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Synthesis and Structural Behaviour of Schiff Base Complexes Derived from Vanillin and Aliphatic Diamines

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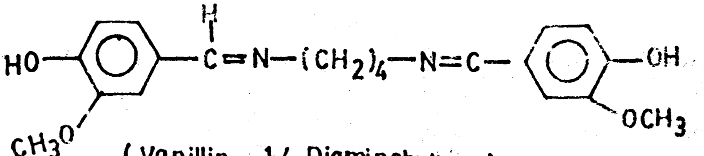
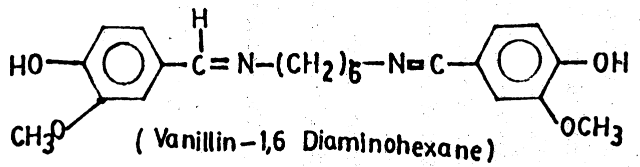
Schiff base complexes derived from ligands vanillin and aliphatic diamines (1,4-diaminobutane and 1,6-diaminohexane) with divalent Co^{2+}, Ni^{2+} and Cu^{2+} ions have been synthesised. Square planar geometry has been assigned to $[M(L_1)_2]SO_4$ and $[M(L_2)_2]SO_4$, where $M = Cu^{2+}$, L_1 = Schiff base ligand derived from vanillin and 1,4-diaminobutane(PMBIB) and L_2 = Schiff base ligand derived from vanillin and 1,6-diaminohexane (PMBIH); whereas octahedral structures have been assigned to $[M(L_1)_2(NO_3)_2]$, $[M(L_2)_2(NO_3)_2]$ and $[M(L_1)_2(CH_3COO)_2]$ complexes ($M = Cu^{2+}$, Co^{2+}, and Ni^{2+}),

INTRODUCTION

In recent years transition metal complexes with Schiff base derived from aromatic aldehyde and aliphatic diamines have been studied widely[1–5]. In the present paper structural properties of cobalt(II), nickel(II) and copper(II) complexes with Schiff bases derived from vanillin, 1,4-diaminobutane(PMBIB) and 1,6-diaminohexane(PMBIH) have been reported.



(Vanillin – 1,4 Diaminobutane)
(PMBIB)



(Vanillin–1,6 Diaminohexane)
(PMBIH)

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EXPERIMENTAL

Synthesis of ligands: An alcoholic solution of vanillin was mixed with 1,4-diaminobutane or 1,6-diaminohexane at room temperature in benzene solution in 2:1 molar solution. Most of the benzene was removed at 30°C under reduced pressure. The resulting Schiff bases (PMBIB and PMBIH), deep orange in colour, appeared as oils which solidified upon storage in the freezer.

Synthesis of complexes: 0.02 Mole of respective Schiff base was mixed separately with the methanolic/ethanolic solution of metal(II) chloride/nitrate/sulphate/acetate (0.01 mole) in 2:1 ratio. All the complexes were prepared by slow addition of the ligand to a warm methanolic/ethanolic solution of metal salts. Slow cooling of the complexes yielded the solid product. The complexes were filtered, washed with a small amount of ethanol and dried under vacuum.

RESULTS AND DISCUSSION

The molecular formulae of the Cu(II), Co(II) and Ni(II) complexes have been assigned on the basis of their analytical data (Table-1) and molar conductance. All the complexes are generally insoluble in common organic solvents. However, some of the complexes have been found to be partialy soluble in methanol, ethanol, dimethyl formaide, DMSO, THF, benzene, CCl_4 and $CHCl_3$ repectively. Most of Cu(II), Co(II) and Ni(II) are non-electrolytic (14–21 ohm^{-1} cm^2 $mole^{-1}$ in DMF, DMSO and THF at 25°C at a concentration of 10^{-2} M) and can be formulated $[M(PMBIB)_2X_2]$ or $[M(PMBIH)_2X_2]$ ($X = Cl^-$, NO_3^- and CH_3COO^-). $Cu(II)(PMBIB)_2SO_4$ and $Cu(II)(PMBIH)_2SO_4$ complexes have been found to be ionic (128–130 ohm^{-1} cm^2 $mole^{-1}$ in DMF at a concentration of 10^{-2} M). The molar conductance values indicate that these complexes behave as 1:2 electrolyte[6].

