

Synthesis and Characterization of Mixed Ligand Complexes of Co(II) and Fe(III) Ions with Malic Acid and Heterocyclic Amines

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Abstract

This paper describes the preparation and characterization of mixed ligand complexes of Co(II) and Fe(III) ions with malic acid and heterocyclic amines. The general formula of the complexes are as follows: $[M(MA)L_2]$ and $K[M(MA)_2L_2]$ (where, M = Co(II) (1-4), Fe(II) (5-8); MA = $C_4H_4O_5$ (1-4), $2C_4H_4O_5$ (5-8); L = C_6H_5N (1), C_6H_7N (2), C_9H_7N (3, 4), $2C_6H_5N$ (5), $2C_6H_7N$ (6), $2C_9H_7N$ (7-8)). The complexes were prepared in the solid form and characterized by elemental analysis, conductivity and magnetic measurements, infrared and electronic spectroscopic studies. The infrared spectra of the complexes confirmed the coordination of metal ion with ligands. The Co(II) complexes are assumed to have tetrahedral and the Fe(III) complexes have octahedral structure based on the electronic spectra and magnetic measurements. Their antibacterial and antifungal activity has also been evaluated by the disc diffusion methods against fourteen pathogenic bacteria (five gram positive and nine gram negative) and fourteen fungi. Complexes $[Co(II)(MA)(4-pico)_2]$ showed the highest antibacterial activity against all bacteria tested (when, MA = $C_4H_4O_5$ and 4-pico = C_6H_7N).

Key words: Co(II) and Fe(III) complexes, Malic Acid, Heterocyclic Amines, Antimicrobial activities.

Introduction

An exhaustive survey of the existing literature reveals that a very little study has been conducted on the metal complexes of dibasic acid. Islam and co-workers reported the magnetic properties of some carboxylic acid derivatives of cobalt (II) and iron(III) (Islam *et al.*, 2004). Novel Malonato-Bridged copper(II) complexes were prepared and characterized by elemental analyses, electronic spectra, magnetic susceptibilities, and X-ray analysis (Catalina *et al.*, 2000). Synthetic chemicals constitute important sources of various bioactive compounds such as antibacterial (Zakaria *et al.*, 2000), antifungal (Islam *et al.*, 2002) and anticancer (Part *et al.*, 1979) compounds. The metal complexes of phthalic acid have been studied both from pharmacological (Sultana *et al.*, 2003) and industrial (Nippon Synthetic Chemical Industry Co. Ltd. Japan, 1980) point of view as indicated by available literature. Some complexes of transition metal ion with malonic (Bhatia *et al.*, 1993 and Reza *et al.*, 2003), phthalic (Sultana *et al.*, 2003; Reza

et al., 2003) and maleic (Islam *et al.*, 2003) acid have been found medicinally important.

Considering these facts, the present work describes the preparation, characterisation and antimicrobial screening of mixed ligand complexes of Co(II) and Fe(III) with malic acid (MAH_2) as primary and heterocyclic amines, viz. quinoline (Q), iso-quinoline (IQ), pyridine (Py), 4-picoline (4-pico) as secondary ligands on the basis of various physico-chemical techniques.

Materials and Methods

All the chemicals were of reagent grade unless otherwise specified 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 $4500-400\text{ cm}^{-1}$ at the Department of Chemistry, University of Dhaka, Bangladesh. Carbon, hydrogen and nitrogen analyses were carried out at the Center for Advance Research on Sciences(CARS), University of

Dhaka, Bangladesh. Metal was determined by weighing as the oxide produced by direct ignition (Scargill, 1961). The molar conductance at 10^{-3} M solutions of the metal complexes in DMF was measured at 30 °C using conductivity meter. Melting points were determined using an electrothermal digital melting point apparatus. Magnetic susceptibility was measured with Magnetic Susceptibility Balance (Model: Mk1, Sherwood Scientific, Cambridge, England) at the department of chemistry, University of Dhaka, Bangladesh at 298 °K. All susceptibilities were corrected for diamagnetic contribution using Pascal's constant (Vogel 1961).

