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Synthesis, Characterisation and Biological Studies of Some Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) Complexes of Schiff Base Derived from Vanillin and 1, 2-Diaminoethane.

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Some transition metal complexes with bis-3-(*p*-hydrosy-*m*-methoxy benzylidene amino)-1, 2-diaminoethame (HMBADE) have been synthesized with the general compostion ML_2X_2 (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}, X = Cl^-, Br^- or I^- and L = HMBADE). Their structural features have been investigated on the basis of elemental analysis, molar conductivity, electronic, ^1H, n.m.r and IR spectral data.

INTRODUCTION

A number of transition metal complexes with Schiff bases derived from 4-hydroxy-3-methoxybenzaldehyde have been studied[1]. In continuation of our studies on transition metal complexes of Schiff bases[2–4], the present paper reports our results on the synthesis, characterisation and biological activity of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes of vanillin-ethylene diamine.

EXPERIMENTAL

The Schiff base ligand HMBADE, bis-3-(*p*-hydroxy-*m*-methoxy benzylidene amino)-1, 2 diamino ethane was prepared by mixing alcoholic solution of vanillin and ethylene diamine in the molar ratio of 2 : 1. The mixture on shaking for 5 to 10 minutes gave yellowish solid and the reaction was exothermic. The ligand was recrystallized using alcohol-dimethyl sulphoxide mixture.

Alcoholic solutions of metal halides (0.005 M) and of ligand (0.01 M) were mixed and kept for several hrs. The solid mass appeared and was filtered, washed with alcohol and dired under vaccum. All the complexes were recrystallised from dimethyl sulphoxide. The compounds were analysed by standard procedures[5].

RESULTS AND DISCUSSION

The molecular formulae of the complexes have been assigned on the basis of their analytical data (Table 1), Mn(II), Fe(II), Ni(II) and Cu(II) complexes are non-electrolytic in nature (15–30 ohm^{-1} cm^2 $mole^{-1}$ in DMSO at 22° ± 1°C at a concentration of (10^{-2}M) and can be formulated as $M(HMBADE)_2X_2$, whereas Co(II) complexes are ionic (210–220 ohm^{-1} cm^2 $mole^{-1}$) and of the type $[M(HMBADE)_2]X_2$ (X = Cl^-, Br^-, I^-). The infrared spectrum of the ligand shows bands at 1610, 3350 and 2800 cm^{-1} attributed to νCH = N, ν–OH and νOCH$_3$ respectively. The downward shift of ν–CH = N band by about 40 cm^{-1} in all the complexes shows co-ordination through azomethine nitrogen[1]. Other bands remain intact in all the complexes thus indicating non-coordination through oxygen of these groups. The co-ordination through nitrogen of ν–CH = N group has been further confirmed by the appearance of νM–N band at 570–635 cm^{-1}. An additional band at 275–320 cm^{-1} in all the complexes may be assigned to νM–X band[7], νM–X band did not split up, so the halogen atoms are at the *trans* position in the complexes.

TABLE 1
ANALYTICAL DATA OF THE COMPLEX

Compound/Colour	M.pt. (°C)	μ_{eff} (B.M.)	% Found (Calc) M	X	N
$Mn(HMBADE)_2Cl_2$ (Faint Pink)	200	5.90	6.98 (7.02)	8.92 (9.07)	7.10 (7.16)
$Mn(HMBADE)_2Br_2$ (Light Pink)	195	5.91	6.18 (6.38)	18.18 (18.37)	6.38 (6.42)
$Mn(HMBADE)_2I_2$ (Yellow)	186	5.91	5.60 (5.69)	26.10 (26.32)	5.75 (5.80)
$Fe(HMBADE)_2Cl_2$ (Brown)	189	5.10	7.00 (7.13)	8.98 (9.06)	7.00 (7.15)
$Fe(HMBADE)_2Br_2$ (Dark Brown)	191	5.15	6.00 (6.40)	18.28 (18.38)	6.38 (6.42)
$Fe(HMBADE)_2I_2$ (Brownish Green)	199	5.18	5.69 (5.78)	26.20 (26.29)	5.68 (5.79)
$Co(HMBADE)_2Cl_2$ (Violet)	200	4.24	7.42 (7.49)	8.98 (9.03)	7.00 (7.12)
$Co(HMBADE)_2Br_2$ (Red)	205	4.26	6.68 (6.73)	18.20 (18.28)	6.38 (6.40)
$Co(HMBADE)_2I_2$ (Blue)	210	4.25	5.70 (5.78)	26.20 (26.29)	5.72 (5.79)
$Ni(HMBADE)_2Cl_2$ (Greenish Brown)	212	3.31	7.12 (7.47)	9.00 (9.03)	6.99 (6.40)
$Ni(HMBADE)_2Br_2$ (Pale Yellow)	202	3.30	6.58 (6.71)	18.00 (18.29)	6.32 (6.40)
$Ni(HMBADE)_2I_2$ (Dark Red)	210	3.31	6.00 (6.06)	26.18 (26.22)	5.69 (5.78)
$Cu(HMBADE)_2Cl_2$ (Green)	196	1.98	7.93 (8.03)	8.88 (8.98)	6.98 (7.08)
$Cu(HMBADE)_2Br_2$ (Greyish Green)	186	1.97	7.00 (7.22)	18.00 (18.19)	6.28 (6.36)

