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Chemical Investigation of Mixed Ligand Complexes of Co(II), Ni(II), Cu(II) with Malonic Acid and Pyridine

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The preparation and characterization of mixed ligand complexes of Co (II), Ni (II) and Cu (II) with malonic acid as primary ligand and pyridine as secondary ligand has been reported. The composition of complexes is confirmed by chemical analysis, AAS, TGA and electrical conductivity. The general formulae of the mixed ligand complexes, malonate complexes and pyridine complexes are $[M(MO)L_2]$, $[M(MO)(H_2O)_4]$ and $[M(L)_2Cl_2]$, respectively where M = Ni(II), Co(II), Cu(II); MO = $C_3H_2O_4$ [malonic acid] and L = C_6H_5N [pyridine]. The magnetic moment values for the M(II) complexes are as per expected spin only values. The IR spectra of the complexes confirm the coordination of metal ion with ligands. The complexes seem to have possible tetrahedral geometry of mixed ligand complexes and pyridine complexes and octahedral geometry of malonate complexes.

Key Words: Co(II), Ni(II), Cu(II), Pyridine, Malonic acid, Mixed lignad complexes.

INTRODUCTION

The work on mixed ligand complexes of Co(II) and Fe(III) with malonic acid as primary and heterocyclic amine like pyridine, quinoline, isoquinoline, 2-aminophenol as secondary ligand[1], on mixed ligand complexes of Co(II) and Ni(II) with malonic acid and pyridine[2] and on simple complexes of Co(II), Ni(II) and Cu(II) with only malonic acid[3] and with only pyridine[4,5] indicated pedagogical potential.

EXPERIMENTAL

All the chemicals were of reagent grade and unless otherwise specified, were used a received. The solvents were purified using conventional methods.

Preparation of mixed ligand complexes: The metal (II) chloride salt (0.952 g for $CoCl_2\cdot 6H_2O$; 0.950 g for $NiCl_2\cdot 6H_2O$; 0.680 g of $CuCl_2\cdot 3H_2O$;

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4 mmol) in 20 mL absolute alcohol were mixed with 5 mL of 2,2-dimethoxypropane. The malonic acid (0.416 g; 4 mmol) was dissolved in 10 mL of absolute ethanol and refluxed on a water bath for an hour. After cooling, a calculated amount of an alcoholic solution of pyridine (0.6 mL; 8 mmol) was added. The mixture was again refluxed for 1 h and then cooled. The formed precipitate was filtered, washed several times with ethanol and then dried in a vacuum desiccator over calcium chloride.

Preparation of malonate complexes: The freshly prepared metal (II) chloride salt (0.238 g for $CoCl_2 \cdot 6H_2O$; 0.238 g for $NiCl_2 \cdot 6H_2O$; 0.170 g of $CuCl_2 \cdot 3H_2O$; 1 mmol) and malonic acid (0.104 g; 1 mmol) were mixed in 50 mL of absolute ethanol and refluxed on a water bath for 1 h. After cooling, calculated amount of ammonia (1:1) was added up to the pH 8-9 is attained and then the solution was concentrated. The precipitate formed was filtered, washed several times with ethanol and then dried in a vacuum desiccator over calcium chloride.

Preparation of pyridine complexes: The metal (II) chloride salt (0.238 g for $CoCl_2 \cdot 6H_2O$; 0.236 g for $NiCl_2 \cdot 6H_2O$, 0.170 g of $CuCl_2 \cdot 3H_2O$; 1 mmol) in 10 mL absolute alcohol were mixed with 2 mL of 2,2-dimethoxypropane. To it was added a calculated amount of pyridine (0.6 mL; 7 mmol). The mixture was refluxed for 1 h on a water bath. The precipitate formed was filtered, washed several times with ethanol and then dried in a vacuum desiccator over calcium chloride.

Metal was determined by titrimetry[6] and AAS as well as from TGA residue. The determination of Co(II) or Ni(II) was done by indirect titrimetry using EDTA and Eriochrome Black-T indicator. The determination of Cu(II) was done by iodometric titrimetry using previously standardized $Na_2S_2O_3$ and starch indicator. For AAS was used Perkin Elmer Model 3100 atomic absorption spectrophotometer. This was done with a setting for a standard at a wavelength, each specific for that metal. They are as -7.0, 7.0 and 4.0 ppm standard and at a wavelength of 240.7, 232.0 and 324.8 nm for cobalt, nickel and copper, respectively and using an air-acetylene flame. The thermo gravimetric analysis was carried out up to 600ºC on a laboratory-constructed balance in air atmosphere.

