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Synthesis and Characterization of Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} Complexes of Schiff base derived from Phenylene Diamines and 3-Carboxaldehyde

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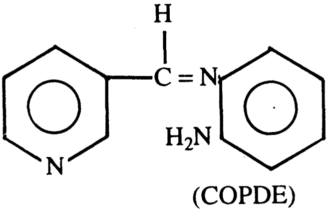
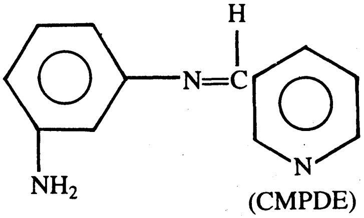
Schiff bases synthesized by the reaction of pyridine-3-carboxaldehyde with *o*-phenylene diamine (COPDE) and *m*-phenylene diamine (CMPDE) form monomeric and dimeric complexes with divalent Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} ions. Square planar geometry has been assigned to $[M(L)_2]Cl_2$ complexes; whereas $M_2(L)_4Cl_2$, $M_2(L)_4(NO_3)_2$ $[(ML_2{\cdot}2H_2O)]SO_4$ and $ML_2(CH_3COO)_2$ complexes are octahedral ($M = Mn^{2+}$, Fe^{2+}, Co^{2+} and Ni^{2+}; L = COPDE or CMPDE). Structures of complexes have been assigned on the basis of elemental analysis, molar conductance, molecular weight determination, IR, UV and magnetic moment values data.

INTRODUCTION

Schiff base and its coordination compounds have gained importance for over several years because of their use as models in biological, biochemical, analytical and antimicrobial system[1]. Keeping the above in view, a number of Schiff base complexes of transition metal cations have been reported[2–4] by us. The present communication deals with the synthesis and characterisation of some Schiff base complexes of Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+}.


(COPDE)


(CMPDE)

EXPERIMENTAL

The analyses of C, H and N contents of compounds were carried out at Bose Institute, Calcutta using a Perkin-Elmer Model 240 C elemental analyser. IR, UV and magnetic susceptibility measurements were carried out at RSIC, Bombay.

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Molecular weights of the complexes were determined by Rast method using camphor as the solvent.

o-Phenylene diamine, *m*-phenylene diamine was of Konch Light, U.K.; pyridine-3- aldehyde was of Sigma, U.S.A., and the metal salts and solvents used were of either B.D.H. or Sarabhai Merck.

Synthesis of Ligands

Pyridine-3-aldehyde-o-phenylene diamine (COPDE): An alcoholic solution of *o*-phenylene diamine and pyridine-3-carboxaldehyde were mixed in 1 : 1 mol ratio. The solution mixture was stirred and was refluxed for 2 h at 30–40°C. It was kept in refrigerator for overnight. A light green precipitate was obtained after recrystallization from acetone and dried over anhydrous $CaCl_2$; m.pt. 25°C.

Pyridine-3-aldehyde-m-phenylene diamine (CMPDE) An alcoholic solution of *m*-phenylene diamine and pyridine-3-carboxaldehyde were mixed in 1 : 1 mole ratio. The solution mixture was stirred and was refluxed for 2 h at 40–50°C. It was kept in refrigerator for 30 h. The precipitate obtained was recrystallized from ethanol and dried over anhydrous $CaCl_2$; m.p. 25°C.

Synthesis of metal complexes with ligands (COPDE, CMPDE): (M = Mn(II), Fe(II), Co(II), Ni(II); X = Cl^-, NO_3^-, SO_4^{2-} and CH_3COO^-): Alcoholic solutions of the respective ligands were prepared separately in dioxane and mixed separately with ethanolic/aqueous solution of the metal salt with constant stirring in 2 : 1 mole ratio. The reaction mixture was kept over water bath for about 3–4 h. After cooling and stirring metal complexes separated out. These were filtered, washed with ethanol, acetone and dried in *vacuo*.

RESULTS AND DISCUSSION

Compounds are partially soluble in common organic solvents, but are soluble in DMF to some extent. Some of the compounds are amorphous in nature and possess high decomposition/melting temperature.

The analytical data of the compounds are shown in Table 1. Molar conductance values of the complexes $M_2L_4(NO_3)_2$, $M_2L_4Cl_2$, $[ML_2{\cdot}2H_2O]SO_4$, $[ML_2(CH_3COO)_2]$ and $ML_2(CH_3COO)_2$ in DMF at 10^{-3} M were observed in the range of 7–17 indicative of their non-electrolytic nature. Molar conductance value of complexes $[ML_2]Cl_2$ and $[(ML_2{\cdot}2H_2O)]SO_4$ were observed in the range 110–115 ohm^{-1} cm^2 $mole^{-1}$ indicating that these complexes behave as 1 : 2 electrolyte.

