

PREPARATION AND CHARACTERISATION OF MIXED LIGAND COMPLEXES OF Co(III), Fe(III), and Cr(III) CONTAINING PHTHALIMIDE AND PHENOLS

M.A. J.MIAH, M.S. ISLAM, S.C. PAL AND T.K. BARMA

Department of Chemistry, Rajshahi University, Rajshahi-6205, Bangladesh

(Received February 27, 1994)

Some novel mixed ligand complexes of Co(III), Fe(III) and Cr(III) containing phthalimide as primary and 2-aminophenol and 3-aminophenol as secondary ligands have been synthesised and characterised on the basis of elemental analyses, conductivity and magnetic measurements and infrared and electronic spectral studies. Complexes containing 2-aminophenol are 1 : 1 electrolyte in N,N dimethylformamide. Spectral studies indicate that all the complexes exhibit octahedral geometry. The complexes have the general composition: $K[M(\text{pim})_2(\text{L})_2]$; where $M=\text{Co(III)}$, Fe(III) and Cr(III) , $\text{pim}=\text{anion of phthalimide}$ and $\text{L}=\text{anion of 2-aminophenol and 3-aminophenol}$.

Key Words: Imide complexes, Co (III), Fe(III) and Cr(III).

Introduction

The wide application of imides and their derivatives in different fields such as, pharmacological [1-3], industrial [4-9] and agricultural [10,11] fields is well recognized. Imide complexes of different metals are also reported to show therapeutic [12] and agricultural [13,14] uses. Different imides and amine bases have been used to prepare mixed ligand complexes Ti(III), V(IV), Cr(III), Ru (III), Cu (II), Co(II), Ni (II), Fe (III), Pt (II), Pd (II), Rd (III) and Ir (III) ions [15-19]. Recently we have reported a number of mixed ligand complexes of Co(II) and Ni (II) containing imides and phenols [20]. Keeping these facts in view, some new mixed ligand complexes of Co(III), Fe(III) and Cr(III) containing succinimide, phthalimide, and aminophenols have been synthesised and characterized.

Experimental

Physicochemical measurements. Infrared spectra were recorded on a Pye-Unicam SP 3- 300 spectrophotometer using KBr discs and electronic spectra on LKB Biochrom Ultrospec Spectrophotometer using nujol mull spread on a filter paper. Conductivity measurements were obtained with a digital conductometer (Conductometer C G 857 Scotte Geratte) and a dip type cell with platinised electrodes at 30° C employing 10-3 M solutions of the complexes. Magnetic measurements were made on a Johnson Mathey magnetic susceptibility balance at 30° C. Metals were estimated using standard procedures [21]. Carbon and hydrogen analyses were obtained on a microanalyser at Central Drug Research Institute, Lucknow, India.

Reagents and Chemicals. All the chemicals were A.R. grade and were used as supplied by E. Merck, Germany, except for ethanol which was purified by refluxing the 99%

crude with iodine and magnesium turnings and then by distillation.

Preparation of the Co(III)Complexes. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.714g, 0.003 mol) was heated with 5 cm³ concentrated HNO_3 to oxidise Co(II) to Co(III) state until the mixture became a paste. 30 cm³ of methanol was added to make a solution of Co(III) ion. To a saturated solution of phthalimide (5.89g, 0.04 mol) in ethanol (30 cm³), an alcoholic solution (30 cm³) of potassium hydroxide (2.24g, 0.04 mol), was added very slowly with stirring. The solid formed was filtered, washed thoroughly with ethanol and dried in oven at 55°C. A solution of potassium phthalimide (1.11g, 0.006 mol) in methanol (50 cm³) was added with stirring to the solution of Co (III) ion. The precipitate of potassium chloride was filtered off. Now a solution (40 cm³) of deprotonated aminophenols (0.655g, 0.006mol) was added to the clear filtrate and the mixture was refluxed for 4 hrs on a water bath at 70°C. The coloured precipitate, that resulted on cooling the mixture, was filtered off, washed several times with ethanol and stored in vacuo over fused CaCl_2 .

Preparation of the Fe (III) complexes. A solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.811g, 0.003 mol) in methanol (30 cm³) was added to a solution of potassium phthalimide (1.11g, 0.006 mol) in methanol (50 cm³) and the mixture was refluxed for 1hr. and then cooled. Potassium chloride that formed was filtered off. To the clear filtrate, the solution of deprotonated aminophenols (0.655g, 0.006 mol) in ethanol (50 cm³) was added with stirring and refluxed for 3-4 hrs on a water bath at ~70° C and then cooled. The resulting coloured solid was filtered, washed several times with ethanol and stored in vacuo over fused CaCl_2 .