TABLE-1
ANALYTICAL AND MAGNETIC MOMENT DATA OF METAL COMPLEXES

Complexes/(Colour)	m.p./ Decomp. 0°C	% Analysis Found (Calcd.) M	C	H	N	μ_{eff} (B.M.)
$[Cu(II)(PMBIB)_2]\ SO_4$ (Indigo)	220	7.02 (7.23)	54.92 (55.10)	4.99 (5.51)	6.12 (6.42)	Diamagnetic
$[Cu(II)(PMBIH)_2]\ SO_4$ (Green)	260	6.72 (6.79)	56.92 (56.95)	5.95 (6.04)	5.88 (6.04)	Diamagnetic
$[Cu(II)(PMBIB)_2Cl_2]$ (Dark green)	205	4.98 (5.08)	56.69 (56.73)	5.64 (5.67)	6.59 (6.61)	1.79
$[Cu(II)(PMBIH)_2Cl_2]$ (Light green)	318	7.42 (7.50)	62.84 (62.93)	6.59 (6.67)	6.54 (6.67)	1.91
$[Cu(II)(PMBIB)_2(NO_3)_2]$ (Light blue)	312	7.35 (7.47)	56.84 (56.93)	5.58 (5.69)	9.88 (9.96)	1.80

Complexes/(Colour)	m.p./ Decomp. 0°C	% Analysis Found (Calcd.)				μ_{eff} (B.M.)
		M	C	H	N	
[Cu(II)(PMBIH)$_2$(NO$_3$)$_2$]	315	6.14	55.40	5.74	8.64	1.89
(Green)		(6.20)	(55.52)	(5.88)	(8.83)	
[Cu(II)(PMBIB)$_2$(CH$_3$COO)$_2$]	325	6.51	59.14	5.90	5.98	1.82
(Green)		(6.63)	(59.39)	(6.07)	(6.29)	
[Cu(II)(PMBIH)$_2$(CH$_3$COO)$_2$]	345	6.01	60.50	6.39	5.41	1.80
(Dark green)		(6.24)	(60.95)	(6.56)	(5.92)	
[Co(II)(PMBIB)$_2$Cl$_2$]	318	6.90	56.98	5.49	6.59	5.30
(Gray)		(7.00)	(57.00)	(5.70)	(6.65)	
[Co(II)(PMBIH)$_2$Cl$_2$]	309	6.43	58.74	6.13	6.20	5.31
(Brown)		(6.57)	(58.79)	(6.23)	(6.23)	
[Co(II)(PMBIB)$_2$(NO$_3$)$_2$]	305	6.48	53.52	5.30	9.21	3.96
(Brown)		(6.59)	(53.63)	(5.36)	(9.38)	
[Co(II)(PMBIH)$_2$(NO$_3$)$_2$]	269	6.52	55.16	5.76	8.74	3.94
(Dark green)		(6.59)	(55.28)	(5.86)	(8.79)	
[Co(II)(PMBIB)$_2$(CH$_3$COO)$_2$]	316	7.00	64.20	6.42	10.10	4.01
(Brown)		(7.18)	(64.31)	(6.57)	(10.23)	
[Co(II)(PMBIH)$_2$(CH$_3$COO)$_2$]	345	5.62	60.90	6.31	5.68	4.00
(Dark brown)		(5.94)	(61.14)	(6.58)	(5.94)	
[Ni(II)(PMBIB)$_2$Cl$_2$]	425	6.80	56.81	5.39	—	2.51
(Light green)		(6.97)	(57.02)	(5.70)		
[Ni(II)(PMBIH)$_2$Cl$_2$]	484	6.51	58.80	6.19	6.16	2.53
(Light green)		(6.53)	(58.81)	(6.23)	(6.23)	
[Ni(II)(PMBIB)$_2$(NO$_3$)$_2$]	348	6.49	49.25	3.91	7.98	2.52
(Light green)		(6.78)	(49.70)	(4.97)	(8.69)	
[Ni(II)(PMBIH)$_2$(NO$_3$)$_2$]	365	5.98	55.28	5.79	8.70	2.50
(Green)		(6.17)	(55.53)	(5.89)	(8.83)	
[Ni(II)(PMBIB)$_2$(CH$_3$COO)$_2$]	309	5.88	61.18	5.48	5.78	2.54
(Brown)		(6.26)	(61.49)	(5.76)	(5.97)	
[Ni(II)(PMBIH)$_2$(CH$_3$COO)$_2$]	316	5.90	60.80	6.19	5.48	2.55
(Brown)		(6.20)	(61.04)	6.54	(5.91)	

