Template Synthesis and Structural Characterization of Homo Binuclear Chromium(III), Manganese(III), Iron(III), Cobalt(III), and Ruthenium(III) Complexes with Octaazamacrocyclic Ligands

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The Schiff base octaazamacrocyclic ligands derived from primary diamines and 3,6-dimethyl/diphenyl-4,5-diazaocta-3,5-diene-2,7-dione, and their binuclear complexes $[M_2LCl_4]Cl_2$ [M = Cr(III), Fe(III), Co(III), or Ru(III)] and $[Mn_2L(AcO)_4](AcO)_2$ were synthesized by template condensation reactions. Attempts to synthesize the corresponding metal-free macrocyclic ligands did not prove successful. The overall geometry and stereochemistry of these complexes were elucidated by elemental analyses, magnetic susceptibilities, electronic spectra, infrared spectra, molar conductance measurements, ^1H NMR, and thermogravimetric analysis. All the trivalent metal ion complexes appear to be 1:2 electrolytes. An octahedral geometry is proposed for all the complexes.

Key Words: Synthesis, chromium, manganese, iron, cobalt, ruthenium, macrocycles.

Introduction

Macrocyclic ligands are polydentate ligands with their donor atoms either incorporated into or attached to a cyclic backbone.[1,2] Macrocyclic ligands are considerably attractive in the quest for new chemistry, because they offer a wide variety of donor atoms, ionic charges, coordination numbers, and geometry of the resultant complexes.[3−7] The understanding of the metal ion chemistry of macrocyclic ligands has important implications for a range of chemical and biochemical applications. Many metal complexes of naturally occurring porphyrins, corrins, and phthalocyanines have been investigated because of their potential as dyestuffs or pigments.[8−10] The macrocyclic ligand complexes are involved in a number of fundamental biological and catalytic systems.[11,12]The importance of such complexes, for example, to the mechanism of photosynthesis,[13] to the transport of oxygen in mammalian and other respiratory systems, and to potency towards DNA binders with a high potential in anti-tumor therapy, has provided a motivation for investigation of the metal ion chemistry of these systems, as well as of cyclic ligand systems.[14,15]

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The design and synthesis of binucleating ligands and their metal complexes have been the subject of great interest.[16,17] Binucleating macrocyclic ligands with similar and dissimilar coordination sites have been reported, and the resulting bimetallic complexes often exhibit characteristic properties, such as magnetic exchange between the adjacent metal ions. These macrocyclic complexes are thermodynamically stabilized and kinetically retarded with regard to metal dissociation and metal substitution relative to metal complexes of acyclic ligands.[18,19] In this paper, we report the synthesis of octaazamacrocyclic complexes of the type $[M_2LCl_4]Cl_2$ [M = Cr(III), Fe(III), Co(III), or Ru(III)], and $[Mn_2L(AcO)_4](AcO)_2$ obtained by the template condensation reactions of 3,6-dimethyl/diphenyl-4,5-diazaocta-3,5-diene-2,7-dione (1) with primary diamines.
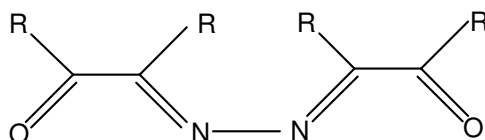
MDDD = 3,6–dimethyl–4,5–diazaocta–3,5–diene–2,7–dione (R = CH_3)
PDDD = 3,6–diphenyl–4,5–diazaocta–3,5–diene–2,7–dione (R = C_6H_5)

(1)