Preparation of Co(II) complexes: The freshly prepared cobalt (II) chloride salt (4.0 m mol) and malic acid (4.0 m mol) 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. 8.0 m mol of Py, Q, IQ and 4-pico). The mixture was again refluxed for an hour and then cooled. The precipitate formed were filtered, washed several times with ethanol and then dried in vacuum over phosphorus pentoxide (P_2O_5).

Preparation of Fe(III) complexes: An ethanolic solution (just dissolved) of Fe(III) chloride (2.0 m mol) and malic acid (4.0 m mol) were mixed in the calculated ratio with constant stirring for 30 minutes. No precipitate was observed after which heteroamine bases (e.g. 4.0 m mol of Q, IQ, Py, 4-pico) was added with constant stirring for an hour. Finally, the solution of complexes was prepared in one equivalent of alcoholic potassium hydroxide. The precipitates were filtered, washed several times with alcohol and then dried in a vacuum desiccator over phosphorus pentoxide (P_2O_5).

Antimicrobial activities: Fourteen pathogenic bacteria as listed in Table 6 were collected from the Department of Pharmacy and Department of Botany, University of Rajshahi respectively and selected for antimicrobial test. The tests were performed at the Plant Pathology Laboratory, Department of Botany, University of Rajshahi. Nutrient agar and potato dextrose agar were used as bacteriological and fungal growth media respectively. The complexes were dissolved separately in dimethyl sulfoxide (DMSO) to get a concentration of 200- $\mu\text{g disc}^{-1}$. Then *in vitro* anti-microbial activity of these complexes was carried out by disc diffusion method (Beur

et al., 1966; Rios et al., 1988). Diameter of zone of inhibition produced by the complexes was compared with Kanamycin (30- $\mu\text{g disc}^{-1}$) and Fluconazol (200- $\mu\text{g disc}^{-1}$) for bacteria and fungi respectively.

Results and Discussion

Elemental analyses and conductivity measurements: Elemental analyses along with other data and their physical properties are presented in Tables- 1 and 2. The molar conductances were measured in N, N'-dimethyl-formamide. The conductance values (Table 1) indicate that the complexes (1-4) are non-electrolyte in nature, while the complexes (5-8) behave as 1:1 electrolytes.

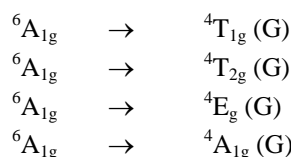
Magnetic moments: The effective magnetic moment of the Co(II) and Fe(III) complexes at room temperature are shown in Table 1. The magnetic measurements indicate that the Co(II) complexes (1-4) are paramagnetic and show magnetic moment between 3.72-4.05BM corresponding to three unpaired electrons and hence, are tetrahedral with sp^3 hybridization. The observed magnetic moment values of Fe(III) (5.68 - 5.93 BM.) indicate that complexes are also paramagnetic with five unpaired electron and therefore, are octahedral structure with sp^3d^2 hybridization (Islam et al., 2004).

Infrared spectral studies: The complexes display $\nu_{C=O}$ band at 1558.4-1625.5 cm^{-1} and ν_{C-O} band at 1342.4-1379.0 cm^{-1} , significantly lower than the values of free malonic acid (1700 and 1440 cm^{-1}), which indicate the coordination of malic acid through their carboxylate anions. Further, the presence of M-O (O = Oxygen in deprotonated malonic acid) bonding is evident from the appearance of ν_{M-O} modes at 446.5-498.6 cm^{-1} in the spectra of the complexes. The broad band observed at 3400-3600 cm^{-1} due to ν_{O-H} of free malic acid or free -OH was disappeared on complexation indicating the metal-oxygen linkage. The extra broad band at ~ 3500 cm^{-1} in the spectrum of the complexes may be due to uncoordinated -OH group. The characteristic ring vibration of the heterocyclic amines in the ring 1400-1600 cm^{-1} generally show significant changes on complexation but in our present complexes these bands could not be distinguished because of overlapping with $\nu_{C=O}$ and ν_{C-O} stretching bands. In plane and out of plane ring deformation modes of the heterocyclic amines observed at ~ 520 and ~ 720 cm^{-1} respectively (Hossain et al., 2004, 2008; Shekh et al.,

2004). Major IR 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 24000-24500 and 30000-30154 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) complexes. Table 4 contains the data of electronic spectra of Co(II) complexes (Reza et al., 2003).