Infrared Spectra

Free ligands (PMBIB and PMBIH) exhibit absorption at 1640–1630, 3550 and 2800 cm^{-1} which correspond to ν(C = N)[7], ν(–OH) and ν(OCH$_3$) respectively. However the IR spectra of all complexes show downward shift of about 20–25 cm^{-1} in ν(C = N) frequency and were observed at 1620–1615 cm^{-1} indicating coordination through nitrogen of azomethine group. However, ν(OH) and ν(OCH$_3$) frequencies remain unaltered. IR spectra of [M(PMBIB)$_2$Cl$_2$] and

$[M(PMBIH)_2Cl_2$ ($M = Co^{2+}$, Ni^{+2} or Cu^{2+}) complexes exhibit additional band at 290–285 cm^{-1}, due to ν(M–Cl) absorption[8]. In $[M(PMBIB)_2(NO_3)_2]$ and $[M(PMBIH)_2(NO_3)_2]$ complexes also exhibit additional band at *ca.* 1480–1475, 1390 and 840–830 cm^{-1}. The difference of 115–110 cm^{-1} between 1480–1475 and 1390 cm^{-1} bands, the two components of ν_3 band of nitrate, suggests unidentate coordination of nitrate[9]. In $[M(PMBIB)_2(CH_3COO)_2]$ and $[M(PMBIH)_2(CH_3COO)_2]$ type complexes additional band at *ca.* 1510, 1445, 1340 and 710 cm^{-1} were observed which can be assigned to ν_{asym}(COO), ν_{sym}(COO), $\delta(CH_3)$ and δ(OCO) vibrations respectively indicating the presence of acetate ion in the coordination sphere[10].

Magnetic moments and Electronic Spectra

$[Cu(PMBIB)_2]SO_4$ and $[Cu(PMBIH)_2]SO_4$ complexes were found to be diamagnetic. Magnetic moment values of $[Cu(PMBIH)_2Cl_2]$ and $[Cu(PMBIB)_2(NO_3)_2]$ complexes were observed to be 1.91 B.M. and 1.89 B.M. respectively. The slightly higher magnetic moments probably resulted from the spin-orbit coupling and absence of spin-spin interaction in the complexes[11]. These values suggest a distorted octahedral geometry for these complexes[12]. The magnetic moment values of other Cu(II) complexes were observed in the range 1.79–1.82 B.M. These values are in accordance with a distorted octahedral geometry[13]. The magnetic moment values of $[Co(PMBIB)_2Cl_2]$ and $[Co(PMBIH)_2Cl_2]$ complexes have been found to be 5.30 B.M. and 5.31 B.M. respectively which suggests an octahedral structure[14]. The magnetic moment values of remaining Co(II) complexes were observed in the range 3.96–4.01 B.M. These are much lower than the values expected for tetrahedral (4.2–3.7 B.M.) or octahedral (4.7–5.2 B.M.) Co(II) complexes. This lowering of magnetic moment may be explained by assuring the co-existence of high spin as well as low spin states[15] of Co(II) ($t_{2g}{}^6e_g^2 \rightleftarrows t_{2g}{}^6e_g$) The presence of antiferromagnetism or the polymeric nature of the complexes[16, 17], μ_{eff} of Ni(II) complexes have been observed in the range (2.50–2.55) B.M., which is lower than the spin-free octahedral values. This may be due to the distortion[18, 19].

$[Cu(PMBIB)_2]SO_4$ and $[Cu(PMBIH)_2]SO_4$ complexes show an intense band at 25,000 cm^{-1} and 26,500 cm^{-1} respectively is assigned to charge transfer from ligand to metal. Other two bands observed by each complex at (18,500, 16,800 cm^{-1}) and (19,000, 17,000 cm^{-1}) respectively may be due to d-d transitions. These bands suggest a square planar geometry[19]. The electronic spectra of other Cu(II) complexes were observed at 16,400–16,000 ($\varepsilon = 15$), 15,800–15,000 ($\varepsilon = 14$), 16,000–15,800 ($\varepsilon = 15$) and 16,200–15,900 ($\varepsilon = 16$) respectively, which are indicative of their distorted octahedral structure.

