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Research Article

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Some Transition Metal Ion Complexes with 4-{(*E*)-[(2-chlorophenyl)imino] methyl}benzene-1,2-diamine

K. George Abraham, Manohar V. Lokhande and Sudhakar R. Bhusare

Department of Chemistry, SIES College, Sion (W), Mumbai(India)
Department of Chemistry, Sathaye College, Vileparle (E), Mumbai(India)
Department of Chemistry, DSM College, Parbhani, Parbhani(India)

ABSTRACT

Many transitional metal ion complexes have been synthesized for their analytical and commercial applications. The complexes of the type $[ML_2.2H_2O]Cl_2$ *{where M= Mn(II), Ni(II), Co(II), Cu(II) and Zn(II) and L=4-{(E)-[(2-chlorophenyl)imino]methyl}benzene-1,2-diamine}have been prepared and characterized on the basis of Elemental analysis,IR, UV-Visible, ESR, Mass, Magnetic susceptibility, Microbial activities, Conductivity measurements, Thermal analysis and X-ray powder diffraction. These complexes are 1:2 ratios, the magnetic data coupled with electronic spectra and ESR suggests that complexes are square planar geometry. IR of the ligand and complexes agree with the co-ordination to be central metal atom through both the nitrogen atoms. The electronic spectra bonding parameter (b½) and nephelauxetic ratio (β) have been also evaluated. Conductance measurements suggest that complexes are 1:1 electrolytic in nature. The X-ray powder diffraction studies indicate that, the unit cell is monoclinic and space group of complexes is* C_2/m *or Pc/m. Microbial activity of ligand and complexes show more activity towards Gram positive and Gram negative.*

INTRODUCTION

During the last decade, there has been a growing interest in the Coordination Chemistry of transition element [1] due to their potential application probes in medicine and biology [2] as contrast agents in magnetic resonance imaging[3-7] and as mild reagents and catalysis in organic synthesis[7]. These applications require a precise knowledge of the coordination properties of transition metal ions. Complexes containing macrocyclic hard donor ligand have been the most studied. This creates our interest in transition metal ions complexes with 4-{(*E*)-[(2-chlorophenyl)imino]methyl}benzene-1,2-diamine.

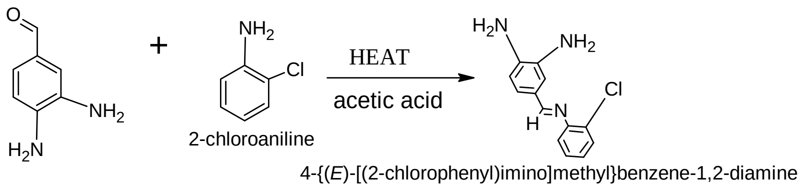
EXPERIMENTAL SECTION

All chemicals were AR grade and some are BDH Grade, The metal salts i.e. $MnCl_2$, $NiCl_2.6H_2O$, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$, and $ZnCl_2$. Methanol, Ethanol, Chloroform and water were used with double distilled.

Preparation of ligand : 0.2 mole of 3,4-diaminobenzaldehyde and 0.2moles of 2-chloroaniline dissolved in ethanol and three cm^3 of acetic acid added in it and reflux for 3 hrs using water condenser. After complete reflection solid separates, wash with ethanol and dry at room temp.

Preparation of complexes*:*
The 0.05 molar of metal chlorides and ligand solutions were prepared in ethyl alcohol. These solutions were mixed in 1: 2 stoichiometric ratios; the solutions were slowly added with constant stirring to an acidic aqueous metal solution. The pH of the solution were adjusted to near about 5.8 to 6.3 by adding 0.01 molar alcoholic ammonia

solution. The resulting mixture was refluxed for three hours in water bath, using water condenser. After three hours the precipitate was obtained. Then this precipitate was cooled, filtered, washed with ethyl alcohol and dried at 60˚c. Most of complexes are colored and Zn(II) complexes are colorless.