Preparation of the Cr(III) complexes. To a methanolic solution (30cm³) of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (0.799g, 0.003 mol), a

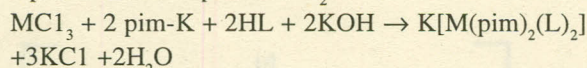
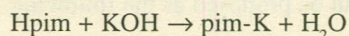
TABLE 1. YIELD AND ANALYTICAL DATA OF THE COMPLEXES
 (CALCULATED VALUES ARE IN THE PARENTHESES)

No	Complexes	Yield(%)	Metal(%)	Carbon(%)	Hydrogen(%)	Nitrogen(%)
1.	K[Co(Pim) ₂ (2-amp) ₂]	60	9.50(9.73)	55.21(55.45)	3.12(3.0)	6.92(7.11)
2.	K[Co(Pim) ₂ (3-amp) ₂]	69	9.43(9.73)	55.15(55.45)	3.02(3.0)	6.97(7.11)
3.	K[Fe(Pim) ₂ (3-amp) ₂]	65	9.12(9.26)	55.50(55.72)	3.2(3.31)	7.01(7.13)
4.	K[Fe(Pim) ₂ (3-amp) ₂]	58	9.00(9.26)	55.53(55.72)	3.15(3.31)	6.95(7.13)
5.	K[Cr(Pim) ₂ (2-amp) ₂]	68	8.72(8.75)	55.92(56.08)	3.30(3.34)	6.92(7.17)
6.	K[Cr(Pim) ₂ (3-amp) ₂]	62	8.63(8.75)	55.82(56.08)	3.25(3.34)	6.96(7.17)

solution of potassium phthalimide (1.11g, 0.006 mol) in the same solvent (50 cm³) was added and refluxed for 1 hr. The solid that formed was rejected by filtration. To the clear filtrate, a solution of deprotonated aminophenol (0.655g, 0.006 mol) in ethanol (50 cm³) was added with stirring and refluxed for 3.5 hrs on a water bath at ~70° C and then cooled. The precipitated coloured complex was filtered, washed several times with ethanol and dried in vacuo over P₄O₁₀.

Results and Discussion

In the light of analytical and other data, the preparation of the complexes can be represented by the following reactions.



where M=Co(III), Fe(III), and Cr(III)

pim=anion of phthalimide

HL=2-aminophenol (2-amp) and 3-aminophenol (3-amp).

Potassium salt of phthalimide is prepared, to enhance the reactivity of the ligand in the salt form, which later on reacts with the metal halide and the secondary ligands to yield the complexes. Here one mole of metal chloride reacts with two moles of K-salt of imide and two moles of aminophenols in the presence of two moles of KOH to produce one mole of complex, three moles of KCl and two moles of H₂O.

Conductivity and elemental analyses. The yields and analytical data are given in Table 1. The complexes are for-

TABLE 2. SOME PHYSICAL PROPERTIES OF THE COMPLEXES

Compound No.	Colour	Melting Point(°C)	Molar conductance, Λ_M (ohm ⁻¹ cm ² mol ⁻¹)	Magnetic moment μ_{eff} (B.M.)
1	Black	310	78.50	0.90
2	Violet	>360	-	0.91
3	Black	290-295(d)	86.80	5.78
4	Yellowish	>360	-	5.87
5	Black	>360	89.2	3.84
6	Green	>285	-	3.93

culated on the basis of these data. Complexes 1, 3, and 5 are soluble in dimethylformamide and dimethylsulphoxide and insoluble in other common solvents, whereas the complexes, 2,4 and 6 are completely insoluble in all common polar and non polar solvents. Molar conductance values of the complexes 1,3 and 5 measured with 10⁻³ M solutions in dimethylformamide (DMF) are found to be in the range of 78-89.2 ohm⁻¹ cm² mol⁻¹. This indicates that the complexes are 1: 1 electrolyte in nature [22] in DMF. Molar conductances of the complexes 2,4, and 6 could not be obtained due to their insolubility in all common solvents. Colour, melting point, molar conductance values and magnetic moments of the complexes are given in Table 2.