The electronic spectra of $[Co(PMBIB)_2(NO_3)_2]$, $[Co(PMBIH)_2(NO_3)_2]$ and $[Co(PMBIB)_2Cl_2]$ complexes exhibit band at 8600–8360 cm^{-1} ($\varepsilon = 4.0$–3.6) 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 C.T. band at 33,000 cm^{-1} ($\varepsilon = 0.6$) was also observed. $[Co(PMBIB)_2(CH_3COO)_2]$, $[Co(PMBIH)_2(CH_3COO)_2]$ and $[Co(PMBIH)_2Cl_2]$ complexes exhibited two bands at (17,100–16,500) ($\varepsilon = 1.1$–1.0) and (21,000–20,500) cm^{-1} ($\varepsilon = 3.0$–2.4) corresponding to

${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_2)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ respectively. The various ligand field parameters; *i.e.* $\nu_1/\nu_2 = (2.00\text{–}2.03)$; $B = (890\text{–}893)$, $B' = (0.69\text{–}0.71)$, $\beta_0 = (20.40\text{–}22.44)$ and $Dq = (860\text{–}830)\ cm^{-1}$ calculated for $[Co(PMBIB)_2 \cdot (NO_3)_2]$, $[Co(PMBIH)_2(NO_3)_2]$ and $[Co(PMBIB)_2Cl_2]$ complexes are indicative of their octahedral structure[20]. Ligand field parameters for $[Co(PMBIB)_2(CH_3COO)_2]$, $[Co(PMBIH)_2(CH_3COO)_2]$ and $[Co(PMBIH)_2Cl_2]$ complexes have been observed to be in the range $\nu_3/\nu_2 = 1.21\text{–}1.24$, $B = 884\text{–}891$; $B' = 0.64\text{–}0.78$, $\beta_0 = 20.10\text{–}22.00$, $Dq = 890\text{–}885\ cm^{-1}$ which are quite consistant with the values reporte for octahedral complexes.

The electronic spectra of all the Ni(II) complexes exhibited bands at 9,300–9,210 ($\varepsilon = 1.5\text{–}1.1$), 16,500–16,100 ($\varepsilon = 3.6\text{–}3.2$), 25,750–24,690 ($\varepsilon = 4.5\text{–}4.0$) corresponding to the transitions $\nu_1\ ({}^3T_{2g} \leftarrow {}^3A_{2g})$, $\nu_2\ ({}^3T_{1g}(F) \leftarrow {}^3A_{2g})$ and $\nu_3\ ({}^3T_{1g}(P) \leftarrow {}^3A_{2g})$ respectively expected for octahdral or distorted octahedral spin free nickel(II) complexes. The ligand field parameters such as $\nu_2/\nu_1 = 1.7\text{–}1.9$, $\beta = 0.84\text{–}0.86$, $\beta_0 = 15.46\text{–}15.65$, $B' = 885.65\text{–}879.33\ cm^{-1}$ were in close agreement with the values required for octahedral complexes.

EPR spectra of Cu(II) complexes were recorded in DMSO, DMF and THF at room temperature and liquid nitrogen temperature. No band corresponding to $M_S = \pm 2$ transition at half field was observed indicating the absence of intramolecular and intermolecular antiferromagnetic interaction. The considerable deviations of g_{11} and g_1 values of the complexes from the free ion value and closeness of those values to those reported for distorted octahedral complexes suggest distorted octahedral geometry for complexes[22]. The σ-bonding parameters α^2 comes out to be in between 0.60–0.64 for all the complexes, suggesting a predominantly covalent nature of metal ligand bond.

The ESR spectra of $[Cu(PMBIB)_2]SO_4$ and $[Cu(PMBIH)_2]SO_4$ complexes show no $M_s = \pm 2$ transition at half field indicating the absence of intramolecular and intermolecular antiferromagnetic interactions. The magnitude of $g_{11} = 2.07\text{–}2.08$ and $g_1 = 2.00\text{–}2.01$ are indicative of square planar environment around metal ion in $[Cu(PMBIB)_2]\ SO_4$ and $[Cu(PMBIH)_2]\ SO_4$ complexes[23].

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