

SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF Co(II) AND Fe(III) IONS WITH MALEIC ACID AND HETEROCYCLIC AMINES

MD. BELAYET HOSSAIN^a, M. SAIDUL ISLAM^b, M. RAFIQUUL ISLAM^c, MD ABDUS SALAM^d AND M. ABU YOUSUF^{a*}

^a*Department of Chemistry, Khulna University of Engineering & Technology, Khulna-9203, Bangladesh*

^b*Department of Chemistry, Rajshahi University, Rajshahi-6205, Bangladesh.*

^c*Department of Botany, Shahzadpur Government Collage, Sirajgang , Bangladesh*

^d*Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh*

Abstract

This paper describes the preparation and characterization of mixed ligand complexes of Co(II) and Fe(III) ions with maleic acid and heterocyclic amines of general formula [M(ME)L] and K[M(ME)L] (where M = Co(II) (1-4), Fe(III) (5-6); ME = C₄H₂O₄ (1-4), 2C₄H₂O₄ (5-6); L = C₃H₆N₂ (1), C₉H₇N (2-3), C₉H₆NO (4), C₅H₅N.H₂O (5), C₆H₇N (6)). The molecular structures of the complexes have been determined by spectral, magnetic studies and elemental analysis.

Introduction

There are many reports on the transition metal malonates with structural and magneto-structural characterization¹. Some references are available on the metal complexes of dibasic acid^{2, 3}. Maleic acid may be used as an analytical reagent⁴ and as a bidentate ligand in the formation of complexes with metal ions.

Fe(III), Ni(II), Co(II) and Cu(II) complexes were reported with thiazoline and their fungicidal activity has also been evaluated⁵. Metal chelates of salicylhydroxamic acids with Cu(II), Ni(II), Co(II), Fe(II), Mn(II) and Zn(II) were studied and have been screened for their antifungal activities⁶. It was observed that chelates are more active than the parent salicylhydroxamic acids being maximum for metal chelates of Co(II) with halo and nitro substituted salicylhydroxamic acids. Moreover, the heterocyclic bases have great importance in biological and industrial fields and their complexes with copper exhibit potent antitumor and antibacterial activities^{7, 8}.

Keeping these facts in view, the present paper describes the preparation and characterization of mixed ligand complexes of Co(II) and Fe(III) with maleic acid (MEH₂) as primary and heterocyclic bases viz., quinoline (Q), Iso-quinoline (IQ), pyridine (Py), 4-picoline (4-pico), 2-aminopyridine (2-apy) and 8-hydroxyquinoline (8-HQ) as secondary ligands on the basis of various physico-chemical techniques.

*Corresponding Author; e-mail: yousuf2716@yahoo.com

Experimental

Chemicals and Reagent

All the chemicals were of reagent grade (Sigma-Aldrich, USA and E-Merck, Germany) and were used as received. The solvents were purified using conventional methods.

Physical Measurement

Infrared spectra were recorded on FTIR spectrophotometer (IR-Prestrige-21) in the region 4500-400 cm^{-1} in the department of chemistry, University of Dhaka, Bangladesh. Carbon, hydrogen and nitrogen analyses were carried out at the Center of Excellence, University of Dhaka, Bangladesh. Metal was determined by weighing as the oxide produced by direct ignition⁹. The molar conductance of 10^{-3} M solutions of the metal complexes in DMF was measured at 30 °C using a WPACM 35 conductivity meter and a dip-cell with a platinized electrode. Melting points were determined using an electro thermal digital Gallenkamp AZ6512 melting point apparatus. Magnetic susceptibility was measured with Magnetic Susceptibility Balance (Model: Mk1, Sherwood Scientific, Cambridge, England) in the department of chemistry, University of Dhaka, Bangladesh at 298 K. All susceptibilities were corrected for diamagnetic contribution using Pascal's constant¹⁰.

