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RESEARCH ARTICLE

SYNTHESIS OF MACROCYCLIC COMPLEXES OF CHROMIUM (III), MANGANESE(II), IRON(III), COBALT(II), NICKEL(II) AND COPPER (II) CONTAINING A TETRA-OXA-OCTA-AZA-CYCLO TETRA-DECANE LIGAND

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ABSTRACT

14–membered macrocyclic complexes of Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) containing tetraoxo octa aza cyclo hexadecane ligand (L = $C_6H_{12}N_8O_4$) have been isolated by the template condensation of oxalo dihydrazide and formaldehyde in the presence of corresponding metal chloride and characterized by elemental analysis, UV–Visible spectroscopic studies, magnetic moments and conductance measurements. The complexes of the type $[M(C_6H_{12}N_8O_4)Cl_2]$ [Where M = Mn, Co, Ni and Cu] and $[M(C_6H_{12}N_8O_4)Cl_2]Cl$ [M=Cr and Fe] are all octahedral in nature.

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INTRODUCTION

Macrocyclic complexes containing nitrogen donor atoms/groups formed by the template condensation between aldehyde or ketone with amine or hydrazide in the presence of a metal ion have been reported (Jadhar, 1994; Ahmed *et al*., 1994; Goedke *et al*., 1973; Patra *et al*., 1991; Mohapatra, 1991 and Rout, 1991). Macrocyclic complexes of transition metals having both oxo and aza groups in a ligand are well known for the ligands having dioxotetraaza (Shourong, 1994; Christodoulou, 1990), tetraoxaoctaaza (Keyes *et al*., 1977), tetraoxotetraaza (Siddiqi, 1994) moieties. Macrocyclic complexes of transition metal(II) ions having oxo and aza groups shows some interesting properties and biological functions, such as being models for metalloproteins and oxygen carrier systems (Shourong, 1994). Macrocyclic complexes of Cr, Mn, Fe, Co, Ni, Cu having ligands, containing octaaza groups are not yet widely explored. Therefore, the present work reports the synthesis and characterization of some new 14–membered macrocyclic complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) having the ligand octaazacyclotetradecane formed by the template condensation of oxalodihydrazide and formaldehyde (2:2) in the presence of corresponding metal chloride.

MATERIALS AND METHODS

All the reagents were of AR grade and used as received from BDH England and Aldrich chemical company. The ligand precursor oxalodihydrazide was prepared by the literature procedure (Adeniyi *et al*., 1993 and Vogel, 1985).

Preparation of complexes of tetraoxoctazacyclo tetra-decane [M(L)Cl$_2$]Cl. M=Cr(III), Fe(III), and [M(L)Cl$_2$], M=Mn(II), Co(II), Ni(II) and Cu(II), complexes 1J6

The solution of oxalodihydrazide (Adeniyi, 1993) $C_2H_6N_4O_2$ (0.48 g, 4 m mol in 25 mL water) was added 37% aqueous solution of formaldehyde (0.33 g). To the above mixture, a solution of chromium trichloride hexahydrate $CrCl_3.6H_2O$ (0.53 g, 2–m mol in 25 mL water) was added and the resultant mixture refluxed for 3 h with constant stirring and then cooled. A light green precipitate (complex 1) was formed immediately. The precipitate was filtered, washed with water and dried in a vacuum desicator over fused $CaCl_2$, m.p. 125°C (decomposed), yield 0.56 g (65%). The same procedure was applied for the complexes 2–6, Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) respectively.

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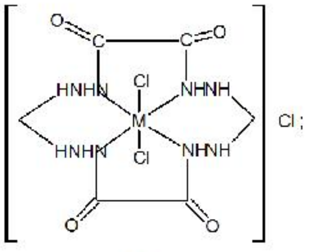
RESULTS AND DISCUSSION

The macrocyclic complexes 1–6 $[Cr(C_6H_{12}N_8O_4)Cl_2]Cl$; $[Mn(C_6H_{12}N_8O_4)Cl_2]$; $[Fe(C_6H_{12}N_8O_4)Cl_2]Cl$; $[Co(C_6H_{12}N_8O_4)Cl_2]$; $[Ni(C_6H_{12}N_8O_4)Cl_2]$;$[Cu(C_6H_{12}N_8O_4)Cl_2]$ were formed by the template condensation of oxalodihydrazide and formaldehyde (2:2) ratio in the presence of the corresponding metal chloride.

Table 1. Characterization data of complexes 1J6

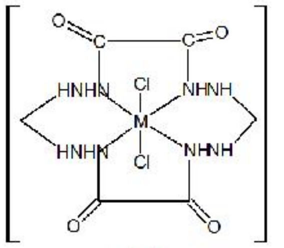
S. No.	Comp. (Colour)	Found (Calc. %				μ_{eff} (BM)	Molar conductance (ohm^{-1} cm^2 mol^{-1})
		M	C	H	N		
1.	$[Cr(C_6H_{12}N_8O_4)Cl_2]Cl$ (Olive Green)	12.31 (12.42)	17.10 (17.20)	2.70 (2.86)	26.63 (26.76)	3.60	35.30
2.	$[Mn(C_6H_{12}N_8O_4)Cl_2]$ (Off White)	14.11 (14.23)	18.50 (18.65)	3.0 (3.10)	28.90 (29.02)	5.72	6.08
3.	$[Fe(C_6H_{12}N_8O_4)Cl_2]Cl$ (Brown)	13.12 (13.22)	16.91 (17.04)	2.70 (2.84)	26.38 (26.51)	5.43	40.13
4.	$[Co(C_6H_{12}N_8O_4)Cl_2]$ (Light Brown)	15.0 (15.11)	18.30 (18.46)	2.91(3.07)	28.58(28.72)	4.70	3.08
5.	$[Ni(C_6H_{12}N_8O_4)Cl_2]$ (Yellowish Brown)	14.88 (15.06)	18.28 (18.47)	2.90 (3.07)	28.60 (28.73)	2.92	4.12
6.	$[Cu(C_6H_{12}N_8O_4)Cl_2]$ (Yellowish Brown)	16.0 (16.10)	18.10 (18.24)	2.90 (3.04)	28.14 (28.38)	2.10	1.00