Infrared spectra

The infrared spectra of Schiff base ligands show bands at 3300 cm^{-1} and 3100 cm^{-1} characteristic of asymmetric and symmetric stretching vibrations of νNH_2 group[4]. However, a strong band at 1540 and 1630 cm^{-1} indicates the presence of ν(pyridine) and νC=N groups[5] respectively. In the spectra of all the complexes no shift was observed in νNH_2 band frequency, ruling out the possibility of coordination through nitrogen. However, downward shift of about 40 and 30 cm^{-1} in νC=N and ν(pyridine) frequency which was observed at 1600

TABLE 1

ANALYTICAL, MOLAR CONDUCTANCE AND MAGNETIC MOMENTS DATA OF SCHIFF BASES COMPLEXES

Complexes	Colour	M.p./Decomp (°C)	% Analyses Found (Calcd)					Λ_M ohm^{-1} cm^{-1} mol^{-1}	μ_{eff} (B.M.)
			Metal	Carbon	Hydrogen	Nitrogen	Mol. Wt		
$Mn_2(COPDE)_4Cl_2$	Brown	330	10.89 (11.33)	58.89 (59.46)	4.23 (4.54)	16.74 (17.33)	905.31 (968.84)	14	2.74
$Mn_2(CMPDE)_4Cl_2$	Brown	305	10.94 (11.33)	58.94 (59.46)	3.98 (4.54)	16.85 (17.33)	901.34 (968.86)	12	2.70
$Fe(CMPDE)_2{\cdot}2H_2O{\cdot}SO_4$	Brownish Orange	300	11.38 (11.73)	60.18 (60.52)	4.39 (4.62)	17.18 (17.65)	438.64 (475.84)	18	5.24
$Fe(CMPDE)_2{\cdot}2H_2O{\cdot}SO_4$	Brownish Orange	319	11.41 (11.73)	60.31 (60.52)	4.40 (4.62)	17.20 (17.65)	458.14 (475.84)	17	5.21
$Co(COPDE)_2(CH_3COO)_2$	Brown	290	12.14 (12.67)	61.34 (71.94)	5.91 (6.02)	17.56 (18.06)	431.04 (464.93)	9	5.8
$Co(CMPDE)_2(CH_3COO)_2$	Brownish Green	325	11.89 (12.67)	61.56 (61.94)	5.75 (6.02)	17.48 (18.06)	428.64 (464.93)	8	5.7
$Co_2(COPDE)_4(NO_3)_2$	Greenish Brown	310	11.98 (12.51)	60.96 (61.15)	4.31 (4.67)	14.51 (14.86)	904.14 (941.86)	10	2.2
$Co_2(CMPDE)_4(NO_3)_2$	Greenish Brown	302	12.14 (12.51)	60.84 (61.15)	1.17 (4.67)	14.28 (14.86)	931.00 (941.86)	12	2.0

Complexes	Colour	M.p./Decomp (°C)	% Analyses Found (Calcd)					Λ_M ohm^{-1} cm^{-1} mol^{-1}	μ_{eff} (B.M.)
			Metal	Carbon	Hydrogen	Nitrogen	Mol. Wt		
$Ni(COPDE)_2Cl_2$	Green	288	13.59 (14.05)	67.84 (68.94)	4.80 (5.26)	19.68 (20.11)	400.08 (417.70)	110	Dia
$Ni(CMPDE)_2Cl_2$	Green	280	13.60 (14.05)	66.00 (68.94)	4.90 (5.26)	19.84 (20.11)	398.97 (417.70)	115	Dia
$Ni(COPDE)_2 \cdot 2H_2O \cdot SO_4$	Dark Brown	303	11.86 (12.26)	59.69 (60.16)	4.98 (5.43)	17.10 (17.54)	429.48 (478.70)	112	3.10
$Ni(CMPDE)_2 \cdot 2H_2O \cdot SO_4$	Brown	309	11.78 (12.26)	59.40 (60.16)	4.68 (5.43)	17.45 (17.54)	440.48 (478.70)	111	3.25
$Ni_2(COPDE)_4(NO_3)_2$	Brownish Green	318	11.96 (12.47)	66.89 (67.13)	4.34 (4.67)	17.38 (17.84)	894.01 (941.48)	9	3.33
$Ni_2(CMPDE)_4(NO_3)_2$	Dark Brown	315	11.90 (12.47)	67.00 (67.13)	4.14 (4.67)	17.60 (17.84)	898.5 (941.43)	7	3.38
$Ni(COPDE)_2(CH_3COO)_2$	Brown	301	11.98 (12.55)	71.00 (71.84)	5.68 (5.98)	17.46 (17.96)	428.60 (467.70)	12	3.43
$Ni(CMPDE)_2(CH_3COO)_2$	Brown	298	12.30 (12.55)	71.48 (71.84)	5.15 (5.98)	17.46 (17.41)	430.00 (467.70)	12	3.40