The electronic spectra of Fe(III) complexes (**5-8**) gave four bands at the range 18500-18725, 21000-21185, 24325-24750 and 25770-25640 cm^{-1} corresponding to the transitions –



respectively. These spectra indicated the octahedral stereochemistry of Fe(III) compound (Reza et al., 2003 and Islam et al., 2003). Table 5 contains the data of electronic spectra of Fe(III) complexes.

On the basis of the above discussion the possible structure of the complexes (**1, 6**) are given in the Figures 1 and 2 respectively.

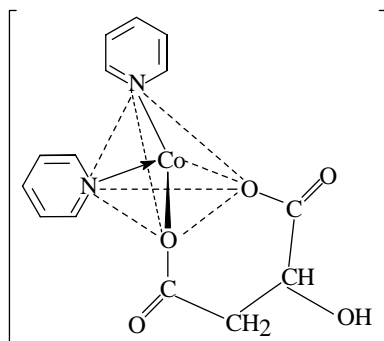


Figure 1. Possible structure of $[\text{Co}(\text{II})(\text{MA})(\text{py})_2]$ complex

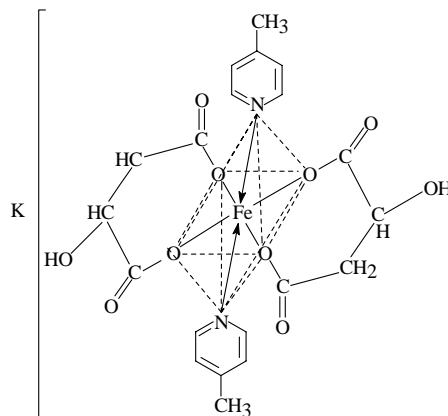


Figure 2. Possible structure of $\text{K}[\text{Fe}(\text{III})(\text{MA})_2(4\text{-pico})_2]$ complex

Antimicrobial activities: The antibacterial activities of these complex compounds were studied and result were presented in Table 6. The highest zone of inhibition 21, 30, 22, 24, 19, 28, 20 and 18 mm were produced by *S. boydii*, *S. dysenteriae*, *B. megaterium*, *S. shiga*, *S. dysenteriae*, *S. shiga*, *S. typhi* and *B. megaterium* respectively. No inhibition zone was found against some bacteria. In the other cases, the complexes showed moderate zone of inhibition. It is evident from the Table to that the complex no. 2 has most and complex no. 7 has least antibacterial effect.

The antifungal activity of these complexes were also studied and result are presented in Table 7. In the case of antifungal activity tells the highest zone of inhibition 28 and 30 mm against *Trichophyton* sp and *Bipolaris sorokiniana* respectively were measured in complex no. 2 while rest of the complexes have more or less moderate antifungal effect against the tested fungi *Aspergillus nidulans*, *Candida albicans* and *Colletotrichum falcatum*. No zone of inhibition was found in some of the tested complexes.

Table 1. Physical properties of the complexes (1-8)

Com. No.	Complexes	Color	Melting point or decomposition temperature ($\pm 5^\circ\text{C}$)	Molar conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	magnetic moment (BM.)
1	$[\text{Co}(\text{II})(\text{MA})(\text{Py})_2]$	Purple	290	9.87	3.98
2	$[\text{Co}(\text{II})(\text{MA})(4\text{-pico})_2]$	Light purple	290	11.93	3.72
3	$[\text{Co}(\text{II})(\text{MA})(\text{Q})_2]$	Light purple	190	14.58	4.05
4	$[\text{Co}(\text{II})(\text{MA})(\text{IQ})_2]$	Light purple	180	12.13	3.91
5	$\text{K}[\text{Fe}(\text{III})(\text{MA})_2(\text{py})_2]$	Yellow	220	65.89	5.78
6	$\text{K}[\text{Fe}(\text{III})(\text{MA})_2(4\text{-pico})_2]$	Yellow	190	79.63	5.68
7	$\text{K}[\text{Fe}(\text{III})(\text{MA})_2(\text{Q})_2]$	Cream	185	72.81	5.82
8	$\text{K}[\text{Fe}(\text{III})(\text{MA})_2(\text{IQ})_2]$	Cream	180	69.86	5.93

