December 2009 *Volume 4 Issue 4*

Trade Science Inc.

Inorganic CHEMISTRY

An Indian Journal

Short Communication

ICAIJ, 4(4), 2009 [191-193]

Synthesis and characterization of copper (II), cobalt (II) and nickel (II) complexes with Schiff bases

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Received: 15th August, 2009 ; Accepted: 25th August, 2009

ABSTRACT

A few complexes of Cu(II), Co(II) and Ni(II) have been prepared by reacting with their metal (II) chlorides with 2-(phenyl/4-methylphenylimino)-1H-indene-1, 3(2H)-dione and 2-[(2-hydroxyphenyl)imino]-1H-inene-1, 3(2H)-dione(Schiff bases) in alcoholic medium. All the chelates are coloured solids and are non-electrolytic in DMF and DMSO. Elemental analysis confirms to the 1:2-stoichiometry of the type ML_2. The IR spectra of the ligands and the complexes suggest the involvement of o-hydroxy group, carbonyl group and azomethine group in bonding through oxygen and nitrogen atoms respectively. The electronic spectra and magnetic data suggest the octahedral and square planar configuration.

INTRODUCTION

The literature[1-6] probe indicates that there is scanty information on the reaction of ninhydrin with aromatic amines and their complexes. Hence, it is thought worth while to prepare of few complexes of transition metals viz. Co(II), Ni(II) and Cu(II) with the Schiff bases formed of ninhydrin and aromatic amines.

In view of the considerable physiological and biological importance of the ninhydrin and the Schiff bases[7-12] it is proposed to prepare some ligands and the complexes.

EXPERIMENTAL

Synthesis of ligands

A mixture of (0.01mole) and various amines (0.02mole) containing a few drops of concentrate hydrochloric acid was refluxed in the alcoholic medium for 5hrs on a steam bath. The reaction mixture was cooled to room temperature the Schiff bases separated were filtered, washed with distilled water and recrystallised from alcohol/benzene.

Synthesis of complexes

To a (0.02mol) ligand in alcohol (0.01mol) an alcoholic solution of metal chloride (Cu, Co and Ni) was added and refluxed for about 4hr on a steam bath [In the case ligand for 2.5g of sodium acetate (anhydrous) was added]. The resulting mixture was further refluxed for an hour. The reaction mixture was transferred into a beaker and the precipitate of complex was initiated by adding a few ml of distilled water. The precipitated complex was filtered, washed with distilled water, then with ethanol and dried over fused calcium chloride.

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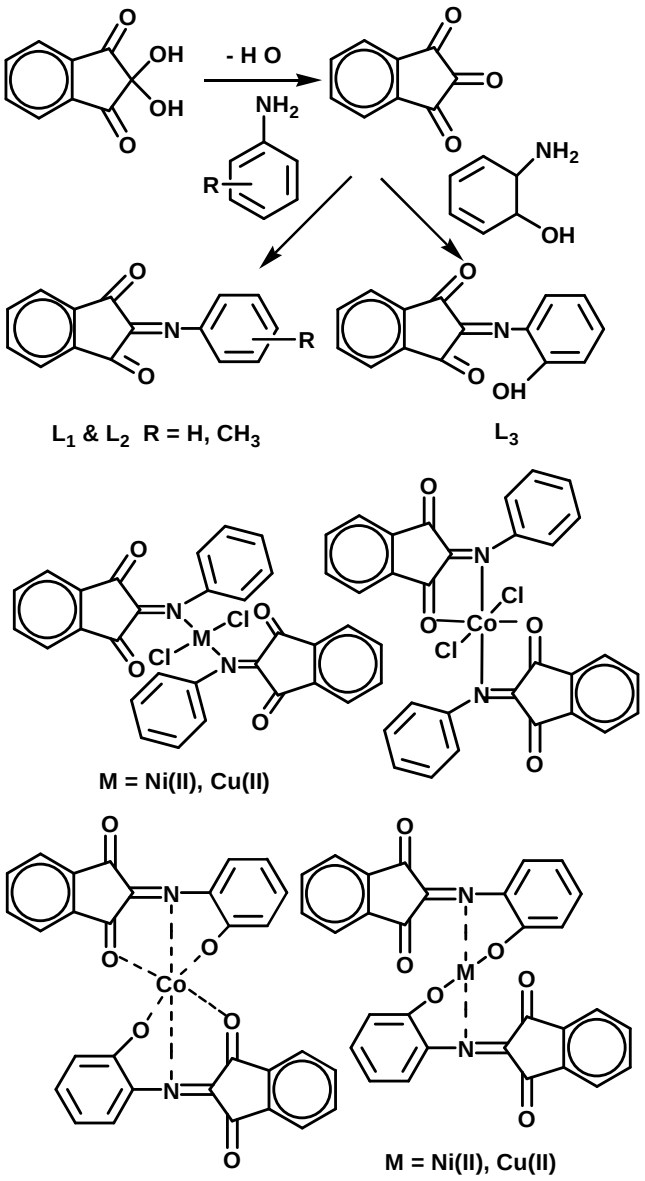

of Cu(II) complexes in the region 15390-15650 cm^{-1}. The nature and shape of band maxima compare well with the characteristic square planar Cu(II) complexes. Hence these Cu(II) complexes are square planar configuration.

