

## Mixed ligand chelates of Fe (III) and Co (III) diphenates with 5-methyl-1,10-phenanthroline and 4-methyl-2,2'-Dipyridyl

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### ABSTRACT

Mixed ligand chelates of Fe (III) and Co (III) diphenates with 5-methyl-1,10-phenanthroline and 4-Methyl-2,2'-Dipyridyl have been isolated. Different physico-chemical studies reveals their octahedral geometry. I.R. studies indicate dibasic nature of diphenic acid, while 4-methyl-2,2' dipyridyl and 5-methyl-1,10-phenanthroline works as a neutral ligand, coordinated through tertiary nitrogen atom.

**Key words:** Mixed ligand chelates, tertiary nitrogen atom.

### INTRODUCTION

Diphenic acid has been used as an analytical reagent for the gravimetric and amperometric determination of Th (IV) and Pd(II) and in the separation studies of some common bivalent transition metal ions<sup>(1-3)</sup> studies on the composition and stability of diphenic acid complexes with a few metal ions<sup>(4-7)</sup> have also been reported. We report here the preparation and characterization of mixed ligand chelates of Fe(II) and Co(II) diphenates with 4-methyl-2,2'-dipyridyl and 5-methyl-1,10-phenanthroline.

### EXPERIMENTAL

Cobalt (III) complexes were prepared by refluxing a mixture of cobalt (iii) chloride and diphenic acid (1.1) in methanol for 30 minutes at ~70°C. Hydrogen peroxide (slightly more than the calculated amount) required for the oxidation of Co(II) was added and mixture again refluxed for one hour. The fresh solution of amine (2.5fold excess) was added and the mixture was cooled in

ice for about a week. A methanolic solution of sodium perchlorate was then added to this cooled when yellow coloured crystals with a bright lustre immediately precipitate. These were filtered washed several times with methanol and then dried at 80°.

Iron (III) complexes were also similarly prepared using dioxane as the solvent. Addition of hydrogen peroxide and sodium perchlorate was not necessary and no refluxing was carried out. The mixture was allowed to stand overnight and reddish brown precipitate formed was filtered, washed several times with dioxane and then dried in vacuo over concentrated sulphuric acid.

### RESULTS AND DISCUSSION

Cobalt (III) complexes were soluble in common organic solvents. The molar conductance values in methanol ranging between 90 and 100 mhos cm<sup>2</sup> mol<sup>-1</sup> indicated (1:1) electrolytic nature of the complexes. The molecular weight determined cryoscopically corresponded to monomer formula of the complexes.

### Magnetic and Electronic Spectral Studies

The absorption spectra of the diamagnetic octahedrally coordinated cobalt (III) complexes in methanol showed three (d-d) transition at 28500 ( $\epsilon_{\max}=140$ ), 18500 ( $\epsilon_{\max}=110$ ), and 14000 $\text{cm}^{-1}$  in the case of 4-methyl dipridyl complex and at 32400 ( $\epsilon_{\max}=145$ ), 20500 ( $\epsilon_{\max}=120$ ), and 14500 $\text{cm}^{-1}$  in case of 5-methyl -1,10 phenanthroline complex corresponding to the transitions  ${}^1A_{1g} \rightarrow {}^1A_{2g} \rightarrow {}^1A_g \rightarrow {}^1A_{1g}$  and  ${}^1A_{1g} \rightarrow {}^3A_{1g}$  respectively. Considering an average octahedral field, the value of 10Dq,  $[\text{Co}(\text{C}_{14}\text{H}_8\text{O}_4)(\text{C}_{11}\text{H}_{10}\text{N}_2)_2]\text{ClO}_4$  and  $[\text{Co}(\text{C}_{14}\text{H}_8\text{O}_4)(\text{C}_{13}\text{H}_{10}\text{N}_2)_2]\text{ClO}_4$  complexes were found to be 22500 and 23500  $\text{cm}^{-1}$  respectively. (8,9).

Iron (III) complexes were soluble in DMF but insoluble in other organic solvents and they did not decompose or melt upto 360°C. Conductance measurement showed their (1:1) electrolytic nature.

