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Synthesis and Characterization of Cobalt(II), Nickel(II) and Copper(II) Complexes derived from Aromatic Diamines and Heterocyclic Aldehyde

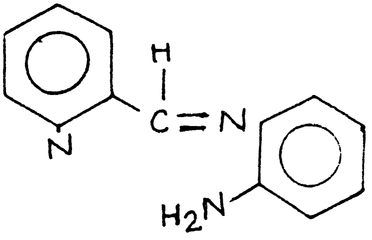
M. KUMAR* and A.K. SINHA†
Department of Chemistry
L.N.T. College, Muzaffarpur-842 002, India

Ligands derived from pyridine-2-aldehyde, *o*-phenylenediamine (Palophen) and *m*-phenylenediamine (Palmphen) have been prepared. Complexes of Cu(II), Co(II) and Ni(II) have been synthesised and characterized on the basis of elemental analysis, molar conductance, IR, UV and magnetic moment data. $[Cu(Palophen)_2]Cl_2$, $[Cu(Palmphen)_2]Cl_2$, $[Ni(Palophen)_2]Cl_2$ and $[Ni(Palmphen)_2]Cl_2$ were diamagnetic and square-planar. However, rest of Cu(II), Ni(II) and all the Co(II) complexes showed μ_{eff} indicative of their octahedral or distorted octahedral structure.

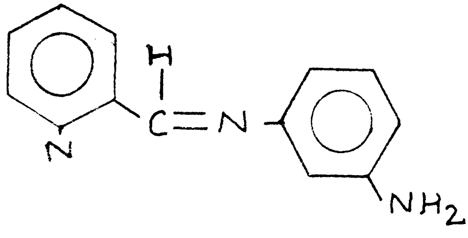
INTRODUCTION

Schiff bases and related complex compounds have gained importance because of their use as models in analytical, biological, biochemical and antimicrobial system.[1]

A number of Schiff base complexes of transition metal cations have been reported[2–4] due to their multi-faceted applications. The present communication deals with the ligational behaviour of pyridine-2-aldehyde, *o*-phenylene diamine and *m*-phenylene diamine with Co(II), Ni(II) and Cu(II).



Palophen (L_1)



Palmphen (L_2)

EXPERIMENTAL

All chemicals used were of AnalaR grade or of chemically pure quality.

**Address for correspondence*: Adarsh Nagar, Majhaulia, P.O. Khabra, Muzaffarpur-843 146.
†Department of Chemistry, M.D.D.M. College, Muzaffarpur-842 002.

Ligands (Palophen) and (Palmphen) were prepared as follows:

Pyridine-2-carboxaldehyde was mixed with *o*-phenylene diamine and *m*-phenylene diamine respectively in equimolar amounts at temperatures between 0–5°C. Both the solution mixtures were stirred for $\frac{1}{2}$ h. The resulting Schiff base deep in colour appeared as oil which solidified upon storage in the freezer. The melting point was observed to be 46°C. It was kept in vacuum.

Preparation of Complexes

The respective Schiff base (0.02 mole) was dissolved in dioxane and mixed separately with the ethanolic solution of metal(II) chloride/nitrate/acetate (0.01 mole) in 2 : 1 ratio. The reaction mixture was kept over water bath for about $1\frac{1}{2}$ h. After cooling and stirring the solution, metal chelates were seperated out. These were filtered, washed with ethanol, ether and dried in *vacuo*.

RESULTS AND DISCUSSION

The analytical data of the complexes (Table-1) reveal that the four complexes of Cu(II) and Ni(II) formed with pyridine-2-aldehyde, *o*-phenylene diamine and *m*-phenylene diamine, *i.e.*, [Cu(Palophen)$_2$]Cl$_2$, [Cu(Palmphen)$_2$]Cl$_2$, [Ni(Palophen)$_2$]Cl$_2$ and [Ni(Palmphen)$_2$]Cl$_2$ have 1 : 2 stoichiometry, which is also evident from high conductance values (115–131 ohm^{-1} cm^2 mole^{-1}) showing the electrolytic nature of complexes. The rest of the complexes have 1 : 1 stoichiometry and their solutions are non-electrolytes as inferred from their low conductance values ranging from 9–21 ohm^{-1} cm^2 mole^{-1}. Most of the compounds have high decomposition temperature (245°–325°C). These compounds are insoluble in most solvents and partially soluble in DMSO and DMF.