Table 2. Elemental analyses data of the complexes(1-8)

Com. No.	Complexes	Yields %	Metal %	Carbon %	Hydrogen %	Nitrogen %
1.	[Co(II)(MA)(Py) ₂]	63	16.88 (16.76)	48.15 (48.09)	4.04 (4.01)	8.02 (8.05)
2.	[Co(II)(MA)(4-pico) ₂]	59	15.62 (15.55)	50.93 (50.82)	4.81 (4.92)	7.43 (7.33)
3.	[Co(II)(MA)(Q) ₂]	65	13.11 (13.02)	58.80 (58.73)	4.04 (3.96)	6.24 (6.18)
4.	[Co(II)(MA)(IQ) ₂]	56	13.11 (13.05)	58.80 (58.73)	4.04 (4.01)	6.24 (6.16)
5.	K[Fe(III)(MA) ₂ (py) ₂]	72	10.80 (10.73)	41.79 (41.71)	3.50 (3.38)	5.42 (5.38)
6.	K[Fe(III)(MA) ₂ (4-pico) ₂]	69	10.24 (10.19)	44.04 (44.09)	4.05 (4.09)	5.14 (5.03)
7.	K[Fe(III)(MA) ₂ (Q) ₂]	73	9.05 (9.01)	50.57 (50.48)	3.60 (3.52)	4.58 (4.48)
8.	K[Fe(III)(MA) ₂ (IQ) ₂]	71	9.05 (9.09)	50.57 (50.61)	3.60 (3.58)	4.54 (4.44)

Table 3. Infrared spectral data of the complexes(1-8) (band maxima in cm⁻¹)

Com. No.	Complexes	$\nu(\text{OH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
1	[Co(II)(MA)(Py) ₂]	3508.5	1599.8	1371.3	515.9	409.8
2	[Co(II)(MA)(4-pico) ₂]	3517.8	1608.5	1342.4	568.0	416.1
3	[Co(II)(MA)(Q) ₂]	3507.3	1595.0	1377.1	488.0	400.2
4	[Co(II)(MA)(IQ) ₂]	3505.9	1625.9	1366.5	518.8	402.1
5	K[Fe(III)(MA) ₂ (py) ₂]	3520.2	1558.4	1373.2	574.7	415.2
6	K[Fe(III)(MA) ₂ (4-pico) ₂]	3515.6	1577.7	1379.0	504.4	412.7
7	K[Fe(III)(MA) ₂ (Q) ₂]	3514.6	1576.7	1379.0	504.4	411.8
8	K[Fe(III)(MA) ₂ (IQ) ₂]	3512.8	1599.6	1365.3	505.2	402.1

Table 4. Electronic spectral data of Co(II) complexes(1-4)

Com. No.	Complexes	Spectral band (cm ⁻¹) with assignment	
		⁴ A _{2g} (F) → ⁴ T _{1g} (P) (ν ₃)	Charge transfer band
1	[Co(II)(MA)(Py) ₂]	24039	30045
2	[Co(II)(MA)(4-pico) ₂]	24500	30070
3	[Co(II)(MA)(Q) ₂]	23950	29948
4	[Co(II)(MA)(IQ) ₂]	23945	29860

Table 5. Electronic spectral data of Fe(III) complexes(5-8)

