) complexes, three d–d transitions observed at 19000, 24200 and 31800 are assigned to $^6A_{1g} \to {}^4T_{1g}$(G), $^6A_{1g} \to {}^4E_g$(G) and $^6A_{1g} \to {}^4E_g$(P) respectively. A band at 31800 cm^{-1} is due to the charge transfer. This suggests a distorted O_h symmetry for Mn(II) complex.

In the case of Fe (III) complex, three bands are observed at 1300, 2100 and 3000 cm^{-1}. These bands may be assigned to the transitions: $^6A_{1g} \to {}^4T_{1g}$, $^6A_{1g} \to {}^4T_{2g}$ and $^6A_{1g} \to {}^4T_g$ respectively. This shows octahedral geometry for Fe (III) complex.

The electronic spectral bands for Co(II) complexes are observed at 800 and 2050 cm^{-1} which are assigned to the transitions: $^4T_{1g} \to {}^4T_{2g}$ (ν_1) and $^4T_{1g} \to {}^4T_{2g}$ (P) (ν_3) respectively. However, we could not observe the band arising from the transition $^4T_{1g} \to {}^4A_{2g}$ probably because of it being a two electron transition. These data indicate an octahedral environment around Co (II) ion [14]. From the values of ν_3 and ν_1, values of Dq, $B^|$ and ν_2 work out as 800, 836 and 1600 cm^{-1} respectively. The ν_2/ν_1 ratio 2.0 lies well within the limit reported for octahedral structure of Co (II) complexes. [15]
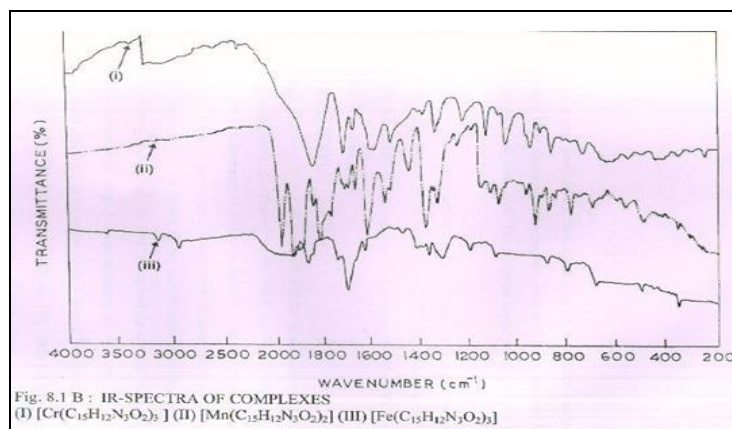

Figure 2

Three bands were observed for Ni (II) complex at 1300, 1850 and 2600 cm^{-1}. These are assigned to the transitions: $^3A_{2g} \to {}^3T_{2g}$ (ν_1), $^3A_{2g} \to {}^3T_{1g}$ (F)(ν_2) and $^3A_{2g} \to {}^3T_{1g}$ (P) (ν_3) respectively. The ratio of ν_2/ν_1 (1.42) usually observed for O_h Ni (II) complexes [16]. From these frequencies we have calculated the values of Dq (1300 cm^{-1}), $B^|$ (866 cm^{-1}) and β (19.8%).

The electronic spectral data of the Cu (II) complex are characterized by a broad band in the region 1560 cm^{-1} and a strong band near 2200 cm^{-1}. The d–d bands for complex for which a planar structure has been proposed [17–21] occur in the range 1400–1800 cm^{-1}. Therefore, the above observations are consistent with a essentially planar structure.
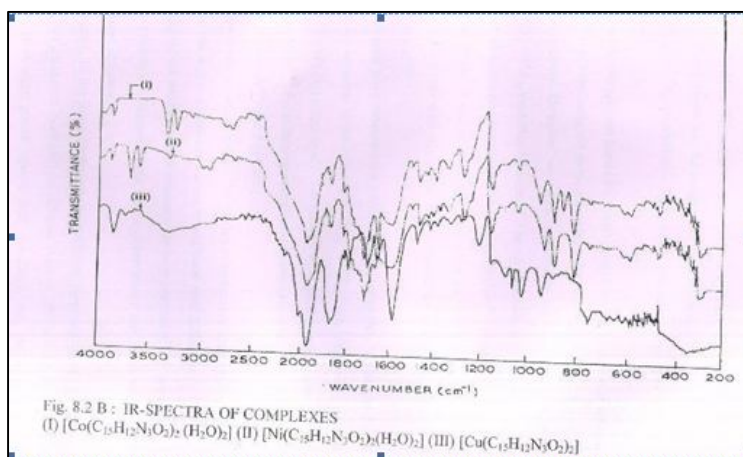

Figure 3

As expected, all the metal chelates had significant fungitoxicity at 1000 ppm but their toxicity decreased markedly on dilution (viz. at 100 and 10 ppm). The metal chelates were more potent against the fungi, viz., A. niger and R. nigracans, than the parent compound and its sodium salt (Table 2). This can be explained on the basis of chelation theory.