### Magnetic and Electronic Spectral Studies

The ground term for a spin free octahedrally coordinated<sup>10</sup> iron (III) system is  $6A_1$ . the values of magnetic moments ( $\approx 5.92\text{B.M.}$ ) indicated a spin free octahedral structures. There was no reduction in magnetic moment below the spin only value due to spin orbit coupling or the higher lying terms. The electronic spectra of the complexes gave three bands at 32800, 39800 and 44100 $\text{cm}^{-1}$  corresponding to the transitions  ${}^6A_{1g} \rightarrow {}^4(P)A_{1g} \rightarrow {}^6A_{1g} \rightarrow {}^4A_{1g} \rightarrow (F)$  and  ${}^6A_{1g} \rightarrow {}^4A_{2g} \rightarrow (F)$  respectively<sup>(11)</sup>.

### NMR-Spectral Studies

The value of isomer shift ( $\delta$ ) and quadrupole splitting ( $\Delta E$ ) obtained from the Mossbauer spectra of the present and some similar Fe(III) complexes are given in table (2). The value of  $\delta$  for the complexes are close to the values reported<sup>12</sup>

Table 1: Analytical data of the complex

S. No	Complex	% Chemical Analysis found (Calcd.)				$\Omega\text{M ohm}^{-1}$ $\text{Cm}^2 \text{mol}^{-1}$ (Caled)	$\mu_{\text{eff}}$ B.M.	Mol. Wt. found
		C	H	N	Metal			
1.	$[\text{Co}(\text{C}_{14}\text{H}_8\text{O}_4)$	58.35	3.62	7.50	7.82	92.31	0.48	725
2.	$(\text{C}_{11}\text{H}_{10}\text{N}_2)_2]\text{ClO}_4$	(58.50)	(3.79)	(7.58)	(7.98)			(738.43)
3.	$[\text{Co}(\text{C}_{14}\text{H}_8\text{O}_4)$	60.90	3.42	7.00	7.35	97.20	0.52	770
4.	$(\text{C}_{13}\text{H}_{10}\text{N}_2)_2]\text{ClO}_4$	(61.03)	(3.56)	(7.12)	(7.49)			(786.43)
5.	$[\text{Fe}(\text{C}_{14}\text{H}_8\text{O}_4)$	61.75	3.93	7.85	7.96	95.12	5.90	685
6.	$(\text{C}_{11}\text{H}_{10}\text{N}_2)_2]\text{NO}_3$	(61.89)	(4.01)	(8.02)	(8.02)			(698)
7.	$[\text{Fe}(\text{C}_{14}\text{H}_8\text{O}_4)$	64.25	3.62	7.43	7.42	100.35	5.92	738
8.	$(\text{C}_{11}\text{H}_{10}\text{N}_2)_2]\text{NO}_3$	(64.34)	(3.75)	(7.50)	(750)			(746)

Table 2: Chemical shift ( $\delta$ ) and quadrupole splittings ( $\Delta E$ ) at 25°C with respect to sodium nitroprusside absorber

S. No.	Complex	$\delta(\text{mm sec}^{-1})$	$\Delta E(\text{mm sec}^{-1})$
1	$[\text{Fe}(\text{C}_{13}\text{H}_{10}\text{N}_2)(\text{C}_{14}\text{H}_8\text{O}_4)]\text{NO}_3$	0.65	0.90
2	$[\text{Fe}(\text{C}_{14}\text{H}_8\text{N}_4)(\text{C}_{11}\text{H}_{10}\text{O}_2)_2]\text{NO}_3$	0.64	0.85
3	$[\text{Fe}(\text{C}_{15}\text{H}_2\text{N}_2)(\text{C}_{12})\text{ClO}_4^*$	0.63	0.0
4	$[\text{Net}_4[\text{Fe}(\text{C}_{16}\text{H}_8\text{N}_2)\text{C}_{14}]^*$	0.65	0.0
5.	$[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{C}_{10}\text{H}_4)_3\text{H}_2\text{O}^*$	0.31	0.0
6.	$[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{CN})_2]\text{NO}_3^*$	0.25	0.0
7.	$[\text{Fe}(\text{C}_{13}\text{H}_2\text{O})]$	0.65	0.50

