

## CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF Cr(III) AND Fe(III) WITH PYROGALLOL AND HETEROCYCLIC AMINES

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The octahedral mixed ligand complexes of the type  $K[Cr(PGH)_2L_2]$ ,  $K[Cr(PGH)_2L']$ ,  $K[Cr(PGH)_2L'']$  and  $K[Fe(PGH)_2L_2]$ ,  $K[Fe(PGH)_2L']$ ,  $K[Fe(PGH)_2L'']$ ; where PGH = Deprotonated pyrogallol; L = Quinoline (Q), Isoquinoline (IQ),  $\alpha$ -picoline ( $\alpha$ -Pic),  $\gamma$ -picoline ( $\gamma$ -Pic); L' = 2-aminopyridine (2-APY), 3-aminopyridine (3-APY), L'' = Pyridine (PY), were prepared in the solid form and characterized on the basis of elemental analysis, conductivity measurements, magnetic measurements, infrared and electronic spectral studies.

**Key words:** Complexes, Phenols, Amines.

### Introduction

It was found from the survey of literature that the complexes of pyrogallol and amine bases with transition metal ions have activities on various fields. The mixed ligand complexes using nitrilotriacetic acid (NTA) as primary and heterocyclic bases, amino acids and some phenols as secondary ligands have been prepared and characterized on the basis of various physico chemical techniques [1,2]. Mixed ligand chelates of Cu(II) with piperidine-2-carboxylic acid and glycine, alanine, phe-alanine, proline, hydroxyproline and 2,2'-bipyridyl catechol were prepared [3]. Metal complexes of heterocyclic amine bases have been prepared by several workers [4-7]. Mixed ligand complexes of Fe (III) succinate with amino acids have also been reported by Islam *et al.* [8]. It has been found that heterocyclic amines can be used as corrosion inhibitors [9-11], the complexes of heterocyclic amines with platinum and copper have been tested as antitumour and antibacterial [12] agents.

On the basis of this literature survey, some new mixed ligand complexes of Cr(III) and Fe(III) with pyrogallol and amine bases have been prepared and characterized.

### Experimental

**Physical measurements.** Infrared spectra of the present complexes were recorded on a Pye Unicam SP3-300 infrared spectrophotometer as KBr pellets. The electronic spectra of the complexes were run on a K4053 spectrophotometer as Nujol Mull carried out on a piece of filter paper. Magnetic measurements were carried out on a Princeton Applied Research Model VSM-155 digital vibrating sample magnetometer with an attachment of EG and G, PARC model-152 cryogenic temperature controller, under a magnetic field of 5000 gauss produced by polytronic electromagnet type H.E.M. 200. Conductivity measurements were carried out at room temperature using a WPA CM35 conductivity meter and dipcell

with a platinized electrodes in DMF. Melting points were obtained with an electrothermal melting point apparatus.

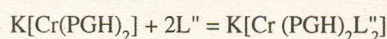
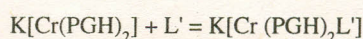
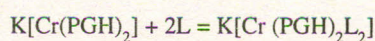
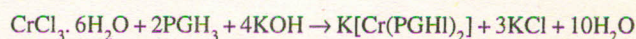
**Reagents and chemicals.** Pyrogallol and heterocyclic amines were of BDH (AR) grade. All other chemicals obtained from BDH and used as supplied but ethanol which was purified by refluxing the 99% crude with magnesium turnings and resublimed iodine and finally distilled and stored over molecular sieves.

**Preparation of complexes.** The complexes have been prepared according to the similar method developed in our laboratory [13]. A solution of chromium (III) chloride (.001 mole) in distilled water (20 ml) was mixed with the solution of pyrogallol (0.002 mole) containing 0.004 mole KOH in water (30 ml) and the mixture was refluxed for 15 mins. Then the solution L (0.002 mole) or L' (0.001 mole) or L'' (0.002 mole) in ethanol (20 ml) was added. The resulting mixture was heated at 70° for about half an hour. The precipitates formed were removed by filtration, washed several times with dis-tilled water and then alcohol and dried in an oven at 150°.

The similar procedures was applied for the preparation of Fe(III) complexes as described earlier [13, 14].

### Results and Discussion

The Cr(III) complexes were obtained according to the following equations:



Where

PGH = Deprotonated pyrogallol



L = Quinoline (Q), Isoquinoline (IQ),  
 $\alpha$ -Picoline ( $\alpha$ -Pic),  $\gamma$ -Picoline ( $\gamma$ -Pic)

L' = 2-amino pyridine (2-APY),  
 3-amino pyridine (3-APY)

L'' = Pyridine (PY)

Similarly Fe(III) complexes are also prepared from  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  with pyrogallol (0.002 mole) and L (0.002 mole) or L'' (0.002 mole) or L' (0.001 mole).

The complexes of Cr(III) and of Fe(III) were insoluble in water and other common organic solvents but soluble in dimethyl formamide (DMF). The molar conductance values

indicate the complexes are 1:1 electrolytes [15]. Analytical data of the complexes and some physical properties, viz., melting points, molar conductance and magnetic moments are given in Table 1.