Preparation

a) Preparation of the Co(II) complexes

The freshly prepared cobalt (II) chloride salt (0.952 g) and maleic acid (0.464 g) were mixed in 100 mL of absolute ethanol and refluxed on a water bath for an hour and then the calculated amount of an alcoholic solution of heteroamine bases was added (e.g. 8 m mol of Q, IQ and 4 m mol of 2apy, 8-HQ). The mixture was again refluxed for an hour and then cooled. Complex 4 was precipitated when one equivalent of alcoholic potassium hydroxide was added. The precipitate formed were filtered, washed several time with ethanol and then dried in a vacuum over phosphorus pentoxide (P_2O_5).

b) Preparation of the Fe(III) complexes

An ethanolic solution (Just dissolved) of Fe(III) chloride (0.540 g) and ethanolic potassium hydroxide solution (Just dissolve) of maleic acid (0.464 g) were mixed in the calculated ratio with constant stirring for 30 minutes. No precipitates was observed, after which heteroamine bases (4 m mol of Py, 4-pico) was added with constant stirring for an hour. Precipitate appeared were filtered, washed several times with alcohol and then dried in a vacuum desiccator over phosphorus pentoxide (P_2O_5).

Results and Discussion

Elemental Analysis and Conductivity Measurement

The complexes of Co(II) and Fe(III) were soluble in N, N' dimethyl formamide. Analytical results for metal, carbon, hydrogen and Nitrogen are given in Table-2 and

some physical properties viz., color, melting points, molar conductance and magnetic moments are given in Table-1. The molar conductance was measured in N, N' dimethyl formamide. The conductance value (Table-1) indicated that the complexes (1-3) were non-electrolyte in nature, while the complexes (4-6) behaved as 1:1 electrolytes.

Magnetic Moments

The effective magnetic moments of the Co(II) and Fe(III) complexes at room temperature are shown in Table-1. The magnetic measurement indicate that the Co(II) complexes (1-4) are paramagnetic and the magnetic moment value was 3.95-4.00 B.M. corresponding to three unpaired electron and hence, are tetrahedral structure with sp^3 hybridization¹¹ and this value of magnetic moment of Fe(III) complexes (5.66-5.76 B.M.) indicate that the complexes (5-6) are also paramagnetic with five unpaired electrons and hence, are of octahedral structure with sp^3d^2 hybridization¹².

Infrared Spectral Studies

Since the antisymmetric -COO stretching frequency is most sensitive to a change in the radius, mass and electronegativity of the metal, the strong bands at 1720 and 1410 cm^{-1} in the spectrum of maleic acid due to $\nu_{C=O}$ and ν_{C-O} were shifted to \approx (1665.9-1680.0) and \approx (1465.9-1380.3) cm^{-1} in the spectrum of all the complexes. This indicated the coordination of maleic acid through the carboxyl group. The coordination are also evident from ν_{M-O} (O = Oxygen in deprotonated maleic acid) at (479.2-530.1) cm^{-1} in all the complexes¹³ (Table-3). The frequency of the stretching O-H vibration observed at \sim 3370.5 cm^{-1} should disappear in the spectra of complex 5 because of the coordination of water¹⁴.

The infrared spectrum of amino pyridine shows ν_{N-H_2} modes at \sim 3400 and \sim 3300 cm^{-1} . Both of these bands are shifted to lower frequencies in the complex 1 at (3380.5-3115.3) cm^{-1} which indicate the coordination of amino nitrogen. The -NH₂ complexation inferred from the appearance of ν_{M-N} modes (400.0-421.1) cm^{-1} in the complexes¹⁵⁻¹⁶.

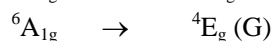
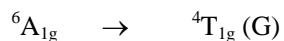
The characteristic ring vibration of the heterocyclic amines in the range 1400-1600 cm^{-1} generally show significant changes on complexation¹⁷ but in our present complexes these bands could not be distinguished because of overlapping with $\nu_{C=O}$ and ν_{C-O} stretching bands. The in plane and out of plane ring deformation modes of the heterocyclic amines are observed at \sim 520 and \sim 720 cm^{-1} respectively. Major I.R. spectral data for the complexes are given in Table-3.