Instruments:
The C, H,N of Schiff base and metal complexes were determined by using micro analytical methods at IIT-Mumbai. IR spectra of the ligand and their complexes were carried out by using KBr pellets by using Perkin Elmer. Chlorides were estimated by Mohr's methods. The electronic spin resonances were recorded at IIT, Electronic spectra recorded at UICT-Mumbai using DMSO and water as solvent. TGA/DTA spectra were carried on Mettler Toledo Star system in the temperature range of 20-900 °C. The Mass spectra were recorded by ESI technique at IICT- Hyderabad and IPCA laboratories. Melting points of the ligand and decomposition temperature of complexes were determined at sathaye college laboratory. The Molar conductance measurements were carried out in DMSO and water (10^{-3} M) using Electronic Digital conductivity meter and cell is calibrated with KCl. The Magnetic susceptibilities of complexes were determined on Gouy balance using Hg [Co $(SCN)_4$] as a calibrate.

RESULTS AND DISCUSSION

The physical and analytical data given in table no.1 the obtained analytical data shows 1:2[M: L] ratio. The conductance measurements of the complexes were carried out in DMSO solvent and the obtained values (Table-1) were taken as a good evidence for the existence of a 1:1 in electrolytic in nature.

IR Spectra: The IR spectra [11-14] of Schiff bases and itscomplexes havebeenstudied assignments are given in below. The IR spectraof the complexes indicate that the Schiff base behaves as bidentate and co-ordinate to themetal *via* C=N and with amine group**.** The shift of the n(C=N) and n(N-H) by10-15 cm-1 in the complexes indicating that these groups are involved in the complexation.In theSchiff bases band appearing at 3455 cm-1 and 3300 due to NH stretching in the complexes. The band due to n(C=N) in the ligand at 1585 cm-1 isshifted to lower wave number at 1585-1550 cm-1 in the complexes there by confirmingthe coordination through the azomethine nitrogen atom. The newband appearing atregion 3485 and 3565 cm-1 may be due to two coordinated water molecules. The appearance ofbands in the far IR region at 435-415 cm-1 in the complexes may be assignable toM-N frequency. Additional bands in the complex in the region 623-603 cm-1 comparedwith IR spectra of free ligand have tentatively been assigned to M-O frequency. The other values are listed below in the table: (IR-spectral bands (cm-1) and frequencies of the Schiff bases and metal complexes)

	v(NH)	v(N-H)	v(C=N)	v(M-N)	v(M-O)	(H2O)
$C_{13}H_{22}ClN_6O_3$	3455	3300	1585	-	-	-
$[Mn(C_{13}H_{22}ClN_3)_2.2H_2O]Cl_2$	3415	3285	1575	422	615	3490 ,3545
$[Co(C_{13}H_{22}ClN_3)_2.2H_2O]Cl_2$	3418	3290	1570	418	609	3482,3542
$[Ni(C_{13}H_{22}ClN_3)_2.2H_2O]Cl_2$	3412	3278	1578	415	618	3485,3550
$[Cu(C_{13}H_{22}ClN_3)_2.2H_2O]Cl_2$	3440	3287	1572	408	620	3485,3555
$[Zn(C_{13}H_{22}ClN_3)_2.2H_2O]Cl_2$	3435	3285	1570	410	622	3475,3545

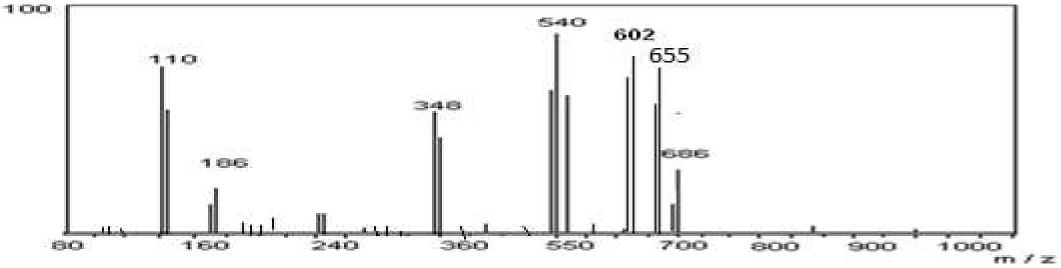
Complexes	Bands (cm^3)	Assignments	Parameters
$[Ni(C_{13}H_{22}ClN_3)_2.2H_2O]Cl_2$	8750 12600 21200	$^3A_{2g}$ (F)→$^3T_{2g}$ (F) $^3A_{1g}$ (F)→$^2T_{2g}$ $^3A_{2g}$ (P)→$^3T_{2g}$ (P)	β =0.9687 $b^{1/2}$=0.1250, δ % =3.2311 η = 0.01605
$[Co(C_{13}H_{22}ClN_3)_2.2H_2O]Cl_2$	5430, 8775 19850	$^4A_2$→$^4T_2$ (F), $^4A_2$ →$^4A_2$ (F) $^4A_2$→$^4T_1$ (P).	β =0.9715 $b^{1/2}$ = 0.1193 δ % =2.9336 η = 0.0140