Com. No.	Complexes	Spectral band (cm ⁻¹) with assignment			
		⁶ A _{1g} → ⁴ T _{1g} (G)	⁶ A _{1g} → ⁴ T _{2g} (G)	⁶ A _{1g} → ⁴ E _g (G)	⁶ A _{1g} → ⁴ A _{1g} (G)
5	K[Fe(III)(MA) ₂ (py) ₂]	18725	21000	24325	25770
6	K[Fe(III)(MA) ₂ (4-pico) ₂]	18500	21185	24750	25640
7	K[Fe(III)(MA) ₂ (Q) ₂]	18625	21050	24550	25675
8	K[Fe(III)(MA) ₂ (IQ) ₂]	18675	21150	24645	25750

where, MA = C₄H₄O₅, Py = C₅H₅N, 4-pico = C₆H₇N, Q = C₉H₇N, IQ = C₉H₇N

Table 6. Antibacterial activity of complexes(1-8)

Bacteria code	Name of the bacteria	Diameter of inhibition zone of bacteria in different complexes* (mm)									
		1	2	3	4	5	6	7	8	Kanamycin 30μg/disc	
A001	<i>Staphylococcus aureus</i>	0	16	8	16	0	20	8	17	22	
B001	<i>Strptococcus-β-haemolyticus</i>	14	15	0	16	8	11	0	14	18	
C001	<i>Bacillus megaterium</i>	13	31	12	20	12	18	10	18	25	
D001	<i>Bacillus subtilis</i>	12	9	22	12	0	8	10	8	24	
E001	<i>Sarcina lutea</i>	18	32	16	16	10	10	10	10	23	
F001	<i>Salmonella typhi</i>	10	18	16	20	12	14	20	14	19	
G001	<i>Shigella dysenteriae</i>	14	30	16	20	19	13	10	10	20	
H001	<i>Shigella boydii</i>	21	26	20	22	0	12	0	12	24	
I001	<i>Shigella flexneri</i>	13	31	12	16	12	18	10	18	18	
J001	<i>Shigella sonnei</i>	15	10	16	14	12	10	0	10	23	
K001	<i>Shigella shiga</i>	8	12	20	24	8	28	10	30	26	
L001	<i>Klebsiella sp</i>	0	9	20	10	0	8	8	8	21	
M001	<i>Pseudomonas aeruginosa</i>	8	18	12	14	10	11	10	10	20	
N001	<i>Escherichia coli</i>	8	15	10	8	10	8	0	8	20	

*Complexes name see Table 1

Table 7. Antifungal activity of the complexes(1-8)

Fungi code	Name of the fungi	Diameter of inhibition zone of fungi in different complexes* (mm)								
		1	2	3	4	5	6	7	8	Fluconazol
A002	<i>Fusarium</i> sp.	0	7	0	8	8	0	0	0	15
B002	<i>Trichophyton</i> sp.	7	28	8	0	10	0	8	0	0
C002	<i>Penicillium</i> sp.	0	8	0	6	8	7	0	0	22
D002	<i>Mucor</i> sp.	0	8	0	0	8	0	0	0	0
E002	<i>Aspergillus flavus</i>	0	10	0	8	0	0	0	0	22
F002	<i>Aspergillus terreus</i>	0	8	7	0	8	0	0	0	10
G002	<i>Aspergillus versicolor</i>	7	8	0	10	10	0	7	0	0
H002	<i>Aspergillus niger</i>	0	0	0	0	0	0	0	7	22
I002	<i>Aspergillus nidulans</i>	8	8	0	8	0	0	0	0	18
J002	<i>Candida albicans</i>	0	0	0	0	0	0	0	0	0
K002	<i>Trichoderma viride</i>	8	8	0	10	0	8	0	6	16
L002	<i>Colletotrichum falcatum</i>	0	0	0	0	8	0	0	0	35
M002	<i>Bipolaris sorokiniana</i>	0	30	8	8	0	10	8	0	18
N002	<i>Sclerotium rolfsii</i>	0	0	0	0	8	0	0	6	28

Conclusion

From the above discussion the structure of Co(II) and Fe(III) complexes are assignable tetrahedral and of octahedral respectively. Similarly the structure of other complexes may also be given. Some of these complexes(1-8) demonstrated strong antibacterial and antifungal activities.

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