



Mixed Ligand Complexes of Co(II) and Ni(II) Containing Organic Acids and Amine Bases as Primary and Secondary Ligands

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Abstract: The synthesis and characterization of mixed ligand complexes of Co(II) and Ni(II) have been described. Organic dibasic acid, malic acid plays role as primary ligand and Heterocyclic amine bases play role as secondary ligands in the complexes. Melting points, Elemental analysis, Magnetic susceptibility measurements, IR, UV and ¹H-NMR spectral analysis were used in determining their physico-chemical properties. The prepared complexes of Co(II) and Ni(II) were found to form octahedral structure.

Keywords: Mixed Ligand Complexes, Organic Acids, Amine Bases

1. Introduction

The bonding nature of the α -amino acid complexes of Co(II) ion and their spectroscopic investigation have been the subject of much interest since long time perhaps because of their biochemical importance. A knowledge of the interaction between biologically active molecules and metals is needed when preparing biomaterials or considering certain aspects of biocompatibility. The study of model species such as the simple amino acids can assist in the interpretation of more complex system. Amino acid has the neutral donor N at one end and acidic replaceable H at the other end and are sufficient length to span two adjacent coordinating site and the resulting complexes is a non-electrolyte chelate or inner complex compound. Such metal chelates are characterized by great thermal stability [1], are intensely colored, insoluble in water but soluble in organic solvents are of practical importance. Amino acids form complexes with metal atoms and exhibit significant biological and enzymatic activities [2]. The synthesis, spectrochemical properties, structure,

stability, thermochemical study, and characterization of complexes of Ni(II) with histidine, glycine, alanine, and other amino acids have previously been reported [3–9]. Standard molar enthalpies of formation of glycine and alanine in the gaseous phase on the basis of theoretical calculations have also been studied [10].

Recently, we studied few mixed ligand complexes containing heterocyclic amine as secondary ligands and few Schiff base containing complexes [11-20]. We report here, the synthesis and characterization of several new mixed ligand complexes of Co(II) and Ni(II) with Organic dibasic acid, malic acid as primary ligand and Heterocyclic amine bases as secondary ligands.

2. Experimental

2.1. Reagents and Chemicals

All the reagents used were of analytical or chemical grade

purity. Solvents were purified and dried according to the standard procedures.

2.2. Physical Measurements

Melting points of all metal complexes were measured by an electro thermal melting point apparatus model no. AZ6512. The SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance was used for the present study. Infrared spectra (KBr) were recorded in a SIMADZU FTIR-8400 (Japan) spectrophotometer in the range 4000–400 cm^{-1} . The absorbance's of the complexes were recorded on SHIMADZU Spectrophotometer (Model UV-1800). Carbon, hydrogen, nitrogen analysis and ^1H NMR were carried out from the Liverpool University, Liverpool, England.

2.3. General Method for the Preparation of the Complexes

An ethanolic solution (just dissolved) of M(II) chloride salts (2 m.mol) and ethanolic potassium hydroxide solution (just dissolved) of malic acid (4 m.mol) were mixed and gently heating with stirring for half an hour. No precipitate was observed, and then secondary ligand (Pyridine/2-Aminopyridine) in calculated ratio was added and stirred until complex precipitated. The precipitates were filtered, washed several times with alcohol and then dried in vacuum desiccator over phosphorus pentaoxide (P_2O_5).

3. Results and Discussion

3.1. Elemental Analysis and Conductivity Measurement

The analytical data and their physical properties of the complexes are tabulated in tables 1 and 2 respectively. The analytical data are in good agreement with the proposed empirical formula of the prepared complexes. The molar conductance of 10^{-3} M solution of the complexes in DMSO were measured at 30°C . The molar conductance values (Table 2), lies in the range 107.73-102.61 indicating electrolytic nature of the complexes.

3.2. Magnetic Moment and Electronic Spectra

The observed values of effective magnetic moment (μ_{eff}) of the complexes at room temperature are given in Table 2. The magnetic moment values of the complexes 1.79 to 5.57 B.M indicate that these complexes were paramagnetic. In nature suggesting that there were no changes in the oxidation states of the metal ions upon complexation.

The Co(II) complexes possesses magnetic moment in the range 4.98 to 5.57 B.M. in agreement with octahedral geometry. The three transitions observed in the electronic spectra of the Co(II) complexes indicate the octahedral environment around the metal ion. The electronic spectra showed strong peak between 315 to 590 nm assignable to the transitions $^4\text{T}_{1g} \rightarrow ^4\text{A}_{2g}$ (F) and $^4\text{T}_{1g} \rightarrow ^4\text{T}_{2g}$ (F).