Electronic spectra and magnetic moment

The electronic spectral data of the Schiff base and its complexes were recorded in DMF and Ethanol. (0.001 Mole /lit) the nature of electronic spectra of all the complexes indicates an octahedral geometry**[20]** around the central metal ions in the complexes. The Mn(II), Ni(II) , Co(II) and Cu(II) complexes *magnetic moment* recorded at room temperature they are paramagnetic in nature, magnetic value are listed in table no: 1**.** This indicates that the all complexes of 6-coordinate and probably octahedral. Bonding parameter ($b^{1/2}$), Nephelauxetic parameter (β) Angular covalency and sinha's covalency parameter (η) and (δ%) **[21]**have been calculated and values are listed as above:

Mass Spectrum

Mass spectra of **[Co** ($C_{13}H_{22}ClN_3$) $_2$.2H_2O]Cl_2 Line # 1 R.Time 3.1 (Scan# : 368)
Mass peak : 654 base peak : 655 (21114)
Raw Mode Averaged 3.1-3 (478-498)
BG Mode Calc. From PeakMass Spectra :



ESR spectra :

The ESR spectra of Cu (II) and Ni (II) complex recorded at nitrogen temperature when compared to that of room temperature in exhibiting all the hyperfine lines. The calculated Values [15-16]ofg_{II}, g_I , g_{av}, A_o, A_{II} , A_I,K, $ά^2$ and $β^2$.(ESR parameters, isotropic contact and molecular orbital coefficient)

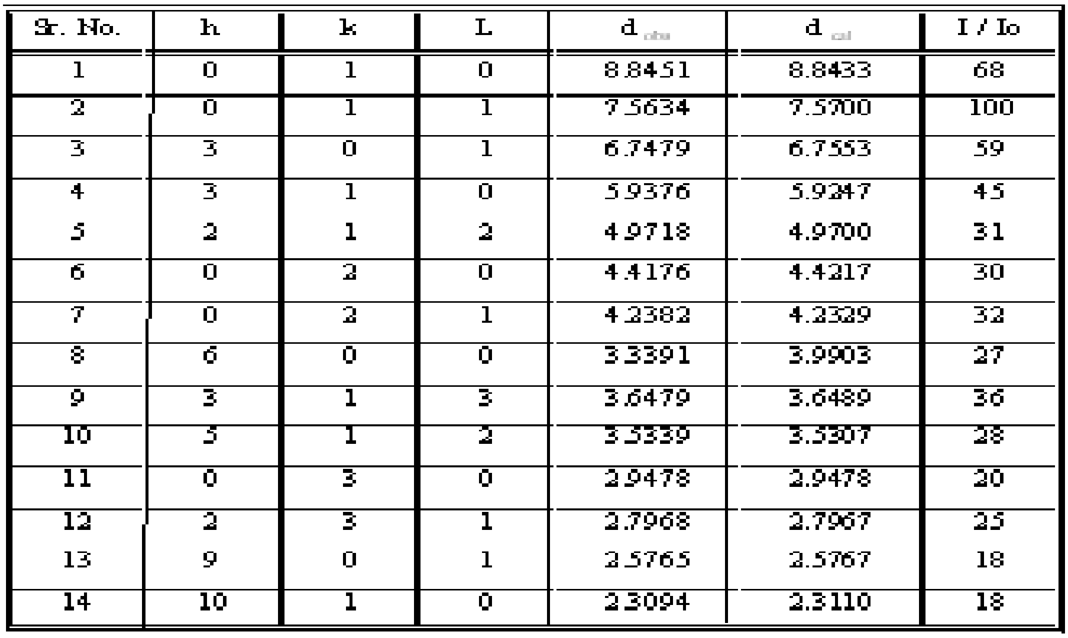
	g_{II}	g_I	g_{av}	A_o	A_{II}	A_I,	K,	$ά^2$	β2
Ni (II)	2.07	1.91	2.05	121	165	94	0.87	0.68	0.99
Cu (II)	1.96	1.95	2.09	127	187	84	0.82	0.59	0. 95