The ESR–spectra of Cu (II) complex was recorded in DMSO at 300K and 77K. The spectra of the copper complex at 300K show one intense absorption band in the high field and are isotropic due to the tumbling motion of the molecules. However, the complex in the frozen state show four well resolved pears with low intensities in the low field region and one intense peak in the high field region. No band corresponding to $m_S = \pm 2$ transition was observed in the spectra, ruling out any Cu–Cu interaction. The spin Hamiltonian parameters of the complex $A_\parallel$ (143×10^4 cm^{-1}); $A_\perp$ (42×10^4 cm^{-1}); A_{iso} (76); $g_\parallel$ (2.31); $g_\perp$ (2.06); g_{iso} (2.14) α^2 (0.59); β^2 (0.86).[22–23]

The g–tensor values of copper (II) complex can be used to derive the ground state. In square planar complexes, the unpaired electron lies in the dx^2-y^2 orbitals giving $^2B_{1g}$ as the ground state with $g_\parallel > g_\perp > 2.0$ while the unpaired electron lies in the dz^2 orbital giving $^2A_{1g}$ as the ground state with $g_\perp > g_\parallel > 2.0$ which suggests that the complex is present in square planar geometry. Further it is also supported from the fact that the unpaired electrons lies predominantly in the dx^2-y^2 orbital. [24]

The molecular orbital coefficients viz. inplane π–bonding (β^2) and inplane σ–bonding (α^2) were calculated using the following expressions.[25–27]

$\alpha^2 = (A_{11} / 0.036) + (g_{11} - 2.0023) + 3/7 (g_\perp - 2.0023) + 0.04$

$\beta^2 = (g_\parallel - 2.0023) E/- 8\lambda\alpha^2$

Where $\lambda = 823$ cm^{-1} for free ion and E is the electronic transition energy of $^2B_{1g} \rightarrow ^2A_{1g}$. α^2 and β^2 – values indicate that there is substantial interaction in the inplane σ–bonding where as the inplane π–bonding is almost ionic. The results are anticipated because there are no appropriate ligand orbitals to combine with dxy orbital of copper ion.

4. References

1. Adolf Hubels (Ciba–Geigy AG), Ger. Offen, 2317391 (1973); Chem. Abst. 83, 10164j (1975).
2. Wakae, O., Matsuura, K., Kitamura, K. & Ishida, Y., (Takeda Chemical Industries Ltd., Japan) 7427333 (1974); Chem. Abstr. 83, 2233 (1975).
3. Roeder, K., Puttner, R., Pieroh, E.A. (Schering A.G.), Ger. Offen, 2347386 (1975); Chem. Abstr., 83, 43325 (1975).
4. Roeder, K., Puttner, R., Pieroh, E.A. (Schering A.G.), Ger. Offen, 2349919 (1975); Chem. Abstr., 83, 43330 (1975).
5. Frederic, J.B. (du Pont de Nemours E.I. & Co. US), 3932448 (1976); Chem. Abstr., 84, 160596 (1976).
6. Tadeo, I. (Meiji Confectionary Co. Ltd. Japan), 7428192 (1974), Chem. Abstr., 83, 140141 (1975).
7. Chatrath M.S., & Mohan, M., Indian Phytopathol, 24, 174 (1971).
8. Ost, W., Thomas, C. & Jerchel, D., Ger. Offen, 2031912 (1971); Chem. ABstr., 74, 125690 j (1971).
9. Srivastava, R.S., Inorg. Chim. Acta, 46, L43 (1980).
10. Phillips, M.A., Chem. Soc., 172, 2393 (1928).
11. Singh, P.P., Srivastava, A.K. & Pathak, L.P., J. Coord. Chem. 9, 75 (1979).
12. Aggarwal, R.C. & Singh, N.K., Indian J. Chem. 13, 931 (1975).
13. Tanabe, Y. & Sugano, S., J. Phys. Soc. Japn, 9 (1954) 753.
14. Singh, P.P. & Khan, S.N., Inorg. Chim. Acta, 14, 143 (1975).
15. Patel, K.C. & Goldberg, D.E., J. Inorg. Nucl. Chem., 34, 637 (1972).
16. Sacconi, L., Transition Met. Chem. 4, 199 (1968).
17. Doraswamy, U. & Bhattacharya, P.K., J. Inorg. Nucl. Chem. 37, 1665 (1975).
18. Matsumura, S., Sakamoto, S., Ueno, A. & Miharu, K., Chem. Eur. J. 6, 1781 (2000).
19. Cotton, F.A., Lin C. & Murillo, C.A., Acc. Chem. Res. 34, 759 (2001).
20. Kumari, N., Prajapati, R. & Mishra, L., Polyhedron 27, 241 (2008).
21. Mishra, L., Bindu, K. & Bhattacharya, S., Inorg. Chem. Commun. 7, 777 (2004).
22. Chas, M., Platas, Iglesias, C., Peinador, C. & Quintela, J.M., Tetrahedron Lett; 47, 3119 (2006).
23. Ghosh, S., Ibatten, S.R., Turner, D.R. & Mukherjee, P.S., Organometallics 26, 3252 (2007).
24. Hathway, B.J. & Billing, D.E., Coord. Chem. Rev; 5, 143 (1970).
25. Ray, R.K., & Kauffman, G.R., Inorg. Chim. Acta 173, 207 (1990).
26. Anthonisamy, N.S.X. & Murugesan, R., Chem. Phys. Lett. 287, 353 (1998).
27. Anthonisamy, V.S.X., Anantharam, R. & Murugesan, R., Spectrochim. Acta A55, 135 (1999)