The electronic spectra of Ni(II) complexes showed peaks characteristic of octahedral geometry. The reflectance spectra both types of complexes consist of bands range between 312 to 545 nm assignable to the transitions $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}$ and $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}$ (F) respectively. The range of magnetic moment between 2.85 to 3.78 B.M. in agreement with octahedral geometry of the complexes

3.3. Infrared Spectral Spectra

Salient features of the IR spectra of the complexes are tabulated in the Table 4. The complexes display bands 1645-1598 and 1427-1303 cm^{-1} due to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ stretching respectively, significantly lower than that of free ligand $\nu(\text{C}=\text{O}) = 1700$ and $\nu(\text{C}-\text{O}) = 1600$ cm^{-1} indicating the coordination of metal ion through its carboxylate anion. The symmetric stretching of $\nu(\text{COO}^-)$ frequencies are observed at 1473-1403 cm^{-1} . The disappearance of the $\nu(\text{O}-\text{H})$ mode observed in the free phthalic acid and amino acid molecule clearly indicate the loss of proton for O-H group upon coordination, revealing those acids are dinegative bidentate ligand coordinating through the carboxylate anion. The complexes showed $\nu(\text{N}-\text{H})$ bands at 3445-3166 cm^{-1} which are significantly lower than the free ligand (amine base bands from 3100-3400 cm^{-1}), clearly suggests the coordination of amino groups through nitrogen atoms of amino base. The in-plane and out-of-plane ring deformation modes of heterocyclic amines observed at 668 and 639 cm^{-1} respectively undergo a positive shift in mixed ligand complexes confirming their coordination through nitrogen. The presence of metal nitrogen bonding in the complexes are evident from the appearance of $\nu(\text{M}-\text{N})$ modes at 388-359 cm^{-1} and 379-418 cm^{-1} respectively in the spectra of the complexes.

3.4. ^1H NMR Spectra

The ^1H NMR spectra of the complex $2\text{K}^+[\text{Co}(\text{MaH})_2(\text{Py})_2]^{2-}$ was recorded in DMSO- d_6 solution at room temperature. Complex $2\text{K}^+[\text{Co}(\text{II})(\text{MaH})_2(\text{Py})_2]^{2-}$: 8.67-8.54 (m, 4H, Ar-H), 8.09-8.06 (m, 2H, Ar-H), 7.30-7.28 (m, 4H, Ar-H), 5.12 (brs, 2H, -CHOH), 3.71-3.56 (m, 2H, CH), 2.21 (d, 4H, J = 6.4 -CH₂).

Protons of pure pyridine molecule, showed peaks for the ortho hydrogen at $\delta = 8.47$ ppm. But after complexation with the Co(II) ion the same protons have detected at $\delta = 8.67$ -8.54 ppm. From the nature of the ^1H NMR spectra of the proposed complex it is clear that the N atom in pyridine ring has involved in complexation. The same effect has observed for the protons of malic acid. According to the peak heights of the protons in ^1H NMR spectra of complex molecule it can be assumed that malic acid have taken part in complexation with the metal ion. Because, ten protons of pyridine and eight protons of malic acid molecule are found in the same spectra of the complex.

Table 1. Analytical data of Co(II) and Ni(II) complexes.

Complexes	Yield%	M%	C%	H%	N%
$2K^+[Co(II)(MaH)_2(2-Apy)_2]^{2-}$	71	16.70 (16.60)	23.05 (24.01)	2.43 (2.97)	6.28 (6.78)
$2K^+[Co(II)(MaH)_2(Py)_2]^{2-}$	75	10.78 (10.02)	45.89 (46.04)	4.79 (4.45)	4.38 (4.94)
$2K^+[Ni(II)(MaH)_2(2-Apy)_2]^{2-}$	72	10.12 (10.02)	27.69 (27.80)	2.06 (2.18)	5.11 (5.23)
$2K^+[Ni(II)(MaH)_2(Py)_2]^{2-}$	67	9.69 (9.75)	40.59 (40.65)	3.75 (3.80)	4.76 (4.88)

MaH = Malic Acid, Py = Pyridine, 2-Apy = 2- Aminopyridine

Table 2. Physical properties of Co(II) and Ni(II) complexes.