In the macrocyclic complexes, four N atoms of the ligand octazacyclotetradecane, is coordinated to the metal. The complexes $[Cr(C_6H_{12}N_8O_4)Cl_2]Cl$; $[Mn(C_6H_{12}N_8O_4)Cl_2]$; $[Fe(C_6H_{12}N_8O_4)Cl_2]Cl$ are 1:1 electrolyte and complexes $[Mn(C_6H_{12}N_8O_4)Cl_2]$ and $[Co(C_6H_{12}N_8O_4)Cl_2]$; $[Ni(C_6H_{12}N_8O_4)Cl_2]$; $[Cu(C_6H_{12}N_8O_4)Cl_2]$ are non–electrolyte in nature. Elemental analyses (Table 1) of the complexes are consistent with the proposed formula and the suggested structures of the complexes are octahedral in nature (Structure I, II).



(I)

M = Cr(III), Fe(III)



(II)

M = Mn(II), Co(II), Ni(II), Cu(II)

The magnetic moment (Table 1) of Cr(III) compound is 3.60 B.M. corresponding to three unpaired electrons which is observed for nearly all known mononuclear Cr(III) complexes(17) irrespective of the strength of the ligand field. The observed magnetic moments for the compounds of Mn(II) and Fe(III) are 5.72 and 5.43 B.M. respectively, suggesting the high–spin d^5–configuration of octahedral symmetry. Magnetically, Mn(II) and Fe(III) compounds are high–spin in nearly all of their compounds, except those with strong ligands. The magnetic moment of compound $[Co(C_6H_{12}N_8O_4)Cl_2]$ is 4.70 B.M. corresponding to a Co(II) high–spin octahedral environment of three unpaired electrons. A little higher value than the spin only moment for the three unpaired electrons (3.89 B.M.) may be attributed to the orbital contribution which is generally observed for Co(II) compounds(13-17). Compounds $[Ni(C_6H_{12}N_8O_4)Cl_2]$; and $[Cu(C_6H_{12}N_8O_4)Cl_2]$ showed magnetic moment of 2.92 and 2.10 B.M. for the Ni(II) and Cu(II) complexes representing two and one unpaired electron respectively (Chanda *et al.*, 1993; Adams *et al.*, 1968; Adams, 1968; Hill, 1968; Alcock, 1988 and Cotton *et al.*, 1988). The UV–visible spectral bands of the compounds $[Cr(C_6H_{12}N_8O_4)Cl_2]Cl$; $[Mn(C_6H_{12}N_8O_4)Cl_2]$; $[Fe(C_6H_{12}N_8O_4)Cl_2]Cl$; $[Co(C_6H_{12}N_8O_4)Cl_2]$; $[Ni(C_6H_{12}N_8O_4)Cl_2]$; $[Cu(C_6H_{12}N_8O_4)Cl_2]$ for the d–d transitions indicated octahedral geometry(18). Compounds $[Cr(C_6H_{12}N_8O_4)Cl_2]Cl$; $[Mn(C_6H_{12}N_8O_4)Cl_2]$; $[Fe(C_6H_{12}N_8O_4)Cl_2]Cl$ display d–d bands at 576, 515 nm for $[Cr(C_6H_{12}N_8O_4)Cl_2]Cl$, at 600, 483 nm for $[Mn(C_6H_{12}N_8O_4)Cl_2]$ and at 545 nm for $[Fe(C_6H_{12}N_8O_4)Cl_2]Cl$ which are characteristic of an octahedral geometry for Cr(III), Mn(II) and Fe(III) respectively (Lever, 1984). Compounds $[Co(C_6H_{12}N_8O_4)Cl_2]$ and $[Ni(C_6H_{12}N_8O_4)Cl_2]$ showed bands at 686, 585 nm for Co(II) and at 544, 474 nm for Ni(II) complexes. These bands are assigned for the $^4T_{1g}$ (F)→ $^4A_{2g}$ (F), $^4T_{1g}$ (F)→ $^4A_{2g}$ (P) transition for Co(II) and $^4A_{2g}$ (F)→ $^4T_{1g}$ (F), $^4A_{2g}$ (F)→ $^4T_{1g}$ (P) for Ni(II) respectively, which are suggested for the octahedral Co(II) and Ni(II) complexes(19–24). For octahedral Co(II) and Ni(II) $^4T_{1g}$ (F)→ $^4T_{2g}$ (F) and $^4A_{2g}$ (F)→ $^4T_{2g}$ (F) transitions occur in the near IR region, which is seldom observed because it is in an inconvenient region(17) of the spectrum (1000–2000 nm). The copper compound showed a d–d transition at 523 nm for the $^2E_g \rightarrow {}^2T_{2g}$ for d^9–configuration of Cu(II) in an octahedral geometry.(10,25)

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