Experimental

Materials

The metal salts $CrCl_3\cdot6H_2O$, $FeCl_3\cdot6H_2O$, $CoCl_2\cdot6H_2O$, and $RuCl_3\cdot3H_2O$ (Merck) were commercially pure samples. The chemicals diacetyl, benzil, acetonitrile, hydrazine hydrate, ethylenediamine, propylenediamine, and o-phenylenediamine (Acros) were used as received. Methanol was distilled before use. $Mn(AcO)_3\cdot2H_2O$ was prepared[20] by the oxidation of $Mn(AcO)_2\cdot4H_2O$. The diketone 3,6-dimethyl/diphenyl-4,5-diazaocta-3,5-diene-2,7-dione was prepared by the method given by Stratton and Busch.[21] The elemental analyses were obtained from the microanalytical laboratory of CDRI, Lucknow, India. Metals and chlorides were measured volumetrically and gravimetrically.[22,23] Electronic spectra were recorded using dimethylformamide solutions in 1 cm cells with a Perkin-Elmer Lambda 15 UV/Vis spectrometer. IR spectra were scanned as a KBr pellet on a Perkin-Elmer PC-16F FTIR spectrometer in the 4000-350 cm^{-1} region. ^{1}H NMR spectra were obtained with a Bruker DRX 300 spectrometer using deuterated dimethylsulfoxide (DMSO-d_6) as the solvent and TMS as the internal reference. Magnetic susceptibility measurements were carried out at room temperature with a Gouy balance using $Hg[Co(SCN)_4]$ as the calibrant. The conductivity measurements were made using a Systronic conductivity meter with a dip-type cell, using approximately 10^{-3}M solution of the complexes in DMF. The thermogravimetric data were obtained in air at 10 °C min^{-1} in the 25-750 °C range using a Shimadzu TG-50 thermobalance.

Syntheses of the Complexes

Syntheses of tetra chloro/acetato (2,3,6,7,12,13,16,17-octamethyl/octaphenyl-1,4,5,8,11,14,15,18-octaazacycloeicosane-1,3,5,7,11,13,15,17-octaene)dimetal(III) di chloride/acetate.
$[M_2LCl_4]Cl_2$ [M = Cr(III), Fe(III), Co(III) or Ru(III)] and $[Mn_2L(AcO)_4](AcO)_2$:

To a hot solution of 3,6-dimethyl/diphenyl-4,5-diazaocta-3,5-diene-2,7-dione (0.02 mol, 0.3/0.4 g) in acetonitrile (25 cm^3) was added drop-wise a solution of CrCl$_3$·6H$_2$O (0.02 mol, 0.53 g), Mn(AcO)$_3$·2H$_2$O (0.02 mol, 0.53 g), FeCl$_3$·6H$_2$O (0.02 mol, 0.54 g), CoCl$_2$·6H$_2$O (0.02 mol, 0.47 g), or RuCl$_3$·3H$_2$O (0.02 mol, 0.52 g) in methanol (30 cm^3) with the help of a dropping funnel. The mixture was refluxed while stirring for 30 min and ethylenediamine (0.02 mol) was added slowly. In the CoCl$_2$·6H$_2$O reaction mixture, H$_2$O$_2$ (30%, 0.02 mol, 6 cm^3) was added. All reaction mixtures were refluxed and stirred for 12-14 h, which resulted in the formation of colored precipitate. The mixture was cooled in an ice bath and filtered. The precipitate was washed by stirring in hot CH$_3$CN (20 cm^3), then filtered and rewashed with diethyl ether, and dried in vacuo in a desiccator over anhydrous calcium chloride at room temperature.

Syntheses of tetra chloro/acetato (2,3,6,7,13,14,17,18-octamethyl/octaphenyl-1,4,5,8,12, 15,16,19-octaazacyclodecosane-1,3,5,7,12,14,16,18-octaene)dimetal(III) di chloride/acetate. **[M$_2$LCl$_4$]Cl$_2$ [M = Cr(III), Fe(III), Co(III) or Ru(III)] and [Mn$_2$L(AcO)$_4$](AcO)$_2$:**

These complexes were prepared by procedures similar to those discussed above, but using propylene-diamine.

Syntheses of tetra chloro/acetato (2,3,6,7,12,13,16,17-octamethyl/octaphenyl-1,4,5,8,11, 14,15,18-octaazacycloeicosane-1,3,5,7,11,13,15,17-octaene)dimetal(III) di chloride/acetate. **[M$_2$LCl$_4$]Cl$_2$ [M = Cr(III), Fe(III), Co(III) or Ru(III)] and [Mn$_2$L(AcO)$_4$](AcO)$_2$:**

These complexes were prepared by procedures similar to those discussed above, but using o-phenyle-nediamine.