X-Raypowder Diffraction: **X-ray powder diffraction:**

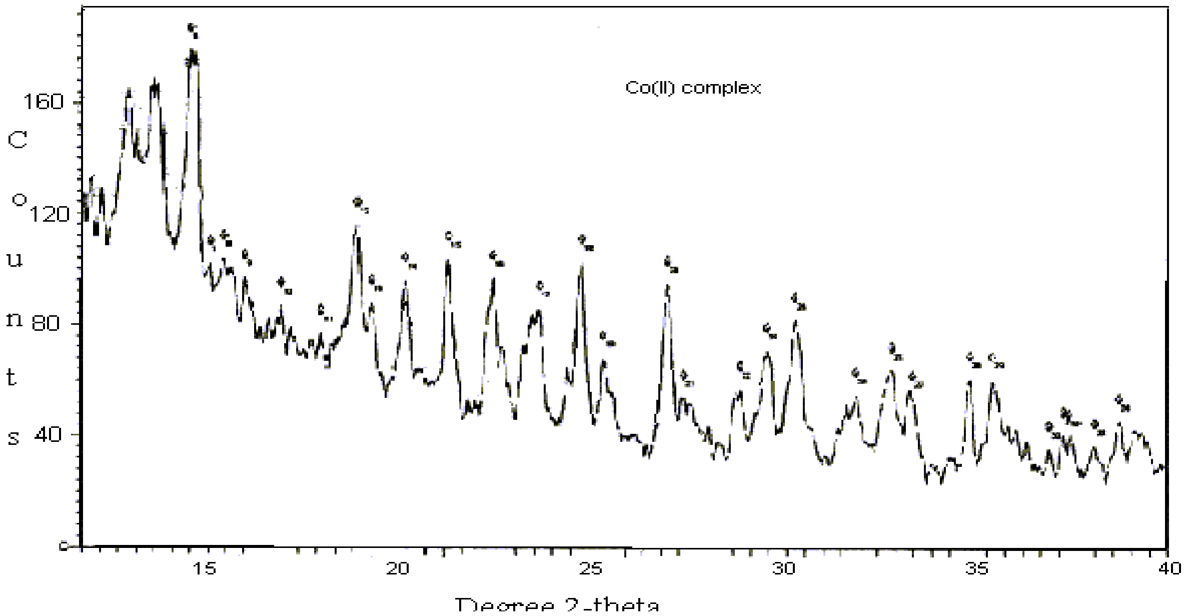
The X-ray powder diffraction of **[Mn** ($C_{13}H_{22}ClN_3$) $_2$.2H_2O]Cl_2complex indicate high crystallinity. The major reflexes were measured and corresponding " d " values were obtained by Bragg's equation (n λ = 2d sin θ). The indexing of major reflexes were carried out using unit least square method the miller indices h, k, l were calculated and refined by using various program on computer like Back-cal, powdin, &cerelef[31-33]. The complexes are monoclinic crystal system with formula factor Z = 8. The lattice parameters along with d_{obs} and d_{cal} values are summarized in table. The correct ness of these values was confirmed by matching with the observed density for **[Co** ($C_{13}H_{22}ClN_3$) $_2$.2H_2O]Cl_2 complexis = 2.193 g/cm^3. The unit cell is monoclinic and space group of complexes is $C_{2/m}$ or $P_{c/m}$ [34].

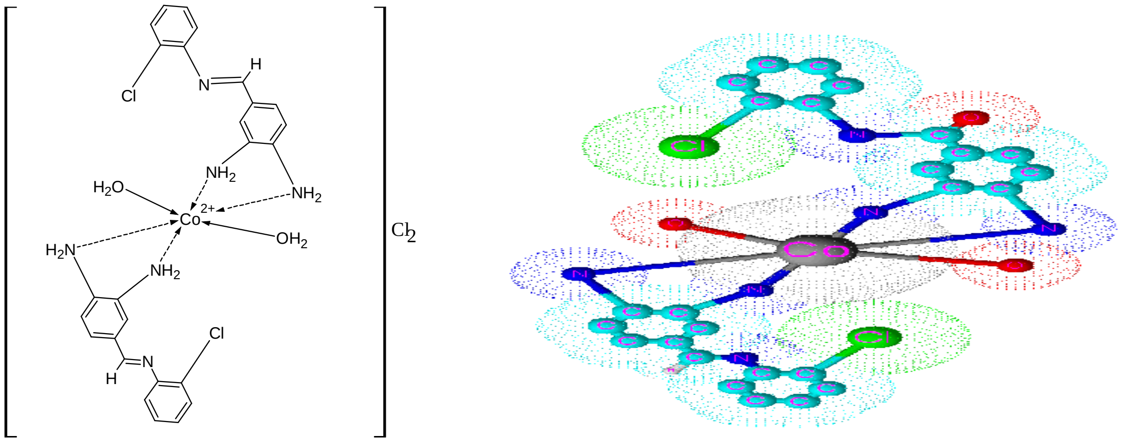
***X-ray powder diffraction data for*[Co** ($C_{26}H_{28}O_4N_6Cl_2$) $_2$**]** Cl_2