Electronic Spectra

The electronic spectra of Co(II) complexes (1-4) gave two intense bands at 23940-24555 and 29845-30040 cm^{-1} corresponding to the transition $^4A_{2g}(F) \rightarrow ^4T_{1g}(P)$ (ν_3) and

charge transfer band respectively. These spectra indicated the tetrahedral stereochemistry of Co(II) complexes⁶. Table-4 contain the data of electronic spectra of Co(II) complexes.

The electronic spectra of Fe(III) complexes (**5-6**) gave four bands in the range (18500–18740), (21033–21165), (24300–24777) and (25690–25757) cm^{-1} corresponding to the transitions.



respectively. These spectra indicated the octahedral stereochemistry of Fe(III) compound^{6,12}. Table-5 contain the data of electronic spectra of Fe(III) complexes.

Table 1. Physical properties of the complex

Com. No.	Complexes	Color	Melting point or decomposition temperature (\pm 5°C)	Molar conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	magnetic moment (B.M.)
1	[Co(II)(ME)(2apy)]	Violet	285	15.30	3.99
2	[Co(II)(ME)(Q) ₂]	Light blue	205	20.90	3.95
3	[Co(II)(ME)(IQ) ₂]	Light blue	193	18.90	4.00
4	K[Co(II)(ME)(8-HQ)]	Thai chocolate	290	80.49	3.98
5	K[Fe(III)(ME) ₂ (Py)H ₂ O]	Mushroom	255 (d)	77.90	5.76
6	K[Fe(III)(ME) ₂ (4-pico) ₂]	Mushroom	255 (d)	65.78	5.66

Table 2. Elemental analyses data of the complexes

Com. No.	Complexes	Yields %	Metal	%Carbon	%Hydrogen	%Nitrogen
1	[Co(II)(ME)(2apy)]	68	22.06 (22.50)	40.44 (40.10)	2.99 (2.78)	10.49 (10.42)
2	[Co(II)(ME)(Q) ₂]	68	13.66 (13.86)	61.27 (61.20)	3.71 (3.62)	6.49 (6.41)
3	[Co(II)(ME)(IQ) ₂]	60	13.66 (13.88)	61.27 (61.15)	3.71 (3.59)	6.49 (6.43)
4	K[Co(II)(ME)(8-HQ)]	72	16.56 (16.80)	43.83 (43.88)	2.25 (2.25)	3.93 (3.95)
5	K[Fe(III)(ME) ₂ (Py)H ₂ O]	68	13.29 (13.38)	37.16 (37.03)	2.62 (2.05)	3.33 (3.30)
6	K[Fe(III)(ME) ₂ (4-pico) ₂]	61	10.96 (10.80)	47.15 (47.22)	3.56 (3.51)	5.50 (5.41)

Table 3. Infrared spectral data of the complexes (band maxima in cm^{-1})

Com. No.	Complexes	$\nu(\text{OH})$	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C-O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
1	[Co(II)(ME)(2apy)]	-	3380.5 3115.3	1670.8	1460.2	479.2	400.0
2	[Co(II)(ME)(Q) ₂]	-	-	1667.2	1477.8	482.0	400.3
3	[Co(II)(ME)(IQ) ₂]	-	-	1665.9	1480.3	481.0	403.0
4	K[Co(II)(ME)(8-HQ)]	-	-	1680.0	1465.9	530.1	421.1
5	K[Fe(III)(ME) ₂ (Py)H ₂ O]	3370.5	-	1666.9	1470.6	478.0	405.6
6	K[Fe(III)(ME) ₂ (4-pico) ₂]	-	-	1670.9	1445.8	480.4	412.5