IR Spectra

IR spectra of both the ligands exhibit strong band around 1640–1635 cm^{-1}, which is indicative of the presence of ν(C═N) group, diagnostic of Schiff base formation. A band at about 1530 cm^{-1} is observed in the IR spectra of the ligand which may be assigned as ν(pyridine).[6] Both the ligands show two sharp bands around 3340–3330 cm^{-1} and 3120–3100 cm^{-1} which may be assigned to asymmetric and symmetric stretching vibrations of ν(NH$_2$) group respectively.[7] IR spectra of all the complexes exhibit downward shift of about 40–35 cm^{-1} in ν(C═N) frequency and observed at 1600 cm^{-1} indicating co-ordination through nitrogen of azomethine group in [M(L$_2$)Cl$_2$], [M(L$_2$)$_2$(NO$_3$)$_2$] and [M(L$_2$)$_2$(CH$_3$COO)$_2$] complexes [M = Cu(II), Co(II) and Ni(II)].

Pyridine frequency was observed at 1500 cm^{-1}, indicating co-ordination through nitrogen of pyridine ring. In [M(L$_1$)$_2$]Cl$_2$, [Cu(L$_1$)$_2$(NO$_3$)$_2$] and [M(L$_1$)$_2$(CH$_3$COO)$_2$] complexes there is lower shift of the asymmetric stretching band and observed at 3290–3280 cm^{-1} and 3090–3080 cm^{-1}; indicative of participation of NH$_2$ group in the metal-ligand band. Further the ligands display a band at 1580 cm^{-1} due to —NH$_2$ group deformation and undergo higher shift by 40–20 cm^{-1} in the complexes which support the involvement of the NH$_2$ group in bonding.[8, 9] The presence of a band near 500–450 cm^{-1} in the far infrared region is indicative of co-ordination through nitrogen atom of $>C{=}N$, $—NH_2$ group as well as of pyridine.

In $[M(L_1)_2(NO_3)_2]$ and $[M(L_2)_2(NO_3)_2]$ complexes additional bands at 1490–1485, 1380–1375 and 840–830 cm^{-1} have been observed. The difference of about 10 cm^{-1} between 1490–1485 and 1380–1375 cm^{-1} bands, the two components of ν_3 band of nitrate, suggests unidentate co-ordination of nitrate.[10,11]

In $[M(L_1)_2(CH_3COO)_2]$ and $[M(L_2)_2(CH_3COO)_2]$ complexes additional bands at 1510, 1445, 1340 and 710 cm^{-1} which can be assigned to $\nu_{asym}(COO)$, $\nu_{sym}(COO)$, $\delta(CH_3)$ and $\delta(OCO)$ vibrations respectively indicating the presence of acetate ion in the co-ordination sphere.[12]

Magnetic moment and electronic spectral data—$[Cu(L_1)_2]Cl_2$ and $[Cu(L_2)_2]Cl_2$ complexes show intense band at 24,900 cm^{-1} respectively—may be assigned to charge transfer from ligand to metal. Other bands shown by both of the complexes at (18,450–18,500) and (16,800–16,850) respectively may be due to d-d transitions. The appearance of these bands suggests square-planar geometry for both these complexes.

Square-planar geometry of $[Cu(L_1)_2]Cl_2$ and $[Cu(L_2)_2]Cl_2$ complexes is quite consistent with the diamagnetic character of these complexes.

Electronic spectral data of $[Cu(L_1)_2(NO_3)_2]$, $[Cu(L_2)_2(NO_3)_2]$, $[Cu(L_1)_2(CH_3COO)_2]$ and $[Cu(L_2)_2(CH_3COO)_2]$ complexes have been observed in the range 16,000–15,200 cm^{-1}. This is indicative of their distorted octahedral structure. The magnetic moment values of $[Cu(L_2)_2(NO_3)_2]$ and $[Cu(L_1)_2(CH_3COO)_2]$ complexes have been reported to be 1.91 and 1.90 respectively. The slightly higher magnetic moment probably results from the spin-spin interaction in the complexes.[13] The magnetic moment values of $[Cu(L_1)_2(NO_3)_2]$ and $[Cu(L_2)_2(CH_3COO)_2]$ complexes have been observed to be 1.80 B.M. and 1.85 B.M. respectively. These values suggest a distorted octahedral geometry for the complexes.[14]