Complexes	Colour	Melting point $^{\circ}C$ (± 0.52)	Molar conductance $\Omega\text{ cm}^2\text{ mol}^{-1}$	Magnetic moment μ_{eff} (B.M.)
$2K^+[Co(II)(MaH)_2(2-Apy)_2]^{2-}$	Brown	275	106.02	5.57
$2K^+[Co(II)(MaH)_2(Py)_2]^{2-}$	Green	230	102.61	5.47
$2K^+[Ni(II)(MaH)_2(2-Apy)_2]^{2-}$	Green	290	107.73	3.60
$2K^+[Ni(II)(MaH)_2(Py)_2]^{2-}$	L.Green	260	103.36	2.98

MaH = Malic Acid, Py = Pyridine, 2-Apy = 2- Amino pyridine

Table 3. Electronic spectral data of Co(II) and Ni(II) complexes.

Complexes	λ_{max} (n.m)		
$2K^+[Co(II)(MaH)_2(2-Apy)_2]^{2-}$	385	448	578
$2K^+[Co(II)(MaH)_2(Py)_2]^{2-}$	371	459	587
$2K^+[Ni(II)(MaH)_2(2-Apy)_2]^{2-}$	341	443	530
$2K^+[Ni(II)(MaH)_2(py)_2]^{2-}$	332	431	545

MaH = Malic Acid, Py = Pyridine, 2-Apy = 2- Amino pyridine

Table 4. IR spectral data of Co(II) and Ni(II) complexes.

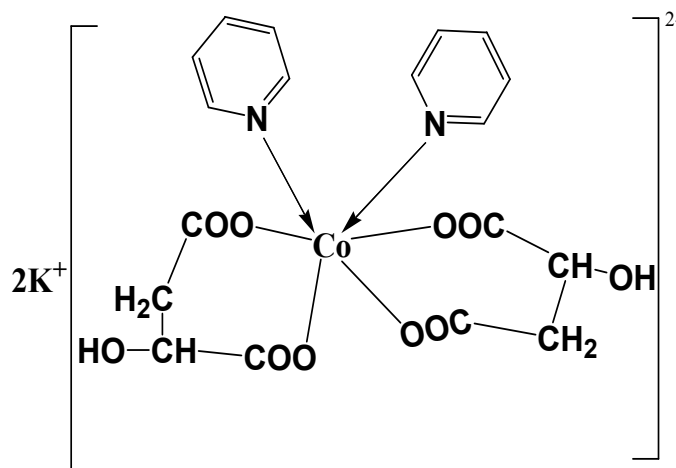
Complexes	$\nu(\text{N-H})\text{ cm}^{-1}$	$\nu(\text{C=O})\text{ cm}^{-1}$	$\nu(\text{M-N})\text{ cm}^{-1}$	$\nu(\text{C-O})\text{ cm}^{-1}$	$\nu(\text{COO}^-)\text{ Symmetry cm}^{-1}$	Aromatic ring cm^{-1}
$2K^+[Co(II)(MaH)_2(2-Apy)_2]^{2-}$	3367	1624	381	1323	1421	897
$2K^+[Co(II)(MaH)_2(Py)_2]^{2-}$	3316	1632	387	1303	1403	827
$2K^+[Ni(II)(MaH)_2(2-Apy)_2]^{2-}$	3198	1625	376	1340	1449	840
$2K^+[Ni(II)(MaH)_2(Py)_2]^{2-}$	3335	1559	388	1356	1415	851

MaH = Malic Acid, Py = Pyridine, 2-Apy = 2- Amino pyridine

4. Conclusion

Elemental analysis correspond to metal: ligand stoichiometry for Co(II) and Ni(II) complexes are 1:2:2. Magnetic susceptibility measurement shows that the complexes are paramagnetic. The IR spectral data shows that the ligands coordinate to the metal through O and N atoms.

The electronic spectral data are in conformity with the transitions of octahedral complexes. The $^1\text{H-NMR}$ studies of the complex indicates two pyridine and two malic acid molecules coordinate with Co(II) metal ion and represents the complex as $2K^+[Co(II)(MaH)_2(Py)_2]^{2-}$. Based on the above analysis the structure of complex $2K^+[Co(II)(MaH)_2(Py)_2]^{2-}$ has been proposed as shown in Fig. 1.

**Figure 1.** Structure of the complex $2K^+[Co(II)(MaH)_2(Py)_2]^{2-}$.

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