and 1500 cm^{-1}, indicating coordination through $\nu C{=}N$ and ν(pyridine) ring. Coordination through nitrogen of pyridine and azomethine groups has been further confirmed by the appearance of $\nu M{-}N$ band at 510–540 cm^{-1} in far infrared region of complexes. $[M_2L_4Cl_2]$ complexes show band at 275–280 cm^{-1} which may be assigned to $\nu M{-}Cl$. As M–Cl band did not split up so halogen atoms are at *trans* position. The IR spectra of nitrato complexes show bands at 1640, 1220, 1000 and 940 cm^{-1} suggesting the presence of coordinated nitrate anion[6]. In $[ML_2{\cdot}2H_2O]SO_4$ complexes additional band in the 3650–3400 cm^{-1} region indicates the presence of water molecule. The appearance of one more band at 830 cm^{-1} (rocking and wagging) suggests that it is present in the coordination sphere[7]. $[ML_2(CH_3COO)_2]$ complexes also exhibit additional bands at 1510, 1440, 1335 and 715 cm^{-1} which can be assigned to $\nu_{as}(COO)$, $\nu_s(COO)$, $\delta(CH_3)$ and $\delta(OCO)$ vibrations respectively indicating the presence of acetate ion in the coordination sphere[8].

Magnetic Moment and Electronic Spectra

The subnormal magnetic moment values of Mn(II) complexes under study have been reported in the range 2.70–2.74 B.M. which is indicative of the presence of π type antiferromagnetic and ferromagnetic exchange interaction respectively between metal atoms in a dimetallic structure[9]. The electronic spectra of Mn^{II} complexes exhibit bands at (ν_1) 16700–800 ($\varepsilon = 1.1$–1.2), (ν_2) 26400–26450 ($\varepsilon = 2$), and (ν_3) 28700–28740 ($\varepsilon = 3.9$–4.0) cm^{-1} which may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4A_{1g}(G)$ transitions respectively for the Mn(II) ion in an octahedral environment[10]. The different crystal field parameters $\frac{\nu_2}{\nu_1} = 1.58$, $Dq = 1137\ cm^{-1}$ and $\beta = 25.97\%$ are in accordance with octahedral structure of the Mn^{II} complexes.

The magnetic moment values of Fe^{II} complexes were observed in the range of 5.21–5.24 B.M. The electronic spectra of Fe^{II} complexes exhibit band at 10,700–10,730 ($\varepsilon = 1.5$) in visible region and two broad peaks with low intensity 31,450–31,500 ($\varepsilon = 2.3$–2.4) and 40,350–40,365 ($\varepsilon = 2.7$–2.8) respectively, corresponding to the transitions ${}^5T_{2g}(D) \rightarrow {}^5E_g(D)$, ${}^5T_{2g}(D) \rightarrow {}^3T_{1g}(H)$ and ${}^5T_{2g}(D) \rightarrow {}^3E_g(H)$ respectively. These transitions are spin forbidden and are possibly due to $n{-}\pi^*$ and $\pi{-}\pi^*$ transitions of the ligand or due to merger of both the transitions. Dq value of 1070 cm^{-1} is very close to the Dq value for octahedral Fe^{II} complexes[11, 12]. The μ_{eff} values of $[Co_2L_4(NO_3)_2]$ complexes have been found to be 2.2 B.M. Subnormal magnetic moment values of these complexes can be ascribed to the partial quenching of paramagnetism due to metal-metal interaction in a polymeric structure. The μ_{eff} values of $[CoL_2(CH_3COO)_2]$ complexes have been observed in the range 5.7–5.8 B.M., which suggests an octahedral structure[13]. The electronic spectra of complexes exhibit band at 8180–8620 ($\varepsilon = 1.4$–1.8), 17,000–17,730 ($\varepsilon = 0.3$–0.4) and 20,800–21,500 cm^{-1} ($\varepsilon = 4.0$–4.2) corresponding to the transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F)$

$\rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ respectively. In addition a charge-transfer band at 33,000 cm^{-1} ($\varepsilon = 0.6$) was also observed.

The ligand field parameters $\nu_2/\nu_1 = 2.0–2.07$, $B = 884–891$, $\beta = 0.78–0.79$, $\beta_0 = 20.44–21.07$ and $Dq = 8180–8620\ cm^{-1}$ are quite consistant with octahedral geometry.