Structural studies of complexes: Magnetic studies were carried out at room temperature using the Faraday technique using mercury (II) tetrathiocyanatocobaltate (II) as calibrant[7]. The electrical conductance measurements were performed in a 1×10^{-3} M DMF solutions using a Systronics direct reading conductivity meter model 303 calibrated with potassium chloride solution. IR spectra (KBr disc) were recorded on Shimadzu FTIR 8400 spectrophotometer in the region 4000-350 cm^{-1}.

RESULTS AND DISCUSSION

Elemental analyses along with other data and the physical properties are given in Table-1.

The TG curves for the mixed ligand complexes show two steps-first step (in the range 100-180ºC) for decomposition of malonate group and later loss (200ºC onwards) due to pyridine ligand. The pyridine complexes show two-step loss due to two pyridine groups. The malonate chelates show loss in the first step due to dehydration while the loss in the second step due to decomposition. The temperature ranges for them are changing as per the metal ion.

The molar conductances were measured in N, N'-dimethylformamide indicate that the complexes are non-electrolyte in nature.

The effective magnetic moments of the metal complexes (Table-1) indicate tetrahedral geometry for mixed ligand complexes and pyridine complexes while octahedral geometry for malonate complexes. The effective magnetic moments of Co(II) complexes are higher than the expected values and it is rather unexpected[8-10].

TABLE-1
ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE COMPLEXES

Complex	Yield (%)	Metal Found (Calcd.) (%)	Δ_M (ohm^{-1} mol^{-1} cm^2)	μ_{eff} (BM)
$[Co(II)(MO)(Py)_2]$	74	20.63 (18.65)	12.25	6.22 (4.05)^1
$[Co(II)(MO)(H_2O)_4]$	68	21.21 (20.45)	10.82	6.28
$[Co(II)(Py)_2Cl_2]$	65	28.21 (29.91)	11.45	6.26
$[Ni(II)(MO)(Py)_2]$	67	17.60 (18.40)	10.07	3.49
$[Ni(II)(MO)(H_2O)_4]$	69	24.21 (28.22)	9.98	2.88
$[Ni(II)(Py)_2Cl_2]$	70	19.92 (20.39)	12.24	3.11
$[Cu(II)(MO)(Py)_2]$	65	18.10 (19.62)	11.37	1.54
$[Cu(II)(MO)(H_2O)_4]$	68	27.98 (26.74)	12.76	1.62
$[Cu(II)(Py)_2Cl_2]$	65	21.70 (20.65)	11.05	1.74

The malonate complexes show a broad band at 3160 cm^{-1} with broad shoulder at 3400 cm^{-1}. This is due to the hydroxyl of water associated. The mixed ligand complexes display ν(C=O) band at 1580 cm^{-1} and ν(C–O) band at 1350 cm^{-1}, significantly lower than the values of free malonic acid (1712 and 1423 cm^{-1}) (Table-2). This indicates that coordination of malonic acid through their carboxylate anions. The presence of (M–O) bonding is evident from the appearance of ν(M–O) modes at 446-498 cm^{-1} in the spectra of the complexes. The complexation through nitrogen of pyridine is inferred from the appearance of ν(M–N) modes at 402 cm^{-1} in the spectra of the complexes[11]. The IR values show slight difference than values of free pyridine. This indicates coordination through nitrogen.

The characteristic ring vibration of the heterocyclic amine in the range 1600-1400 cm^{-1} generally shows significant changes on complex formation. But in the present complexes these bands could not be distinguished because of overlapping with ν(C=O) and ν(C–O) stretching bands. The in plane and out-of-plane ring deformation modes of the heterocyclic amine are observed at 520 and 720 cm^{-1}, respectively.

TABLE-2
SIGNIFICANT INFRARED SPECTRAL BANDS (cm^{-1})
OF METAL COMPLEXES

Complex	ν(O–H)	ν(N–H)	ν(C=O)	ν(C–O)	ν(M–O)	ν(M–N)
$[Co(II)(MO)(Py)_2]$	–	–	1600	1369	680	402
$[Co(II)(MO)(H_2O)_4]$	3151	–	1575	1369	449	–
			1577	1367		
$[Co(II)(Py)_2Cl_2]$	–	3037	–	–	–	428
$[Ni(II)(MO)(Py)_2]$	–	–	1571	877	478	439
$[Ni(II)(MO)(H_2O)_4]$	3460	–	1579	881	499	–
	3184					
$[Ni(II)(Py)_2Cl_2]$	–	–	–	–	–	439
$[Cu(II)(MO)(Py)_2]$	–	3039	1604		644	441
$[Cu(II)(MO)(H_2O)_4]$	3323	–	–	1373	563	–
	3161	–				
$[Cu(II)(Py)_2Cl_2]$	–	3041	1604	–	–	441

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