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MIXED-LIGAND COMPLEXES OF CHROMIUM(III), IRON(III) AND RUTHENIUM(III) WITH HOMOPHTHALIC ACID AND HETEROCYCLIC AMINES

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Several new mixed-ligand complexes of chromium(III), iron(III) and ruthenium(III) with homophthalic acid (hpH_2) and nitrogen-containing heterocyclic bases have been prepared and characterised by elemental analyses, conductometric, magnetic, infrared and electronic spectral studies. The complexes have the composition $K[M(hp)_2.L_2]$, where M=Cr(III), Fe(III) or Ru(III); hp=dianion of homophthalic acid; L=quinoline (Q), isoquinoline (IQ), pyridine (Py), 2-picoline (2-Pic) or 4-picoline (4-Pic). A proposed octahedral structure for all the complexes is supported by magnetic and spectral data.

Key words: Mixed-ligand, Complexes, Amines.

Introduction

Metal ions, coordinated with carboxylic acid groups have antiseptic properties on films, fibres and fabrics. Metal complexes of phthalic acid have insecticidal properties [1]. Heterocyclic bases are well known therapeutic agents [2] and their activity is generally enhanced when they are allowed to form complexes with metal ions [3]. Most of the heterocyclic amines are used as corrosion inhibitors [4].

The mixed-ligand complexes of Co(II) and Ni(II) with different carboxylic acids and heterocyclic bases have been prepared [5-7]. Recently, we have reported the preparation and characterisation of mixed-ligand complexes of Co(II), Ni(II), Ti(III), V(IV), Cu(II), Pd(II) and Pt(IV) with homophthalic acid and heterocyclic amines [8-10]. We are interested to extend our study to chromium(III), iron(III) and ruthenium(III) ions. Keeping these facts in view, we report herein the syntheses of the complexes of Cr(III), Fe(III) and Ru(III) with homophthalic acid and nitrogen-containing heterocyclic bases. The complexes were characterised on the basis of elemental analyses, conductivity measurements, magnetic measurements, infrared and electronic spectral studies.

Experimental

Physical measurements. The IR spectra were recorded with a Pye-Unicam SP3-300 IR spectrophotometer; spectra between 4000 and 600 cm^{-1} were recorded as KBr pellets and between 600 and 200 cm^{-1} as Nujol mulls sandwiched between CsI plates. Electronic spectra in N, N'-dimethylformamide (DMF) were recorded on a Ultrospec K-4053 spectrophotometer. Magnetic measurements were carried out on a Johnson-Matthey magnetic susceptibility balance. Conductivities of 5×10^{-4} mole dm^{-3} solutions of the complexes in DMF were measured at 28° using a WPA CM35 conductivity meter and dip-type cell with platinized electrodes. Melting points of the complexes were recorded with an electrothermal melting point apparatus.

Reagents and chemicals. All chemicals used were of reagent grade. Homophthalic acid was obtained from Fluka Chemika (Switzerland), ruthenium(III) chloride was obtained from Aldrich Chemical Co. and all other chemicals were used as supplied by E. Merck.

Preparation of the complexes. A solution of metal(III) chloride (0.002 mole) in distilled water (20 cm^3) was mixed homogeneously with a solution of homophthalic acid (0.004 mole) in ethanol (20 cm^3) and refluxed for 1 hr. A solution of L (0.004 mole) in ethanol (20 cm^3) was then added slowly to the above mixture with continuous stirring followed by the addition of a solution of potassium hydroxide (0.008 mole) in ethanol (20 cm^3). The resulting mixture was heated at 70° for 1 hr. and then cooled. The precipitate formed was filtered, washed several times successively with distilled water and ethanol and dried in a vacuum desiccator over anhydrous silica gel. The prepared complexes were isolated in pure state as indicated by TLC (using DMF-methanol [3:1] solvent system) which shows a single spot in all the cases.

Results and Discussion

Elemental analysis and conductivity. The analytical data and other physical properties of the complexes are given in Tables 1 and 2, respectively. All the complexes are soluble in DMF and dimethylsulfoxide but insoluble in water and other common organic solvents. The molar conductance values (Table 2) indicate that all the complexes are 1:1 electrolytes in DMF [11]. The analytical data and molar conductance values of the complexes are consistent with their general formula, $K[M(hp)_2.L_2]$.

IR studies. Salient features of the IR spectra of the complexes are shown in Table 3. Free homophthalic acid (hpH_2) shows a broad band at 3400-3550 cm^{-1}, a very strong band at 1700 cm^{-1} and a strong band at 1440 cm^{-1} due to υ(O-H), υ_{as}(COO) and υ_s(COO), respectively. The complexes display υ(C=O) bands at 1620-1640 cm^{-1} and υ(C-O) bands at

1390-1420 cm^{-1}, significantly lower than the free ligand value which indicates the coordination of homophthalic acid through its carboxylate anions. The disappearance of υ(O-H) mode observed in the free hpH_2 molecule clearly indicates the loss of the protons from both O-H on coordination revealing that homophthalic acid is a bidentate, dinegative ligand coordinating through both carboxylate anions. Further, the presence of M-O bonds in the complexes are evident from the appearance of υ(M-O) modes at 380-420 cm^{-1} in the spectra of the complexes [12].