$[NiL_2]Cl_2$ complexes have been found to be diamagnetic. Magnetic moment for $[NiL_2{\cdot}2H_2O]SO_4$ and $[NiL_2(CH_3COO)_2]$ type complexes have been observed in the range 3.10–3.43 B.M. These values are expected for Ni^{II} octahedral complexes. The magnetic moment values of $[Ni_2L_4(NO_3)_2]$ complexes have been observed in the range 2.08–2.12 B.M. Subnormal magnetic moment value of these complexes can be ascribed to partial quenching of paramagnetism to metal-metal interaction in a polymeric structure[14].

The electronic spectra of $[NiL_2]Cl_2$ complexes under study exhibit band at 21,200–21,250 cm^{-1} (broad) ($\varepsilon = 12.0–12.3$) which may be due to ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition, suggestive of square planar geometry[15].

The electronic spectra of $[NiL_2{\cdot}2H_2O]{\cdot}SO_4$ complexes exhibit band at 10,416–10,420 ($\varepsilon = 7.1$), 14,920–14925 ($\varepsilon = 7.2$) and 23,850–23,854 cm^{-1} ($\varepsilon = 17.2$) corresponding to transitions (${}^3T_{2g} \leftarrow {}^3A_{2g}$), (${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$) and (${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$) respectively, expected for Ni^{II}octahedral complexes. Out of these low energy band (ν_1) has been equated to 10 Dq. Ligand field parameters $\nu_2/\nu_1 = 1.43$, Racah parameter[16], $B = 501.46$, $\beta = 0.48$ and $\beta_0 = 51.78\%$ are also suggestive of octahedral structural of Ni^{II} complexes.

Electronic spectra of $[Ni_2L_4(NO_3)_2]$ and $[NiL_2(CH_3COO)_2]$ complexes exhibit band at 10,010–10,400 ($\varepsilon = 5.8–7.1$), 14,380–15,000 ($\varepsilon = 7.0–7.5$) and 24,400–24,700 ($\varepsilon = 14.2–14.0$) cm^{-1} corresponding to the transitions (${}^3T_{2g} \leftarrow {}^3A_{2g}$)($\nu_1$), (${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$)($\nu_2$) and (${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$)($\nu_3$) respectively. Out of these the low energy band ν_1 has been equated to 10 Dq. $\frac{\nu_2}{\nu_1}$ for these complexes have been observed in the range 1.45 and 1.42 respectively, which are close to that required for octahedral geometry[17]. B, β and β_0 values were observed in the range (560.66–598.66) cm^{-1}, $\beta = (0.53–0.57)\ cm^{-1}$ and $\beta_0 = (42.48–45.9)$ are also suggestive of octahedral structure of Ni^{II} complexes.

The molecular weight determination also suggests dimeric nature of $M_2L_4Cl_2$, $M_2L_4(NO_3)_2$ and $M_2L_4(NO_3)_2$ complexes.

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REFERENCES

1. M. Gulloti, L. Cassella, A. Pasini and R. Ugo, *J. Chem. Soc. Dalton Trans.*, 339 (1977).
2. M. Kumar, H.R. Mahato, Vibha Sharma and T. Sharma, *J. Indian Chem. Soc.*, **66**, 73 (1989).

3. T. Sharma and M. Kumar, *J. Indian Chem. Soc.*, **68**, 539 (1991).
4. J.V. Quagliano. G.V. Svatos and B.C. Curran, *Anal. Chem.*, **26**, 429 (1954).
5. R.P. Sharma and R.N. Prasad, *Polyhedron*, **3**, 714 (1984).
6. K. Nakamoto and P.J. McCarthy, Spectroscopy and Structure of Metal Chelate Compounds, John Wiley & Sons., Inc., New York (1968).
7. R.C. Aggarwal and N.K. Singh, *Indian J. Chem.*, **13A**, 931 (1975).
8. K, Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, New York, p. 229, 231 (1978).
9. P. Mahapatra, B.K. Patel and K.C. Sathpathy, *J. Indian Chem. Soc.*, **66**, 820 (1989).
10. V.J. Patel and M.N. Patel, *Indian J. Chem.*, **28A**, 428 (1989).
11. N.R. Gandhi and K.N. Munshi. *J. Indian Chem. Soc.*, **59**, 1290 (1989).
12. M. Ciampolini, *Structure and Bonding*, **6**, 52 (1969).
13. H.K. Sharma, Sneh Lata, S.N. Reddy and D.M. Puri, *Indian J. Chem.*, **20A**, 1031 (1981).
14. Bipin B. Mahapatra, Sarat Ch. Chaudhury and Basant K. Patel, *Indian J. Chem.*, **28A**, 619 (1989).
15. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, p. 887 (1972).
16. A.B.P. Lever, *J. Chemical Education*, **45**, 711 (1968).
17. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, New York (1968).

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