\*RR Berrett, B.W. Fitzsimmons, A.A. Owusu J. Chem. Soc. A (1968) 1576-7

for complexes 3 and 4 which have octahedral structures. The data for the complexes 3 and 4 indicate that unidentate chloride and phenanthroline nitrogen are electrically too similar to give rise to any quadrupole splitting in highspin iron (III) compounds but the present complexes showed appreciable quadrupole splitting indicating there by a widely different<sup>13</sup> field generated by two different types of ligands (amine and diphenic acid) secondly the  $\Delta E$ -values for these complexes are greater than those reported for  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  because of different donor characteristics of amine and diphenic acid. Further it was observed that the replacement of diphenic acid by phenanthroline lowers the isomeric shift by  $0.34 \text{ mm sec}^{-1}$  which is due to the better  $\pi$ -bonding capacity of phenanthroline as compared to diphenic acid on replacement of diphenic acid by two(14) cyanide ions this value is further lowered by  $0.40 \text{ mm sec}^{-1}$  again indicating a better  $\pi$ -bonding of cyanide ion over phenanthroline. The value of  $\delta$  -for the first two complexes indicate a better coordinating ability of 5-methyl 1:10 phenanthroline than that of 4-methyl-2,21-dipyridyl<sup>15</sup>.

#### IR- studies

The IR-Spectra of amines showed the presence of bands at  $740$  and  $830 \text{ cm}^{-1}$  due to (C-H) out of plane deformation. The former band shifted to  $760$  and  $775 \text{ cm}^{-1}$  in the spectra of cobalt (iii) and iron (iii) complexes respectively<sup>16</sup> while the second band shifted to  $850 \text{ cm}^{-1}$  in the spectra of both the complexes. All these bands gained intensity in the spectra of complexes. Which is also a characteristics feature of 4-methyl dipyridyl<sup>17</sup> and

5-methyl 1:10-phenanthroline complexes. The bands due to nitrate and per chlorate ions obtained at  $1360$  and  $815 \text{ cm}^{-1}$  and  $1010$  and  $670 \text{ cm}^{-1}$  respectively compared to the value  $1370$  and  $820 \text{ cm}^{-1}$  and  $1050$  and  $630 \text{ cm}^{-1}$  respectively reported for  $\text{KNO}_3$  and  $\text{KClO}_4$ . The strong bands obtained at  $1200$  and  $1450 \text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}=\text{O})$  in the spectrum of diphenic acid<sup>18</sup> shifted to  $1600$  and  $1370 \text{ cm}^{-1}$  and  $1600$  and  $1380 \text{ cm}^{-1}$  in the spectra of cobalt (iii) and iron (iii) complexes respectively. The infra red spectra of the complexes indicate the absence of (O-H) stretching vibrations of free carboxylic acids as no band was observed in the region<sup>19</sup>  $3600-3250 \text{ cm}^{-1}$  the coordinate of hydroxyl group to the Co(iii)/Fe(iii) ions was confirmed by observing a shift in the stretching frequency of the OH group of free hydroxyl acids from  $3500$  to  $3200 \text{ cm}^{-1}$ . A strong band due to deformation vibrations which appear at  $935 \text{ cm}^{-1}$  in the spectra of free diphenic acids was found missing in the spectra of complexes. The carbonyl (C=O) stretching frequency expected at  $1710 \text{ cm}^{-1}$  in the free diphenic acid were also found absent in the spectra of complexes. This indicate that carbonyl oxygen of COO group is coordinated.

IR-Spectrum of free ligand in KBr shows a strong band at  $1440 \text{ cm}^{-1}$  which is attributed to the (C=C-N=C-) stretching mode and a shoulder arising at  $1460 \text{ cm}^{-1}$  is attributable to an overtone or combination band. In present case we find the shifts of the order of  $20-30 \text{ cm}^{-1}$  in complexes which imply direct combination of amine nitrogen atoms to metal centres.

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