

STUDIES ON THE MIXED LIGAND COMPLEXES OF Cr (III) AND Co (III) CONTAINING MONOBASIC ACIDS AND TETRAAZA MACROCYCLES

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(Revised 26 November 1995; accepted 20 August 1997)

A few mixed ligand macrocyclic complexes of Cr (III) and Co (III) of the formula $\text{trans} [\text{M}(\text{X}_2)_2\text{L}] \text{Cl}_2$ where $\text{M} = \text{Cr} (\text{III}), \text{Co} (\text{III})$; $\text{X} =$ anion of acetic acid (Ac), propionic acid (Pr), butyric acid (Bu); $\text{L} = 5, 7, 7, 12, 14, 14$ -hexamethyl-1, 4, 8, 11, -tetraazacyclotetradeca-4, 11-diene dihydro dibromide dihydrate ($\text{L} \cdot 2\text{HBr} \cdot 2\text{H}_2\text{O}$) have been synthesized and characterized by elemental analyses, conductometric, magnetic measurements, IR and electronic spectral studies. The complexes are low-spin species with a trans configuration.

Key words: Mixed ligand, Macrocyclic complexes, Low spin species.

Introduction

The preparation and characterization of hexa coordinated complexes of Ni(II), Cu(II), Zn(II), Co(III) with macrocyclic have been reported (Hollinshead and Smith 1960; Curtis and House 1961; Curtis and Hay 1966; Busch 1967; Kolinski and Korybut 1969; Banefield and Busch 1971; Busch *et al* 1971; Lindoy and Busch 1971) in the literature. The complexes with different simple ligands have also been prepared (Curtis and House 1961; Curtis and Hay 1966; Kolinski and Korybut 1969). The studies on these transition metal complexes are of great interest and importance for their ability to the fundamental structural relationship with some natural products like heme proteins, chlorophyll and vitamin B₁₂ (Curtis and Hay 1966; Busch *et al* 1971). Two novel chemical reactions have figured in the synthesis of many of these new complexes coordination template reactions (Busch 1967; Banefield and Busch 1971; Lindoy and Busch 1971) and oxidative dehydrogenation reactions (Banefield and Busch 1971; Busch *et al* 1971; Lindoy and Busch *et al* 1971). The preparation of the complexes of 14-membered macrocyclic tetra amines has been extensively studied (Curtis 1968; Melson 1968). Such ligands normally produce complexes of the type $\text{trans} - [\text{Co}(\text{X})_2\text{L}]^{2+}$ (Where, X=monodentate ligand) and only in the presence of chelating ligands the complexes with a cis-geometry have been reported (Sadasivan *et al* 1967; Hay and Lowrance 1975; Hay and Jeragh 1977). This paper reports the synthesis and characterization of Cr (III) and Co (III) complexes containing simultaneously a monobasic acid and tetradentate macrocyclic ligands.

Experimental

Physical measurements. IR spectra (as KBr disc) were re-

corded on a Pye-Unicam SP3-300 infrared spectrophotometer and the electronic spectra in acetonitrile recorded on a Ultrospec K-4053 spectrophotometer. Magnetic measurements were made on a Johnson-Matthey Magnetic susceptibility balance and the conductivity measurements of the complexes (1×10^{-3} M soln.) recorded in DMSO at room temperature using WPA CM25 conductivity meter and dip-type cell with platinumized electrodes. Melting points of the complexes were recorded with an electrothermal melting point apparatus.

Reagents and chemicals. All the chemicals used were of reagent grade quality. Acetic acid, propionic acid, butyric acid were obtained from the General Chemical and Pharmaceutical Co., ethanol was purified by refluxing the 99% crude with iodine and magnesium turnings, distilled and stored over molecular sieves.

Determination of chromium. (Islam *et al* 1993) A known weight of chromium complex (0.1-0.2g) was pyrolysed with a few drops of concentrated H_2SO_4 . The residue was fused with potassium persulfate and the contents dissolved in water. The dichromate solution thus obtained was used to determine chromium titrimetrically.

Determination of cobalt. (Vogel 1961) The complex salt of known amount was pyrolysed in the same way as above. The residue was taken with H_2O and estimated volumetrically by EDTA titration using xylenol orange as indicator.

Preparation of the complexes. An ethanolic solution of anhydrous metal (II) chloride (0.002 mol) was mixed homogeneously with the ethanolic solution of X (0.004 mol). In this mixture another ethanolic solution of L. $2\text{HBr} \cdot 2\text{H}_2\text{O}$ (0.002 mol) was added dropwise with constant stirring. Then the mixture was refluxed for about 3 h when a solid product appeared. The product was filtered off, washed with ethanol,

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ether and finally dried in vacuum desiccator over P_4O_{10}

Results and Discussion

Elemental analysis and conductivity. The analytical data and some physical properties of the complexes are presented in Table 1 and 2 respectively. Carbon, hydrogen and nitrogen analyses were carried out by the Regional Sophisticated Instrumentation Center, Central Drug Research Institute, Lucknow, India. All the complexes were soluble in dimethylformamide and dimethylsulphoxide. The molal conductance values indicate (Table 2) that all the complexes were 1:1 electrolytes in DMSO.