*I. R. studies.* The O-H band at  $3400\text{--}3500\text{ cm}^{-1}$  of pyrogallol would disappear on coordination but a band at the same regions is observed due to one uncoordinated -OH group. The characteristic ring vibration of the heterocyclic bases in the range  $1600\text{--}1450\text{ cm}^{-1}$  generally show significant changes on complexation [16] which could not be distinguished because of mixing or overlapping with  $\nu_{\text{C-O}}$  stretching bands. The in-plane and out of plane ring deformation modes observed at  $\approx 520$  and  $\approx 720\text{ cm}^{-1}$  respectively, undergo a positive shift in

TABLE 1. ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE COMPLEXES.

Complex No.	Complexes	Colour	Metal	Carbon	Hydrogen	Molar conductance $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$	Magnetic moment (B.M.)
1.	K [Cr (PGH) <sub>2</sub> Q <sub>2</sub> ]	Black	8.67 (8.53)	60.29 (60.21)	3.68 (3.65)	88	3.72
2.	K [Cr (PGH) <sub>2</sub> (IQ) <sub>2</sub> ]	-do-	8.67 (8.62)	60.29 (60.23)	3.68 (3.64)	90	3.71
3.	K [Cr (PGH) <sub>2</sub> ( $\alpha$ -Pic) <sub>2</sub> ]	-do-	9.85 (9.12)	54.84 (54.80)	4.18 (4.13)	95	3.91
4.	K [Cr (PGH) <sub>2</sub> ( $\gamma$ -Pic) <sub>2</sub> ]	-do-	9.85 (9.65)	54.84 (54.81)	4.18 (4.15)	87	3.83
5.	K [Cr (PGH) <sub>2</sub> (2-APY)]	-do-	11.93 (11.85)	47.10 (47.05)	3.23 (3.20)	85	3.86
6.	K [Cr (PGH) <sub>2</sub> (3-APY)]	-do-	11.93 (11.67)	47.10 (47.03)	3.23 (3.21)	82	3.93
7.	K [Cr (PGH) <sub>2</sub> (PY) <sub>2</sub> ]	-do-	10.40 (10.12)	53.10 (52.98)	3.62 (3.59)	93	3.82
8.	K [Fe (PGH) <sub>2</sub> Q <sub>2</sub> ]	-do-	9.25 (9.19)	59.91 (59.87)	3.66 (3.62)	78	5.55
9.	K [Fe (PGH) <sub>2</sub> (IQ) <sub>2</sub> ]	-do-	9.25 (9.18)	59.91 (59.85)	3.66 (3.64)	85	5.69
10.	K [Fe (PGH) ( $\alpha$ -Pic) <sub>2</sub> ]	-do-	10.50 (10.12)	54.43 (54.39)	4.15 (4.12)	82	5.72
11.	K [Fe (PGH) ( $\gamma$ -Pic) <sub>2</sub> ]	-do-	10.50 (10.23)	54.43 (54.40)	4.15 (4.10)	89	5.58
12.	K [Fe (PGH) <sub>2</sub> (2-APY)]	-do-	12.71 (12.37)	46.67 (46.65)	3.20 (3.19)	76	5.62
13.	K [Fe (PGH) <sub>2</sub> (3-APY)]	-do-	12.71 (12.45)	46.67 (46.63)	3.20 (3.17)	91	5.83
14.	K [Fe (PGH) <sub>2</sub> (PY) <sub>2</sub> ]	-do-	10.09 (11.02)	52.69 (52.72)	3.59 (3.60)	73	5.91

PGH =  $\text{C}_6\text{O}_3\text{H}_4$  (deprotonated). Q = Quinoline ( $\text{C}_9\text{H}_7\text{N}$ ). IQ = Isoquinoline ( $\text{C}_9\text{H}_7\text{N}$ ).  $\alpha$ -Pic =  $\alpha$ -Picoline ( $\text{C}_6\text{H}_7\text{N}$ ).  $\gamma$ -Pic =  $\gamma$ -Picoline ( $\text{C}_6\text{H}_7\text{N}$ ). 2-APY = 2-amino pyridine ( $\text{C}_5\text{H}_6\text{N}_2$ ). 3-APY = 3-amino pyridine ( $\text{C}_5\text{H}_6\text{N}_2$ ). PY = Pyridine ( $\text{C}_5\text{H}_5\text{N}$ ). The experimental values are given in the parenthesis.

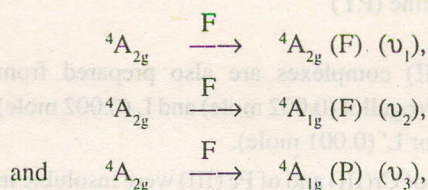


mixed ligand complexes confirming thereby a coordination through nitrogen.

*Magnetic moments and electronic spectral studies.* The magnetic moments of Cr(III) complexes were found to be 3.70-3.90 B.M. at room temperature while the Fe(III) complexes gave 5.50-6.00 B.M. as given in Table 1. The observed values are in good agreement with published values [17].