The bands observed in the range 1530-1575 cm^{-1} in the spectra of the complexes may be due to the ring vibrations of the coordinated heterocyclic bases [13]. The in-plane and out-of-plane ring deformation modes of the heterocyclic bases observed at ~610 cm^{-1} and ~420 cm^{-1}, respectively, undergo shifts to higher frequencies in the spectra of the present complexes confirming their coordination through nitrogen [14]. Further support for M-N bonding in the complexes is evident from the appearance of υ(M-N) modes at 270-315 cm^{-1} in the spectra of the complexes [15].

Magnetic moments. The observed values of effective magnetic moment of the complexes at room temperature are given in Table 2. The magnetic moment values of Cr(III) complexes (3.75-3.93 B.M.) indicate that the complexes (1-5) are paramagnetic with three unpaired electrons [16,17]. The magnetic moment values of Fe(III) complexes (5.70-5.98 B.M.) indicate that the complexes (6-10) are paramagnetic with five unpaired electrons and, hence, are high

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

Compound	No.	Yield %	Metal %	Carbon %	Hydrogen %	Nitrogen %
K[Cr(hp)$_2$ (Q)$_2$]	1	64	6.98 (7.36)	60.75 (61.21)	3.51 (3.68)	3.74 (3.96)
K[Cr(hp)$_2$ (IQ)$_2$]	2	70	7.12 (7.36)	60.87 (61.21)	3.50 (3.68)	3.80 (3.96)
K[Cr(hp)$_2$(Py)$_2$]	3	62	8.20 (8.58)	55.05 (55.48)	3.65 (3.63)	4.43 (4.62)
K[Cr(hp)$_2$(2-Pic)$_2$]	4	76	7.96 (8.20)	56.47 (56.81)	4.18 (4.10)	4.30 (4.41)
K[Cr(hp)$_2$(4-Pic)$_2$]	5	71	7.81 (8.20)	56.35 (56.81)	4.04 (4.10)	4.26 (4.41)
K[Fe(hp)$_2$(Q)$_2$]	6	67	7.54 (7.86)	60.46 (60.88)	3.68 (3.66)	3.70 (3.94)
K[Fe(hp)$_2$(IQ)$_2$]	7	75	7.66 (7.86)	60.52 (60.88)	3.75 (3.66)	3.78 (3.94)
K[Fe(hp)$_2$(Py)$_2$]	8	78	8.83 (9.16)	54.77 (55.13)	3.52 (3.60)	4.45 (4.59)
K[Fe(hp)$_2$(2-Pic)$_2$]	9	80	8.65 (8.75)	56.61 (56.48)	4.15 (4.07)	4.42 (4.39)
K[Fe(hp)$_2$(4-Pic)$_2$]	10	68	8.31 (8.75)	56.08 (56.46)	3.93 (4.07)	4.15 (4.39)
K[Ru(hp)$_2$(Q)$_2$]	11	60	12.95 (13.39)	56.84 (57.23)	3.28 (3.44)	3.56 (3.70)
K[Ru(hp)$_2$(IQ)$_2$]	12	77	13.51 (13.39)	57.08 (57.23)	3.50 (3.44)	3.60 (3.70)
K[Ru(hp)$_2$(Py)$_2$]	13	65	15.16 (15.43)	50.89 (51.32)	3.42 (3.36)	4.05 (4.27)
K[Ru(hp)$_2$(2-Pic)$_2$]	14	72	14.47 (14.80)	52.50 (52.72)	3.85 (3.80)	3.94 (4.10)
K[Ru(hp)$_2$(4-Pic)$_2$]	15	65	14.55 (14.80)	52.34 (52.72)	3.68 (3.80)	3.90 (4.10)

hp = $C_9H_6O_4$,; Q and IQ = C_9H_7N; Py = C_5H_5N; 2-Pic and 4-Pic = C_6H_7N.

TABLE 2. PHYSICAL PROPERTIES OF THE COMPLEXES (d = DECOMPOSE).

Compound	Colour	Melting point (±0.5°)	Molar conductance (ohm^{-1} cm^{2}mole^{-1})	Effective magnetic moment (B.M.)
1	Green	352	83.24	3.75
2	Green	326	80.36	3.81
3	Ash	>360	69.58	3.93
4	Ash	>360	67.95	3.80
5	Ash	>360	73.44	3.78
6	Brown	345	68.55	5.92
7	Brown	327d	75.32	5.98
8	Brown	339	88.14	5.87
9	Brownish red	342	81.75	5.70
10	Brownish red	318d	86.67	5.84
11	Deep grey	345	77.82	2.06
12	Deep grey	330	72.63	1.94
13	Red	354	85.68	1.92
14	Crimson	348	74.26	1.88
15	Crimson	306d	79.82	1.98

TABLE 3. IR SPECTRAL DATA FOR THE COMPLEXES (BAND MAXIMA IN cm^{-1})*.