IR studies. IR spectral data of the complexes has been shown in Table 3. Acid anion may be coordinated through its carbonyl oxygen (Bailar 1956). In the complexes the $\nu(C=O)$, $\nu(C-O)$

mode was found at $\sim 1690\text{ cm}^{-1}$ and $\sim 1390\text{ cm}^{-1}$ as compared with $\sim 1720\text{ cm}^{-1}$ and $\sim 1400\text{ cm}^{-1}$ in the free acetic acid or propionic acid or butyric acid (Alam *et al* 1991). The decrease in frequency may be due to the mass effect (Alam *et al* 1991). The IR spectra of trans complexes (planar geometry) showed more than one $\nu(NH)$ band, but cis complexes (folded geometry) showed more than one $\nu(NH)$ due to the lower symmetry of the molecules (Hung *et al* 1977). The free macrocyclic ligands had $\nu(NH)$ band at 3175 cm^{-1} (L) and $\nu(C=N)$ band at 1660 cm^{-1} (L). The complexes showed a single $\nu(C=N)$ band in the range $1650\text{--}1665\text{ cm}^{-1}$ and a $\nu(NH)$ band in the region $3140\text{--}3155\text{ cm}^{-1}$ significantly lower than the free ligand values indicating the coordination of the macrocycles through nitrogen atom. The presence of M-N bonds vibration at $430\text{--}465\text{ cm}^{-1}$ in the far IR spectra of the complexes (Hay and Tarafder 1991) indicated the coordination of nitrogen with the metals.

Table 1
Analytical data and yields of the complexes (calculated values are given in parentheses)

No.*	Complex	Yield %	Metal %	Carbon %	Hydrogen %	Nitrogen %
1.	[Cr(Ac) ₂ L] Cl	62	10.70 (10.72)	49.43 (49.45)	7.88 (7.85)	11.53 (11.55)
2	[Cr(Pr) ₂ L] Cl	65	10.12 (10.15)	51.40 (51.42)	7.83 (7.85)	(10.90) (10.92)
3	[Cr(Bu) ₂ L] Cl	70	9.59 (9.60)	53.17 (53.15)	8.55 (8.51)	(10.34) (10.30)
4	[Co(Ac) ₂ L] Cl	65	11.96 (11.98)	48.73 (48.75)	7.77 (7.75)	10.21 (10.25)
5	[Co(Pr) ₂ L] Cl	62	11.30 (11.31)	50.72 (50.70)	8.12 (8.14)	11.53 (11.50)
6	[Co(Bu) ₂ L] Cl	70	10.73 (10.75)	52.50 (52.55)	8.45 (8.40)	10.90 (10.92)

Ac = CH_3COO^- , Pr = $C_2H_5COO^-$, Bu = $C_3H_7COO^-$, L = $C_{16}H_{32}N_4$.

Table 2
Physical properties of the complexes

No.*	Colour	Melting point (°C)	Molar conductance $ohm^{-1} cm^2 mol^{-1}$	Effective Magnetic moment (BM)
1	Light green	280 (d)	118.32	3.97
2	Light green	290 (d)	226.44	4.12
3	Light green	295 (d)	202.98	4.02
4	Olive	225	124.44	0.18
5	Olive	235	098.94	0.24
6	Olive	195	113.22	0.48

d = decomposed.

*See Table 1 for complexes.

Table 3
Infrared absorption frequencies (cm^{-1}) (Banefild and Busch 1971)

No.*	ν (NH)	ν (C-O)	ν (C-N)	ν (C-O)	ν (M-N)	ν (M-O)
1.	3150s	1690 s	1650 s	1390 s	445 m	390 m
2	3140s	1680 s	1655 s	1385 m	430 m	395 w
3	3155s	1685 s	1660 s	1380 m	450 w	410 m
4	3135s	1685 s	1665 s	1390 s	460 m	415 w
5	3140s	1680 s	1650 s	1380 s	465 w	405 m
6	3150s	1680 s	1655 s	1385 m	450 m	398 w

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

* See Table 1 for complexes.

The complexes displayed ν (M-O) modes in the region 390-415 cm^{-1} suggesting metal oxygen coordination.

Magnetic moments. The observed values of effective magnetic moments of the complexes at room temperature are given in Table 2. The magnetic moment values of the Cr(III) complexes 3.97-4.12 BM were consistent with published values of six coordinated complexes (Islam *et al* 1993). Co(III) complexes were diamagnetic in nature which indicated the hexa coordination from valence bond theory.

Electronic spectra. The electronic spectral data of the complexes is shown in Table 4. The Cr(III) complexes gave two bands in the regions 17282-17730 cm^{-1} and 23060-23920 cm^{-1} corresponding to the transitions ${}^4A_{2g} \rightarrow {}^4A_{2g}$, ${}^4A_{2g} \rightarrow {}^4A_{1g}$ and (F) respectively (Hourse *et al* 1983; Hay and Tarafdar 1991). The Co(III) complexes also gave a single d-d band ${}^1A_{1g} \rightarrow {}^1A_{1g}$ in the region 16286 cm^{-1} - 17761 cm^{-1} (Hung *et al* 1977; Islam and Uddin 1993) with lower extinction coefficients characteristic of trans substitution.

From the above discussion a trans configuration is assignable to the prepared complexes. Thus suggested structure of the complexes is given in fig-1.

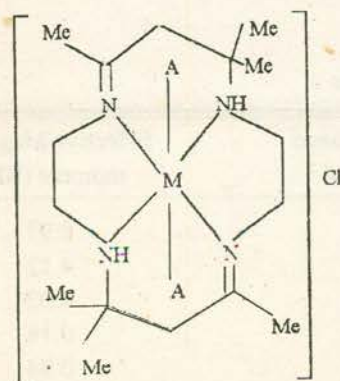


Fig 1. Probable structure of the complexes, M = Cr(III), Co(III), A = Oxygen of Acetic acid or Propionic acid or Butyric acid.

Table 4

Electronic spectral data of the complexes

No.*	Spectral band maxima (cm^{-1})
1	17730 (34), 23060 (47)
2	17282 (25), 23923 (40)
3	1750 (54), 23750 (45)
4	17761 (74)
5	17730 (34)
6	16286 (32)

* See Table 1 for complexes.

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