The magnetic moment values of $[Co(L_2)_2Cl_2]$ and$[Co(L_2)_2Cl_2]$ complexes have been observed in the range 5.0–5.3 B.M. These values are indicative of octahedral structure.[15]

The μ_{eff} values of $[Co(L_1)_2(NO_3)_2]$, $[Co(L_2)_2(NO_3)_2]$, $[Co(L_1)_2(CH_3COO)_2]$ and $[Co(L_2)_2(CH_3COO)_2]$ complexes have been reported in the range 3.96–4.00 B.M. These values are less than the magnetic moment values reported for tetrahedral or octahedral Co(II) complexes and more than reported values for square-planar Co(II) complexes. This lowering of magnetic moment values may be explained by assuring co-existence of high spin as well as low spin state of $Co(II)({}^t2g^5\ eg^2 = {}^tg^2\ eg^1)$, the presence of antiferromagnetic or the polymeric nature of the complexes.[16]

The electronic spectra of Co(II) complexes have shown three bands in the region 8550–8500, 17500–17450, 21550–21450 and 33500–33000 cm^{-1} (C.T. band) respectively.

Complexes $[Co(L_1)_2(NO_3)_2]$, $[Co(L_1)_2(CH_3COO)_2]$, $[Cu(L_2)_2(CH_3COO)_2]$ and $[Co(L_2)_2(NO_3)_2]$ have shown above absorptions corresponding to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_3)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_2)$ respectively.

TABLE-1

ANALYTICAL, CONDUCTANCE AND MAGNETIC MOMENT DATA OF Palophen, Palmphen AND THEIR METAL-COMPLEXES

Analysis % : Found/(calcd)

Compound/Colour	m.p./Decomp. (°C)	Metal	Carbon	Hydrogen	Nitrogen	Halogen	$\Lambda_m\ \Omega^{-1}$ cm^2 mol^{-1} in DMF	μ_{eff} (B.M.)
Palophen (L_1) (Green)	46	—	72.96 (73.09)	5.58 (5.58)	21.20 (21.30)	—	—	—
Palmphen (L_2) (Deep Green)	47	—	72.89 (73.09)	5.48 (5.58)	21.22 (21.32)	—	—	—
$[Cu(L_1)_2]Cl_2$ (Dark green)	212	11.61 (12.02)	54.00 (54.48)	3.98 (4.16)	15.21 (15.89)	12.64 (13.43)	125	Dia
$[Cu(L_1)_2(NO_3)_2]$ (Brown)	218	11.08 (11.39)	47.24 (47.32)	3.59 (3.94)	19.90 (20.08)	—	15	1.80
$[Cu(L_1)_2(CH_3COO)_2]$ (Green)	285	13.26 (13.53)	69.98 (71.55)	4.28 (4.68)	17.24 (17.88)	—	21	1.90
$[Cu(L_2)_2]Cl_2$ (Dark brown)	225	11.49 (12.02)	54.23 (54.48)	3.88 (4.16)	15.49 (15.89)	13.08 (13.43)	131	Dia
$[Cu(L_2)(NO_3)_2]$ (Brown)	230	10.92 (11.39)	46.98 (47.32)	3.48 (3.94)	19.79 (20.08)	—	17	1.91
$[Cu(L_2)_2(CH_3COO)_2]$ (Green)	275	13.36 (13.53)	70.00 (71.55)	4.38 (4.68)	17.54 (17.88)	—	20	1.85
$[Co(L_1)_2Cl_2]$ (Light Green)	245	11.42 (11.78)	52.32 (52.81)	4.00 (4.40)	16.34 (16.80)	13.92 (14.20)	11	5.0
$[Co(L_1)_2(NO_3)_2]$ (Greenish Brown)	300	10.21 (10.85)	47.34 (47.74)	3.58 (3.97)	19.96 (20.25)	—	14	3.96

