

Synthesis and characterization of mixed ligand complexes of Co(II) and Fe(III) ions with malonic acid and heterocyclic amines

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The preparation and characterization of mixed ligand complexes of Co(II) and Fe(III) ions with malonic acid and heterocyclic amines are described here. The general formula of the complexes are: $[M(MO)L]$ and $K[M(MO)L]$, [where, $M=Co(II)$ (1-6), $Fe(III)$ (7-8); $MO=C_3H_2O_4$ (1-6), $2C_3H_2O_4$ (7-8); $L=C_6H_5N$ (1), $C_5H_6N_2$ (2), $2C_9H_7N$ (3,4,7,8), C_6H_6NO (5), C_9H_6NO (6)]. IR spectra of the complexes confirm the coordination of metal ion with ligands. The magnetic measurements indicate that the Co(II) complexes (1-6) are paramagnetic, having magnetic moment 3.91-4.21 B.M. 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.

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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}. Lewis *et al.*⁴ have reported the magnetic properties of some carboxylic acid derivatives of copper(II). Malonate complexes are known with Cu(II) and have been reviewed by Lenstra and Kataeva⁵. Complex formation between iron(III) and oxalate, malonate, succinate and glutarate ions has been studied by Deneux *et al.*⁶. They have shown that the stability order of the chelates of iron(III) is oxalate>malonate>succinate>glutarate. The metal complex of malonic⁷ and succinic acids and their various activities are also reported in the literature⁸⁻¹⁶.

Tiwari has synthesised the benzo thiazole ligand and its metal complexes with bivalent Cu, Co, Ni, Cd, Fe and Zn ions and evaluated the antibacterial and antifungal activities of the complexes¹⁷. The heterocyclic bases have a great importance in biological and industrial field and are used as corrosion inhibitors¹⁸ and as antibacterial, anticonvulsive, antifungal and antifouling agents¹⁹.

The present note describes the preparation and characterization of mixed ligand complexes of Co(II) and Fe(III) with malonic acid (MOH_2) as primary and heterocyclic amines, viz. quinoline (Q), iso-quinoline (IQ), pyridine (Py), 2-aminopyridine (2apy), 2-aminophenol (2aph) and 8-hydroxyquinoline (8-HQ) as secondary ligands on the basis of various physico-chemical techniques.

Experimental

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

IR spectra (KBr disc) were recorded on Shimadzu IR-470, Perkin-Elmer IR-883 and Genesis Series FTIRTM 9423-240-08061 spectrophotometer in the region $4500-400\text{ cm}^{-1}$. Metal was determined by weighing as oxide produced by direct ignition²⁰. The molar conductance of 10^{-3} M solution of the metal complexes in DMF was measured at 30°C using a Jenway 4310 conductivity meter and a dip-cell with platinized electrode. Melting points were determined using an electrothermal digital melting point apparatus. Magnetic susceptibility was measured with a Johnson Matthey magnetic susceptibility balance at 298 K. All susceptibilities were corrected for diamagnetic contribution using Pascal's constant²¹.

Preparation of the Co(II) complexes

The freshly prepared cobalt(II) chloride salt (0.952 g; 4 m mole) and malonic acid (0.416 g; 4 m mole) were mixed in 100 mL of absolute ethanol and refluxed on a water bath for an hour and calculated amount of an alcoholic solution of heteroamine bases was added (e.g. 8 m mole of Py, Q, IQ and 4 m mole of 2apy, 2aph, 8-HQ). The mixture was again refluxed for an hour and then cooled. Then, the solution of the complexes (only 5 and 6) was prepared in one equivalent of alcoholic potassium hydroxide. The formed precipitate was filtered, washed several times with ethanol and then dried in a vacuum desiccator over P_2O_5 .