Table 4. Electronic spectral data of tetrahedral Co(II) complexes

Com. No.	Complexes	Spectral band (cm^{-1}) with assignment	
		${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P}) (\nu_3)$	Charge transfer band
1	[Co(II)(ME)(2apy)]	24555	30040
2	[Co(II)(ME)(Q) ₂]	23980	29845
3	[Co(II)(ME)(IQ) ₂]	23940	29960
4	K[Co(II)(ME)(8-HQ)]	24378	30000

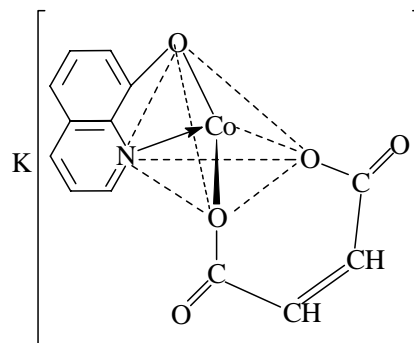
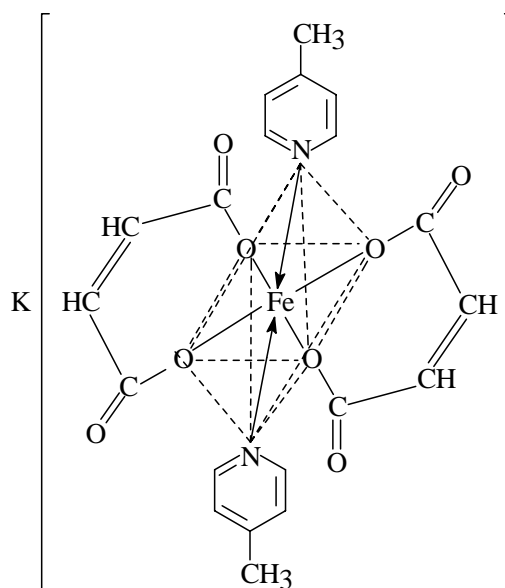
Table 5. Electronic spectral data of octahedral Fe(III) complexes

Com. No.	Complexes	Spectral band (cm^{-1}) with assignment			
		${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$	${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$	${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}(\text{G})$
5	K[Fe(III)(ME) ₂ (Py)(H ₂ O)]	18740	21033	24300	25757
6	K[Fe(III)(ME) ₂ (4-pico) ₂]	18500	21165	24777	25690

Where, ME = C₄H₂O₄ Py = C₅H₅N 2apy = C₅H₆N₂ Q = C₉H₇N
 IQ = C₉H₇N 4-pico = C₆H₇N 8-HQ = C₉H₇NO

Conclusion

The structure of Co(II) and Fe(III) complexes are tetrahedral and octahedral respectively. The possible structure of the complexes **4** and **6** are given in the figure-1(a) and figure-1(b) respectively. Similarly the structure of other complexes may also be given.

a) $K[Co(II)(ME)(8-HQ)]$:b) $K[Fe(III)(ME)_2(4-pico)_2]$:**Fig. 1.** Possible structure of the complexes (a) $K[Co(II)(ME)(8-HQ)]$ (b) $K[Fe(III)(ME)_2(4-pico)_2]$.

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Graphical Abstract

<p style="text-align: center;">SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF Co(II) AND Fe(III) IONS WITH MALEIC ACID AND HETEROCYCLIC AMINES</p> <p>MD. BELAYET HOSSAIN, M. SAIDUL ISLAM, M. RAFIQUUL ISLAM, MD ABDUS SALAM AND M. ABU YOUSUF*</p>	<p>This paper describes the preparation and characterization of mixed ligand complexes of Co(II) and Fe(III) ions with maleic acid and heterocyclic amines of general formula [M(ME)L] and K[M(ME)L] (where M = Co(II) (1-4), Fe(III) (5-6); ME = C₄H₂O₄ (1-4), 2C₄H₂O₄ (5-6); L = C₅H₆N₂ (1), C₉H₇N (2-3), C₉H₆NO (4), C₅H₅N.H₂O (5), C₆H₇N (6)). The molecular structures of the complexes have been determined by spectral, magnetic studies and elemental analysis.</p>
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