Compound/Colour	m.p./Decomp. (°C)	Metal	Carbon	Hydrogen	Nitrogen	Halogen	$\Lambda_m\ \Omega^{-1}$ $cm^2\ mol^{-1}$ in DMF	μ_{eff} (B.M.)
[$Co(L_1)_2(CH_3COO)_2$] (Brown)	325	12.29 (12.87)	61.34 (61.94)	5.86 (6.02)	14.81 (15.35)	—	9	3.98
[$Co(L_2)_2Cl_2$] (Light green)	235	11.32 (11.78)	52.42 (52.81)	4.00 (4.40)	16.34 (16.80)	13.92 (14.20)	12	5.30
[$Co(L_2)_2(NO_3)_2$] (Greenish)	308	10.31 (10.65)	47.38 (47.74)	3.68 (3.97)	12.98 (20.25)	—	15	4.00
[$Co(L_2)_2(CH_3COO)_2$] (Brown)	335	12.22 (12.67)	61.34 (61.94)	5.86 (6.02)	14.98 (15.35)	—	12	4.00
[$Ni(L_1)_2$]Cl_2 (Green)	288	13.59 (14.05)	68.08 (68.94)	4.80 (5.26)	19.68 (20.11)	16.38 (16.99)	115	Diamagnetic
[$Ni(L_1)_2(NO_3)_2$] (Dark green)	305	10.00 (10.62)	47.20 (47.74)	3.25 (3.97)	19.79 (20.25)	—	9	3.30
[$Ni(L_1)_2(CH_3COO)_2$] (Brown)	314	11.98 (12.55)	71.34 (71.84)	5.88 (5.98)	17.47 (17.89)	—	9	3.10
[$Ni(L_2)_2$]Cl_2 (Green)	294	13.54 (14.05)	68.19 (68.94)	4.79 (5.26)	19.80 (20.11)	16.51 (16.99)	120	Diamagnetic
[$Ni(L_2)_2(NO_3)_2$] (Dark green)	308	10.18 (10.62)	47.38 (47.74)	3.45 (3.97)	19.72 (20.25)	—	11	3.40
[$Ni(L_2)_2(CH_3COO)_2$] (Brown)	315	11.89 (12.55)	71.54 (71.84)	5.61 (5,98)	17.54 (17.96)	—	12	3.10

The various ligand field parameters of Co(II) complexes (Table-2) are suggestive of octahdral Co(II) complexes.[14]

TABLE-2
LIGAND FIELD PARAMETERS OF Co(II) COMPLEXES

Complexes	ν_1/ν_2	ν_3/ν_2	B	β	β_0	Dq (cm^{-1})
$[Co(L_1)_2Cl_2]$	2.04	1.23	866.6	0.77	23.66	855
$[Co(L_2)_2Cl_2]$	2.05	1.26	890	0.79	23.21	850
$[Co(L_1)_2(NO_3)_2]$	—	1.23	888	0.79	20.62	889
$[Co(L_2)_2(NO_3)_2]$	—	1.26	889	0.80	20.44	890
$[Co(L_1)_2(CH_3COO)_2]$	—	1.22	890.1	0.70	22.14	872
$[Co(L_2)_2(CH_3COO)_2]$	—	1.24	888.8	0.70	22.32	870

$[Ni(L_1)_2]Cl_2$ and $[Ni(L_2)_2]Cl_2$ complexes have been found to be diamagnetic. The electronic spectra of these complexes exhibit band in the range 21200–21000 cm^{-1} (broad) corresponding to the transition $^1A_{1g} \rightarrow {}^1A_{2g}$ suggestive of square-planar geometry.[17] The magnetic moment values of $[Ni(L_1)_2(NO_3)_2]$, $[Ni(L_2)_2(NO_3)_2]$, $[Ni(L_1)_2(CH_3COO)_2]$ and $[Ni(L_2)_2(CH_3COO)_2]$ complexes have been found in the range 3.10–3.40 B.M. These values are quite consistent with the values reported for octahedral Ni(II) complexes.[19] The electronic spectra of these complexes exhibit bands in the region (10400–10000 cm^{-1}) (ν_1), (15300–14400 cm^{-1}) (ν_2) and (24700–24400 cm^{-1}) (ν_3) 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 Ni (II) octahedral complexes.[19] For all the above stated complex low energy band (ν_1) has been equated to 10 Dq. The ratio of ν_2/ν_1 (1.3–1.5) is in close agreement with the values required for octahedral geometry. The Racha parameter (B) has been found in the range 546.6–613.3. It has been calculated according to the equation[21] $\nu_3 + \nu_2 - 3\nu_1 = 15B$.

The value of β has been observed in the range (0.52–0.65) indicating covalent character of metal ligand bond in the complexes. These values are in agreement with octahedral geometry of the complexes.[18]

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