Preparation of the Fe(III) complexes

An ethanolic solution (just dissolved) of Fe(III) chloride (0.540 g; 2 m mole) and malonic acid (0.416 g; 4 m mole) was prepared with constant stirring for 30 min. No precipitate was observed after

Table 1 — Elemental analysis and physical properties of the complexes

Comp. No.	Complexes (Colour)	Yield (%)	Metal (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Melting point ($\pm 5^\circ\text{C}$)	Λ_M ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	μ_{eff} (B.M.)
1	[Co(II)(MO)(Py) ₂] (Purple)	63	18.46 (18.41)	48.91 (48.85)	3.76 (3.70)	8.78 (8.72)	255(d)	16.29	4.05
2	[Co(II)(MO)(2apy)] (Light purple)	67	23.10 (23.04)	37.66 (37.61)	6.16 (3.08)	10.98 (10.93)	260(d)	14.31	4.21
3	[Co(II)(MO)(Q) ₂] (Light purple)	65	14.05 (13.90)	60.15 (30.09)	3.85 (3.77)	6.68 (6.61)	245	19.50	4.10
4	[Co(II)(MO)(IQ) ₂] (Light purple)	69	14.05 (13.85)	60.15 (60.88)	3.85 (3.79)	6.68 (6.63)	240	20.45	3.98
5	K[Co(II)(MO)(2aph)] (Purple)	67	19.12 (19.08)	54.45 (58.39)	2.62 (2.55)	4.55 (4.54)	210	82.52	3.95
6	K[Co(II)(MO)(8-HQ)] (Thai chocolate)	72	17.12 (17.07)	41.86 (41.80)	2.34 (2.29)	4.07 (4.01)	240(d)	98.38	3.91
7	K[Fe(III)(MO) ₂ (Q) ₂] (Cream)	65	10.02 (9.92)	51.71 (51.67)	2.25 (2.18)	5.03 (5.00)	185	63.15	6.00
8	K[Fe(III)(MO) ₂ (IQ) ₂] (Cream)	68	10.02 (9.95)	51.71 (51.67)	2.25 (2.19)	5.03 (4.99)	183	75.64	6.20

Table 2 — Infrared spectral data of the complexes (band maxima in cm^{-1})

Comp. 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)(MO)(Py) ₂]	-	-	1599.8	1371.3	515.9	409.8
2	[Co(II)(MO)(2apy)]	-	3360.2 2990.1	1608.5	1342.4	568.0	416.1
3	[Co(II)(MO)(Q) ₂]	-	-	1595.0	1377.1	488.0	400.2
4	[Co(II)(MO)(IQ) ₂]	-	-	1625.9	1366.5	518.8	402.1
5	K[Co(II)(MO)(2aph)]	-	3365.2 3099.8	1558.4	1373.2	574.7	415.2
6	K[Co(II)(MO)(8-HQ)]	-	-	1577.7	1379.0	504.4	412.7
7	K[Fe(III)(MO) ₂ (Q) ₂]	-	-	1576.7	1379.0	504.4	411.8
8	K[Fe(III)(MO) ₂ (IQ) ₂]	-	-	1599.6	1365.3	505.2	402.1

which heteroamine base (Q, IQ = 0.576 g; 4 m mole) was added with constant stirring for an hour. Then, the solution of the complexes was prepared in one equivalent of alcoholic potassium hydroxide. The formed precipitates were filtered, washed several times with alcohol and then dried in a vacuum desiccator over P_2O_5 .

Results and discussion

Elemental analyses along with other data and the physical properties are given in Table 1. The molar conductances were measured in $\text{N,N}'$ -dimethylformamide. 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.

The effective magnetic moments of the Co(II) and Fe(III) complexes at room temperature are also shown in Table 1. The magnetic measurements indicate that the Co(II) complexes (1-6) are paramagnetic and

show magnetic moment between 3.91-4.21 B.M. corresponding to three unpaired electrons, and hence, are tetrahedral²² with sp^3 hybridization. The observed magnetic moment values of Fe(III) (6.00-6.20 B.M.) indicate that these complexes are also paramagnetic with five unpaired electrons and hence, have octahedral structure^{23,24} with sp^3d^2 hybridization.

The complexes display $\nu(\text{C=O})$ band at 1558.4-1625.5 cm^{-1} and $\nu(\text{C-O})$ 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 malonic acid through their carboxylate anions. Further, the presence of M-O (O=oxygen in deprotonated malonic acid) bonding is evident from the appearance of $\nu_{\text{M-O}}$ modes at 446.5-498.6 cm^{-1} in the spectra of the complexes²⁵.