In the electronic spectra of Cr(III), have three spin allowed bands can be observed when the ligand is transparent in the ultraviolet region. The transition  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  (P) occurs above  $30,000\text{ cm}^{-1}$  so will be obscured if ultraviolet absorbing ligands are employed. The spin forbidden bands of chromium (III) which are also very well known as 'Ruby lines' are of importance in the development of optical lasers. These bands are extremely narrow and very weak compared with the spin allowed bands. The absorption spectrum of Ruby [18-20] has been analysed by Macfarlane [20] on the basis of trigonal distortion of the octahedral field. Because of the very narrow nature of spin forbidden bands, splitting of the levels by spin-orbit coupling can be observed. The electronic spectra of a very large number of six co-ordinated chromium(III) complexes have been studied [22-30]. The electronic spectra of

solution of the present chromium(III) complexes in DMF gave three bands in the region 17360-18000, 242000-26000 and  $35350\text{-}37890\text{ cm}^{-1}$ . These spectra are typical for octahedral Cr(III) complexes. The three spin allowed transitions expected are:



respectively. The electronic spectra of the Cr(III) complexes are summarized in Table 2.

The spectrum of octahedral iron (III) has not been adequately characterized. The spectra of the Fe(III) complexes generally exhibit a small number of fairly broad bands (as does the solid state spectrum of ferric alum [31] rather than the series of narrow bands expected perhaps the best resolved of octahedral iron(III) is that of  $\text{Fe}^{+3}$  in beryl [32], but the band assignments are in doubt. The electronic spectra of all the Fe(III) complexes of solution in DMF gave four bands at the

TABLE 2. ELECTRONIC SPECTRAL DATA AND PARAMETERS OF Cr (III) COMPLEXES.

Complex No.*	Spectral bands ( $\text{cm}^{-1}$ ) with assignment			10Dq ( $\text{cm}^{-1}$ )	B ( $\text{cm}^{-1}$ )	C ( $\text{cm}^{-1}$ )	$\beta$
	${}^4A_{2g} \rightarrow {}^4T_{2g}$ (F)	${}^4A_{2g} \rightarrow {}^4T_{1g}$ (F)	${}^4A_{2g} \rightarrow {}^4T_{1g}$ (P)				
1	17480	24400	37095	17480	713	2852	0.69
2	18000	25030	35590	18000	735	2940	0.71
3	17360	24803	35503	17360	709	2836	0.69
4	17905	24230	37100	17905	731	2924	0.71
5	17365	24720	35835	17365	709	2836	0.69
6	18000	24670	37215	18000	735	2940	0.71
7	17453	24740	35631	17453	712	2848	0.69

\* As indicated in Table 1.

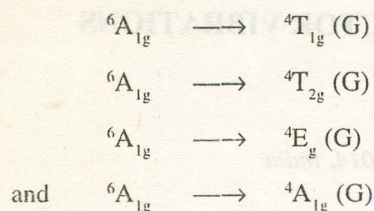
TABLE 3. ELECTRONIC SPECTRAL DATA AND PARAMETERS OF Fe (III) COMPLEXES.

Complex No.*	Spectral bands ( $\text{cm}^{-1}$ )				10Dq ( $\text{cm}^{-1}$ )	B ( $\text{cm}^{-1}$ )	C ( $\text{cm}^{-1}$ )	$\beta$
	${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G)	${}^6A_{1g} \rightarrow {}^4T_{2g}$ (G)	${}^6A_{1g} \rightarrow {}^4E_g$ (G)	${}^6A_{1g} \rightarrow {}^4A_{1g}$ (G)				
8	18725	21000	24325	25770	8580	780	3120	0.60
9	18500	21185	24750	25640	8569	779	3116	0.60
10	18450	21928	25000	25187	8591	781	3124	0.60
11	18110	21365	24028	25970	8294	754	3016	0.58
12	18220	21095	24750	25840	8349	759	3036	0.59
13	18630	21005	24325	25653	8580	780	3120	0.60
14	18713	21158	25340	25445	8569	779	3116	0.60

\* As indicated in Table 1.



range 18115-19011, 21008-21929, 24038-25000 and 25188-25974  $\text{cm}^{-1}$  corresponding to the transition:



respectively. These spectra indicated the octahedral stereochemistry of Fe(III) complexes. The electronic spectral data of Fe(III) complexes are given in Table 3.

From the above discussion the possible structure of Cr(III) complex is given below:

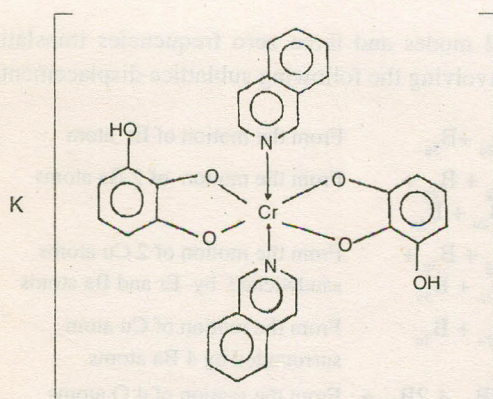


Fig. 1. The structure of  $K [Fe(PGH)_2(IQ)_2]$

Similarly the structures of other complexes may also be given.

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