The electronic spectra of Ni(II) complexes observed in the region 15385-16000 cm^{-1} may be attribute to the $^1A \rightarrow {}^1A_{2g}$ transition. The band due to the $^1A \rightarrow {}^1B_{1g}$ appears around 23529 cm^{-1}. This band has high intensity and may be due to the overlaying of M–L charge transfer bands. These observations suggest that these Ni(II) complexes of ligands I, II and III are square planar configuration. The electronic spectra of Co(II) complexes observed around 15385 cm^{-1} and 20000 cm^{-1} are assigned to $^4T_{1g} \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition, respectively suggesting an octahedral geometry for Co(II) complexes.

All the complexes are dark coloured amorphous substances. Soluble in DMSO and DMF. The elemental analysis confirms to the 1:2 stoichiometry of the type ML_2. The molar conductance values in DMF and DMSO (10^{-3} mole) are in the range of 2.16 - 4.24 $\Omega\ cm^2\ mol^{-1}$ indicating that all these chelates are non-electrolytes. In the IR spectra the frequency shift, splitting and change in the intensity of the ligand fundamental frequencies caused by the complex formation are considered. The analytical data suggest that 1:2 stoichiometry for these complexes. The complexes are non-electrolyte in DMSO and DMF. The electronic and magnetic studies probed together project the following tentative structures for the complexes where in Cu(II) and Ni(II) exhibit square planar configuration and Co(II) shows coordination number of six.

Electronic data

RESULTS AND DISCUSSION

The broadband observed in the electronic spectra

TABLE 1 : Physical, magnetic susceptibility and molar conductance data of ligand (L^1, L^2, L^3) and its complexes.

Comp. No.	Empirical Formula/ Molecular Formula	M.P. Yield (^{0}C), (%)	Elemental Analysis (%)			$\mu_{eff.}$ (B.M.)	Molar. Cond (λ_M) $ohm^{-1}\ cm^2\ mol^{-1}$	Colour
			M	N	Cl			
C1	$Co(C_{30}H_{18}N_2O_4)Cl_2$	289 (72)	9.632 (9.824)	4.49 (4.459)	11.82 (11.80)	5.1	8.0	Green
C2	$Ni(C_{30}H_{18}N_2O_4)Cl_2$	248(d) (62)	9.80 (9.780)	4.50 (4.46)	11.90 (11.82)	Diamag.	3.7	Dark Brown
C3	$Cu(C_{30}H_{18}N_2O_4)Cl_2$	253 (67)	10.62 (10.51)	4.30 (4.276)	11.74 (11.73)	1.90	2.0	Brown
C4	$Co(C_{32}H_{22}N_2O_4)Cl_2$	252(d) (53)	9.390 (9.386)	4.65 (4.667)	11.32 (11.29)	5.34	8.0	Yellow
C5	$Ni(C_{32}H_{22}N_2O_4)Cl_2$	>300 (67)	9.365 (9.350)	4.67 (4.669)	12.56 (12.46)	Diamag.	--	Yellow

Continued

Comp. No.	Empirical Formula/ Molecular Formula	M.P. Yield (^{0}C), (%)	Elemental Analysis (%)			$\mu_{eff.}$ (B.M.)	Molar. Cond (λ_M) ohm^{-1} cm^2 mol^{-1}	Colour
			M	N	Cl			
C6	$Cu(C_{32}H_{22}N_2O_4)Cl_2$	>300 (53)	10.09 (10.04)	4.64 (4.632)	11.13 (11.21)	1.85	2.0	Yellow
C7	$Co(C_{30}H_{16}N_2O_6)$	245 (58)	10.56 (10.54)	5.003 (5.001)	------	5.0	--	Reddish Brown
C8	$Ni(C_{30}H_{16}N_2O_6)$	276 (55)	10.52 (10.50)	5.03 (5.01)	------	Diamag.	3.2	Dark Brown
C9	$Cu(C_{30}H_{16}N_2O_6)$	240 (60)	11.27 (11.25)	4.89 (4.96)	------	1.79	2.9	Dark Brown

TABLE 2 : IR spectral assignments of ligands L^1, L^2, L^3 and its complexes.

Ligand / Complex	OH	C=O	C=N	C-O	M-O	M-N	M-Cl
Ligand (L^1)	--	1690	--	--	--	--	--
Cu-complex (C_1)	--	1668	1620	--	560	417	311
Co-complex (C_2)	--	1667	1587	--	571	411	317
Ni-complex (C_3)	--	1665	1585	--	555	420	314
Ligand (L^2)	--	1690	--	--	--	--	--
Cu-complex (C_4)	--	1659	1598	--	568	415	319
Co-complex (C_5)	--	1666	1604	--	560	422	309
Ni-complex (C_6)	--	1660	1581	--	565	427	310
Ligand (L^3)	3432	1680	1584	1285	--	--	--
Cu-complex (C_7)	--	1663	1588	1320	571	421	--
Co-complex (C_8)	--	1662	1581	1350	557	428	--
Ni-complex (C_9)	--	1664	1586	1335	552	425	--

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