A broad band appears at (2990.1-3099.1) cm^{-1} and 3360.2-3365.1 cm^{-1} in the complexes 2 and 5 in which $\nu(\text{NH}_2)$ bands of the complexes are probably hidden. The NH_2 complexation is inferred from the

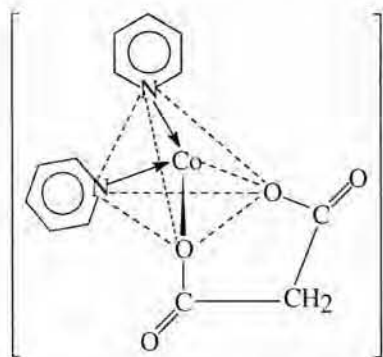


Fig. 1 — Possible structure of the complexes 1-4
[Co(II)(MO)(Py)₂]

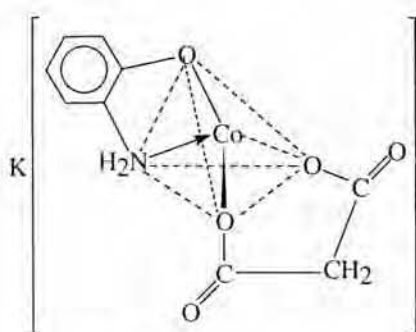


Fig. 2 — Possible structure of the complex 5-6,
K[Co(II)(MO)(2aph)]

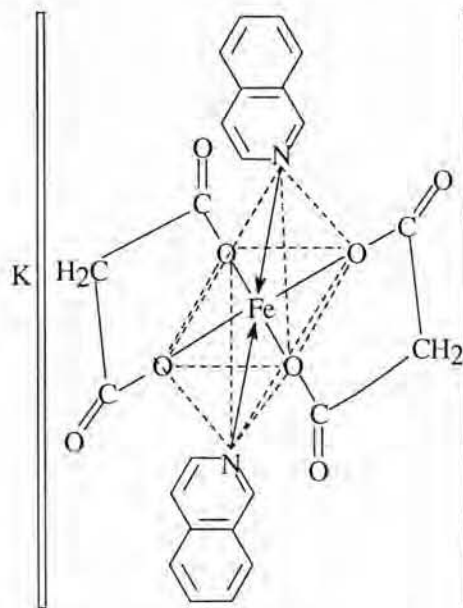


Fig. 3 — Possible structure of the complexes 7-8,
K[Fe(III)(MO)₂(IQ)₂]

respectively. These spectra are very much consistent with the octahedral stereochemistry of Fe(III) compounds^{31,32}.

Possible structures of the complexes (1-8) are given in Figs 1-3.

appearance of $\nu(\text{M-N})$ modes $402.1\text{-}425.2\text{ cm}^{-1}$ in the complexes²⁶⁻²⁸.

The characteristic ring vibration of the heterocyclic amines in the range $1400\text{-}1600\text{ cm}^{-1}$ generally shows significant changes on complexation²⁹ but in the present complexes, these bands could not be distinguished because of overlapping with $\nu(\text{C=O})$ and $\nu(\text{C-O})$ stretching bands. The in-plane and out-of-plane ring deformation modes of the heterocyclic amines are observed at ~ 520 and $\sim 720\text{ cm}^{-1}$ respectively. IR spectral data for the complexes are given in Table 2.

The electronic spectra of Co(II) complexes (1-6) give two intense bands at $24000\text{-}24500$ and $30000\text{-}30154\text{ cm}^{-1}$ corresponding to the transitions ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ (ν_3) and charge transfer band respectively. These spectra indicate the tetrahedral stereochemistry of Co(II) complexes which are consistent with the published structure^{22,30}.

The electronic spectra of Fe(III) complexes (7-8) gave four bands at the range $18500\text{-}18725$, $21000\text{-}21185$, $24325\text{-}24750$ and $25770\text{-}25640\text{ cm}^{-1}$ corresponding to the transitions [${}^6A_{1g} \rightarrow {}^4T_{1g}(\text{G})$; ${}^6A_{1g} \rightarrow {}^4T_{2g}(\text{G})$; ${}^6A_{1g} \rightarrow {}^4E_g(\text{G})$; ${}^6A_{1g} \rightarrow {}^4A_{1g}(\text{G})$],

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