I.R. studies. I.R. spectra of the complexes are shown in the Table 3. The $\nu(\text{C}=\text{O})$ band observed at 1750 cm⁻¹ for free phthalimide is found to be shifted at 1625-1670 cm⁻¹ in the spectra of the complexes. This shift towards the lower frequencies may be due to either coordination through oxygen or formation and coordination of imide nitrogen (N-). Coordination through nitrogen seems to be more logical, since linkage through oxygen is normally hindered by steric factor [23]. In addition to the above fact, coordination of the imide nitrogen to the metals is supported by the appearance of $\nu(\text{CN})$

 TABLE 3. INFRARED SPECTRA OF THE COMPLEXES
 (BAND MAXIMA, CM⁻¹)

Compound No.	$\nu(\text{NH}_2)$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{N})$	$\nu(\text{M}-\text{N})$
1	3380 w 3285 sh	1670 sh	1380 s	360 m
2	3230 m 3140 m	1645 m	1370 m	360 w
3	3220 s 3160 sh	1640 m	1375 s	350 w
4	3260 m 3160 sh	1640 s	1375 s	350 m
5	3240 s 3140 s	1625 sh	1380 s	360 w
6	3370 m 3280 sh	1665 m	1385 m	355 m

Relative band intensities are denoted by s,m,w, and sh meaning strong, medium, weak, and shoulder, respectively.

TABLE 4. ELECTRONIC SPECTRAL PARAMETERS OF Fe (III) COMPLEXES

Compound No.	Transitions			B(cm ⁻¹)	C(cm ⁻¹)	β	Dq
	⁶ A _{1g} → ⁴ T _{1g} (G) ν ₁ (cm ⁻¹)	⁶ A _{1g} → ⁴ A _{2g} ν ₂ (cm ⁻¹)	⁶ A _{1g} → ⁴ A _{1g} ν ₃ (cm ⁻¹)				
3	17047	27390	33000	616.6	2466.4	0.607	1704.7
4	17040	27480	33100	630.67	2522.68	0.621	1704

TABLE 5. ELECTRONIC SPECTRAL PARAMETERS OF Cr(III) COMPLEXES

Compound No.	Transitions			B(cm ⁻¹)	C(cm ⁻¹)	β	Dq
	⁴ A _{2g} → ⁴ T _{2g} (F) ν ₁ (cm ⁻¹)	⁴ A _{2g} → ⁴ T _{1g} (F) ν ₂ (cm ⁻¹)	⁴ A _{2g} → ⁴ T _{1g} (P) ν ₃ (cm ⁻¹)				
5	17980	25400	36100	504	2016	0.55	1798
6	17900	25500	36900	580	2320	0.63	1790

stretching band at ~1380 cm⁻¹ for the complexes significantly lower than the free ligand value (1470 cm⁻¹) [24]. The ν(NH) band at 3400 cm⁻¹ observed for free imide ligand disappeared in the complexes. The metal oxygen linkage in case of aminophenol is indicated by the disappearance of the broad ν(OH) band that occurs at 3500 cm⁻¹ for free aminophenol. The two bands due to ν(NH₂) observed for free aminophenols at ~3390 cm⁻¹ and 3478 cm⁻¹ are shifted to lower frequencies 3140-3285 cm⁻¹ and 3220-3380 cm⁻¹ respectively indicating coordination of nitrogen atom of the NH₂ group to the metal [25]. The metal nitrogen coordination is further supported by the appearance of ν(MN) mode at ~350 cm⁻¹ in the far infrared spectra of the complexes[26].

Magnetic moment and electronic spectra. Magnetic moments of the Co(III) complexes (Table 3) are found to be μ_{eff} = 0.9-0.91 B. M. which includes the orbital contribution. These values reveal that the complexes are low spin diamagnetic in character consistent with the octahedral geometric structure for a d⁶ system. The effective magnetic moments, μ_{eff} of Fe(III) and Cr(III) complexes are in the range of 5.78-5.87 B. M. and 3.84-3.94 B.M. respectively which are essential in favour of the high spin paramagnetic character as well as octahedral stereochemistry for these complexes [27].

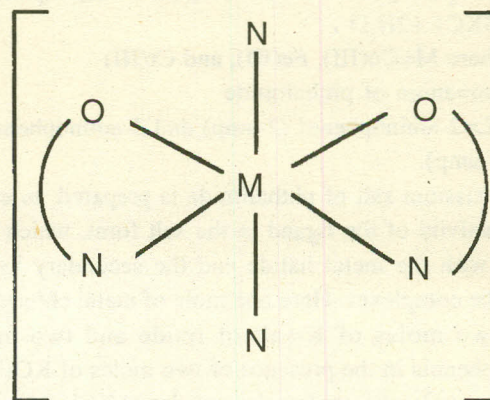
The electronic spectral parameters of Fe(III) and Cr(III) complexes are presented in Table 4 and 5.

The Co(III) complexes exhibit a single d-d band at 16420-16835 cm⁻¹ corresponding to the transition ¹A_{1g} → ¹A_{2g} and they assume largely a trans structure [28]. The cis complexes generally show this d-d band around 20,000 cm⁻¹. This is fairly consistent with octahedral geometry for these complexes [28].