Comp.	ν(O-H)	ν(C=O)	ν(C-O)	ν(M-O)	ν(M-N)
hpH$_2$	3400-3550br	1700vs	1440s	—	—
1		1625s	1410s	400w	290m
2		1620s	1390m	420m	310m
3		1630s	1400s	410m	285m
4		1635vs	1410m	420m	310m
5		1625vs	1420s	410m	315w
6		1620s	1395m	400w	275m
7		1640s	1420m	415m	280w
8		1620s	1405s	390w	290w
9		1625s	1420m	410m	315m
10		1625s	1400s	400w	305m
11		1640s	1395m	380w	275m
12		1635s	1410m	395m	280w
13		1630s	1420m	390m	300m
14		1630s	1400s	400m	290m
15		1635s	1415s	390w	285m

* Relative band intensities are denoted by vs, s, m, w and br, meaning very strong, strong, medium, weak and broad, respectively.

TABLE 4. ELECTRONIC SPECTRAL DATA OF Cr(III) COMPLEXES.

Compound	Spectral band maxima (cm^{-1}) with assignment		
	$^4A_{2g} \rightarrow {}^4T_{2g}$(F)	$^4A_{2g} \rightarrow {}^4T_{1g}$(F)	Charge transfer
1	182181	25188	37453
2	17889	25706	36900
3	18382	25575	36363
4	18148	24813	35714
5	17667	25445	37174

spin complexes [16,18]. The magnetic moment values of Ru(III) complexes (1.88-2.06 B.M.) indicate that the complexes (11-15) are paramagnetic with one unpaired electron and, hence, are low spin complexes [16,19].

Electronic spectra. The electronic spectral data of Cr(III), Fe(III) and Ru(III) complexes are given in Tables 4,5 and 6, respectively. The Cr(III) complexes gave three bands in the regions 17667-18382 cm^{-1}, 24813-25706 cm^{-1} and 35714-37453 cm^{-1} corresponding to the transitions $^4A_{2g} \rightarrow {}^4T_{2g}$(F), $^4A_{2g} \rightarrow {}^4T_{1g}$(F) and charge transfer, respectively. These bands are typical for octahedral Cr(III) complexes [16,17]. The Fe(III) complexes gave four bands in the regions 22883-23529 cm^{-1}, 27548-28653 cm^{-1}, 31055-31847 cm^{-1} and 38610-40322 cm^{-1} corresponding to the transitions $^6A_{1g} \rightarrow {}^4E_g$(G), $^6A_{1g} \rightarrow {}^4T_{2g}$(D), $^6A_{1g} \rightarrow {}^4E_g$(D) and charge transfer, respectively. These bands are consistent with octahedral Fe(III) complexes [16,20]. The Ru(III) complexes produced four bands in the regions 19531-20242 cm^{-1}, 25316-26178 cm^{-1}, 32679-34246 cm^{-1} and 39370-41152 cm^{-1}. The first two bands correspond to the

TABLE 5. ELECTRONIC SPECTRAL DATA OF Fe(III) COMPLEXES.

Compound	Spectral band maxima (cm^{-1}) with assignment			
	$^6A_{1g} \rightarrow {}^4E_g$(G)	$^6A_{1g} \rightarrow {}^4T_{2g}$(D)	$^6A_{1g} \rightarrow {}^4E_g$(D)	Charge transfer
6	22935	28089	31250	40322
7	23255	28653	31746	39215
8	22883	28328	31055	39682
9	23148	27548	31847	38610
10	23529	27855	31545	39062

TABLE 6. ELECTRONIC SPECTRAL DATA OF Ru(III) COMPLEXES.

Compound	Spectral band maxima (cm^{-1}) with assignment			
	$^2T_{2g} \rightarrow {}^4T_{1g}$(G)	$^2T_{2g} \rightarrow {}^4T_{2g}$(G)	Charge transfer	
11	19685	25316	33003	39840
12	20242	25906	34129	39370
13	20161	26178	32679	40322
14	19531	25575	33670	41152
15	19880	25839	34246	40816

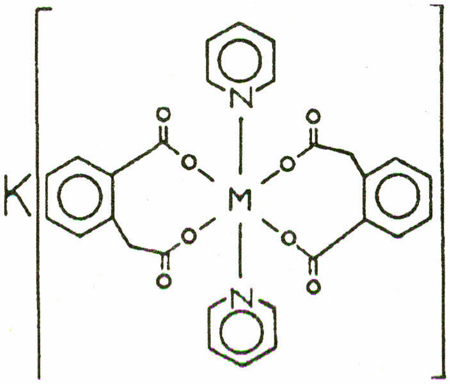

Fig. 1. Possible structure of the complexes.

transitions $^2T_{2g} \rightarrow {}^4T_{1g}(G)$ and $^2T_{2g} \rightarrow {}^4T_{2g}(G)$. The latter two regions correspond to the charge transfer bands. All these bands are consistent with octahedral Ru(III) complexes [16,19].

From the above discussion an octahedral structure is assignable to the prepared Cr(III), Fe(III) and Ru(III) complexes. The suggested structure of the complexes with pyridine is given in Fig. 1. The structures of the complexes with other heterocyclic amines are expected to be similar.

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