X = halogen

Electronic spectra of Mn(II) complexes exhibit bands at 16,100–16,600 cm^{-1} ($\varepsilon = 2.0$), 23,000–23,500 cm^{-1} ($\varepsilon = 4.14$) and 31,800–32,450 ($\varepsilon = 6.0$) are assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$, ${}^6A_{1g} \rightarrow {}^4E_g(G)$ and ${}^6A_{1g} \rightarrow {}^4E_g(P)$ respectively. A band at 31,800–32,450 cm^{-1} is due to the charge transfer. Magnetic moment values for Mn(II) complexes were observed at 5.90–5.91 B.M. suggesting a distorted O_h symmetry for Mn(II) complexes.

There bands were observed in the electronic spectrum of Fe(II) complexes at 10,700–11,000 cm^{-1} ($\varepsilon = 8.81$), 32,500–33,500 cm^{-1} ($\varepsilon = 15.84$) and 38,900–39,000 cm^{-1} ($\varepsilon = 27.21$). The first band is assigned to the ${}^5T_{2g} \rightarrow {}^5E_g$ transition and other two transitions ${}^5T_{2g}(D) \rightarrow {}^3T_{1g}(H)$ and ${}^5T_{2g}(D) \rightarrow {}^3E_g(H)$ respectively. These transitions are spinforbidden and are possibly due to $n-\pi^*$ and $\pi-\pi^*$ transitions of the ligand or due to merger of both the transitions. μ_{eff} values have been observed in the range of 5.10–5.18 B.M. suggesting an octahedral structure.[7]

The electronic spectrum of Co(II) complexes exhibit bands at 16,500–16,900 ($\varepsilon = 18$) and 19,000–19,250 ($\varepsilon = 29$), which are assigned to ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively. μ_{eff} value for Co(II) complexes were observed in the range, 4.24–4.25 B.M. These values are indicative of tetrahedral structure for the complexes[8]. The spectra of Ni(II) complexes show bands at 10,100–10,400 cm^{-1} ($\varepsilon = 6$), 19,400–19,600 cm^{-1} ($\varepsilon = 9$) and 24,900–25,100 cm^{-1} ($\varepsilon = 14.5$) due to the transitions ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(P)$ (ν_3) respectively. μeff value for Ni(II) complexes have been observed in the range, 3.30–3.31 B.M., higher than μ_s values due to orbital contribution. These values are indicative of distorted octahedral structure.

Cu(II) complexes exhibit bands at 10,500–10,600 ($\varepsilon = 6.4$), 13,000–13,100 ($\varepsilon = 9.3$) and 18,100–18,050 ($\varepsilon = 16.0$) cm^{-1} corresponding to ${}^2A_{1g} \rightarrow {}^2B_{1g}(\nu_1)$, ${}^2A_{1g} \rightarrow {}^2E_g(\nu_2)$ and ${}^2A_{1g} \rightarrow {}^2B_{2h}(\nu_3)$ respectively. μ_{eff} values for Cu(II) complexes have been observed in the range, 1.97–1.98 B.M. These values are in accordance with the distorted octahedral geometry.

${}^1H$ NMR spectra of complexes were recorded in DMSO d_6. The ligand shows peak at δ3.8, δ5.6, δ7.5 and δ8.2–8.7 ppm due to OCH_3 proton, Ar–OH (hydroxyl proton), Ar–H protons and azomethine protons respectively. Integrated intensities obtained are in good agreement with the number of different kinds of protons present in the ligand[1]. Two singlets, which were observed for azomethine protons, undergo a down field shift δ(9.0–9.8) ppm and which seems to be due to the co-ordination of both azomethine nitrogen in all the metal complexes. All other protons remained unaffected in the complexes.

Biological Activity

The algacidal effects of $CuCl_2$, $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, the ligand and its complexes on growth of a green alga *Chlorella* species were studied. From the data, it was found that ligand and complexes are less toxic than their corresponding metal chlorides. The hierarchy of toxicity[9] among tested metal chlorides were observed as follows: Cu > Ni > Co > Mn > Fe. The less toxic nature of complexes with respect to their metal salts may be attributed to their larger size[10].

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