a (A°) = 23.0503 D $_{cal(gm/cm^3)}$ = 2.178
b (A°) = 8.7988 D $_{obs(gm/cm^3)}$ = 2.193
c (A°) = 14.8055 Space group = C $_{2/m}$ or P $_{2/m}$
α = 90˚ Crystal system= Monoclinic
β= 95.193˚ γ = 90˚



Sr. No.	h	k	L	d obs	d cal	I / Io
1	0	1	0	8.8451	8.8433	68
2	0	1	1	7.5634	7.5700	100
3	3	0	1	6.7479	6.7553	59
4	3	1	0	5.9376	5.9247	45
5	2	1	2	4.9718	4.9700	31
6	0	2	0	4.4176	4.4217	30
7	0	2	1	4.2382	4.2329	32
8	6	0	0	3.3391	3.9903	27
9	3	1	3	3.6479	3.6489	36
10	3	1	2	3.5339	3.5307	28
11	0	3	0	2.9478	2.9478	20
12	2	3	1	2.7968	2.7967	25
13	9	0	1	2.5765	2.5767	18
14	10	1	0	2.3094	2.3110	18





Proposed structure of the complex

Microbial activity

The studies on antimicrobial activity indicates that amongst other factors, constitution of ligand, its coordination to the metal ion, the nature of metal ion in the complex and strain of the microorganism have important influence on antimicrobial activity. The 4-{(*E*)-[(2-chlorophenyl) imino] methyl}benzene-1,2-diamine and their complexes shows more activity toward Escherichia coli, Bacillus subtilis,Staphylococcus aureus and Salmonella typhi is more inhibition of growth towards Gram-positive bacteria.

Table: 1 Analytical and physical data of Some Transition Metal Ion Complexes with 4-{(*E*)-[(2-chlorophenyl) imino] methyl}benzene-1,2-diamine

	M.P/D.P	**% yield**	**C%**	**H%**	**N%**	**Cl%**	**M%**	**Ω (ohm^{-1} cm^2 mol^{-1}**	**B.M μ_{eff}**
$C_{13}H_{22}ClN_6O_3$	**78**	**255-258**	63.92 (63.75)	08.95 (08.78)	**17.09** (16.98)	14.28 (14.05)	**00**	**47**	**00**
$[Mn(C_{13}H_{22}ClN_3)_2.2H_2O]Cl_2$	59	202-205	47.77 (47.45)	07.35 (07.18)	12.86 (12.58)	16.07 (15.95)	08.42 (08.35)	165	5.78
$[Co(C_{13}H_{22}ClN_3)_2.2H_2O]Cl_2$	54	201-204	47.48 (47.23)	07.30 (07.10)	12.78 (12.54)	15.98 (15.70)	08.96 (08.75)	170	5.22
$[Ni(C_{13}H_{22}ClN_3)_2.2H_2O]Cl_2$	58	195-198	47.47 947.25)	07.29 (07.08)	12.76 (12.55)	15.95 (15.72)	08.93 (08.80)	172	3.24
$[Cu(C_{13}H_{22}ClN_3)_2.2H_2O]Cl_2$	55	192-195	47.12 (46.95)	07.25 (07.03)	12.68 (12.41)	15.86 (15.71)	09.59 (09.41)	168	1.95
$[Zn(C_{13}H_{22}ClN_3)_2.2H_2O]Cl_2$	57	179-182	46.98 (46.94)	07.22 (07.04)	12.65 (12.38)	15.80 (15.58)	09.84 (09.66)	162	00

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