The Fe(III) complexes give three bands at ~17,000, ~27,400 and ~33,000 cm⁻¹ corresponding to the transition ⁶A_{1g} → ⁴T_{1g}(G), ⁶A_{1g} → ⁴A_{1g} and ⁶A_{1g} → ⁴A_{2g} or ⁴E_g respectively. These observations further support the octahedral geo-

metric structures of these complexes [29]. The UV-visible spectra of the Cr(III) complexes display three spin allowed d-d bands at ~18,000, ~25,500 and ~36,000 cm⁻¹. These transition correspond to ⁴A_{2g} → ⁴T_{2g}(F), ⁴A_{2g} → ⁴T_{1g}(F) and ⁴A_{2g} → ⁴T_{1g}(P) respectively. These bands are characteristic of pseudo-octahedral Cr(III) complexes [30].

From the above discussion, the general skeletal structure of the complexes can be proposed as the following.



[M = Cr(III), Fe(III), and Co (III)]

References

1. D.S. Goldman, Biochem. Biophys. Acta, **27a**, 45 (1960).
2. T.Lange, S. Rump, I.Ilezak, J. Lapszewicz, T. Rabsytr and K. Waazyna, Pharmazie, **34** (2), 794 (1979).
3. Parke-Devis and Co. British Patent, 730911 (1955).
4. V.G.Ostroverkhov, E.V. Glavani, O.L. Glavani, L.G. Konovich and P. L. Klimeneo Khim. Teknol, Topl. Masel, **26**, 9 (1980).
5. E.B. Lifshits, D.Y. Shagolova and L.M. Yagupolskii, Dyes Pig., **5**, 377 (1984).
6. R.C. Schlicht and A.P. Schrobul, U.S. Patent, May 1,4446038 (1984).

7. G.A. Hill, British Patent, Appl. Feb. 1,2123429 (1984).
8. Hitachi Patent Engineering and Costt. Co. Ltd. Japan. Jpn Kakai Tokyo Koho JP, Nov. 16, 58196829 (1983).
9. V.N. Tyukaev, B.V. Erzh, I.N. Logachev, I.P. Ivaking, A.P. Maskov, A. M. Egrov, I.S. Epifavonovskii and V.A. Polozov, U.S.S.R. Patent Sept. 15, 763406 (1980).
10. K.Fuzimoto and T. Hosotsuzi, Jap. Patent, Japan, Sept. 26, 145 (62), 15 (1960).
11. G.M. Keitt, Bot. Gaz (Chicago), 51, 122, (1960).
12. A.C.Hollinshed and P.R. Smith, Antibiotics Ann, 313 (1960).
13. P.P. Minieri, U.S. Patent, Mar. 19, U.S.3798327 (1974).
14. P.Rocehi, P.Perocco, W. Alberghini, A. Fini and G. Prodi, Arch. Toxicol, 45, 101 (1960).
15. C.L. Sharma and M.S., Islam, Synthetic React. Inorg.Met-Org. Chem., 16 (9), 1261 (1986).
16. M.S. Islam and M. Masir uddin, Inorg.Met-Org, Chem., 22 (9),1303 (1992).
17. M.S. Islam, Q, Islam, and M.S. Islam, Pak. j. sci. ind. res. 34, 177 (1991).
18. M.S. Islam, M.A. Alam, and M. Masiruddin, J. Bangladesh Chem., Soc., 6 (1), 103 (1993).
19. C. L Sharma, M.S. Islam, J. Indian Chem. Soc., Sept. vol. LXIII (1987).
20. M.A.J. Mia, M.S. Islam, S.C. Pal, T.K. Barma, Bangladesh J. Sci.,Ind., Res. (Accepted).
21. A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis* (Longmans, Green and Co., 1951), 2nd ed., p 453,455,461.
22. W.J. Geary, Coord. Chem. Rev., Elsevier Publishing Company, Amsterdam, 7, 110 (1971).
23. J.C. Bailar, *The Chemistry of Coordination Compounds* (Reinhold, New York, 1956), pp.180
24. P.C.H. Mitchell, J. Inorg. Nucl. Chem., 25, 967 (1963).
25. I.S. Maslennikova, Zh. Fic. Khim., 48, 1510 (1974).
26. K.Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (John Wiley, New York, 1978), pp.215.
27. J. Selbin, Chem. Rev., 65, 153 (1965).
28. A. Uraushiyama, H. Kupka, J. Degen and H. H. Schmidtke, Chem. Phys., 67, 65 (1982).
29. A.B.P. Lever, *Inorganic Electronic Spectroscopy* (Elsevier, Amsterdam 1986), 2nd.ed., pp. 453
30. C.K. Jorgensen, Adv. Chem. Phys., 5, 33 (1963).