Results and Discussion

A systematic study of the reactions of chromium(III) chloride, manganese(III) acetate, iron(III) chloride, and cobalt(III) chloride with octaazamacrocyclic ligands prepared by template synthesis was carried out. The reactions can be represented by the following equations:

2MCl$_3$ + L $\longrightarrow$ [M$_2$LCl$_4$]Cl$_2$

2Mn(AcO)$_3$+ L $\longrightarrow$ [Mn$_2$L(AcO)$_4$](AcO)$_2$
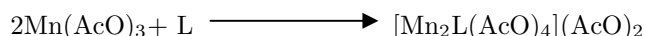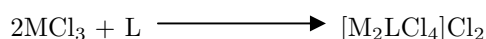
M = Cr(III), Fe(III), Co(III), or Ru(III)

L = MDE, MDP, MDOP, PDE, PDP or PDOP

MDE = Macrocyclic ligand derived from MDDD and ethylenediamine

MDP = Macrocyclic ligand derived from MDDD and propylenediamine

MDOP = Macrocyclic ligand derived from MDDD and o-phenylenediamine

PDE = Macrocyclic ligand derived from PDDD and ethylenediamine

PDP = Macrocyclic ligand derived from PDDD and propylenediamine

PDOP = Macrocyclic ligand derived from PDDD and o-phenylenediamine.

All the above reactions are quite facile and the resulting compounds were isolated in almost quantitative yields. The physical and analytical data of the ligands and complexes are given in Table 1. The complexes are mostly brown, green, or black. The solids are thermally stable, but decompose when heated. The complexes are soluble in chloroform, THF, DMF, DMSO, and nitrobenzene. The conductance measurements in DMF showed that the complexes are 1:2 electrolytes. The analytical results and molecular weights of the compounds (determined by the Rast Camphor method) support the formulations as shown in Table 1. The purity of the compounds was checked by TLC in silica gel-G using diethyl ether and tetrahydrofuran

as solvent. Each of the compounds moves as a single spot, indicating the presence of only one component, and hence their purity.

Magnetic moment

Magnetic susceptibility data for polycrystalline samples of chromium(III) macrocyclic complexes were collected at room temperature. All the complexes of chromium have a magnetic moment of 3.88-3.96 μ_B, smaller than the expected value (5.42 μ_B spin only) for a chromium(III) dinuclear species,[24] and are suggestive of a normal moment for octahedral stereochemistry. The magnetic moment of manganese(III) complexes is around 4.80-4.93 μ_B at room temperature, revealing the high spin nature[25] of the complexes having 4 unpaired electrons. The iron(III) complexes with magnetic moment values of 4.92-5.22 μ_B may attain dimeric structures in the solid state. In this pseudo octahedral geometry, the antiferromagnetic exchange interaction may be present between the 2 iron centers. Similar spin–spin exchange is shown by the binuclear iron(III) complexes reported earlier.[26] Cobalt(III) complexes show diamagnetic behavior, which indicates octahedral surroundings of the donor atoms around the metal ions producing a strong field.[27] The magnetic moment of ruthenium(III) complexes is in the range 1.82-2.13 μ_B. The values indicate the presence of one unpaired electron, confirming a (spin paired) low spin $t_{2g}^5(4d^5)$ configuration and a +3 oxidation state for ruthenium in all of the complexes.[28,29] This further indicates that the 2 ruthenium centers are independent.

Electronic Spectra

The electronic spectral bands of chromium(III), manganese(III), iron(III), cobalt(III), and ruthenium(III) complexes with macrocyclic ligands are summarized in Table 2. The electronic spectra of chromium(III) complexes show 3 absorption bands at 16,560–17,600(ν_1), 21,000–23,520(ν_2), and 30,800–32,630(ν_3) cm^{-1}, respectively. The 3 spin-allowed transitions for chromium(III) in an octahedral field are: $^4A_{2g} \rightarrow {}^4T_{2g}(F)(\nu_1)$, $^4A_{2g} \rightarrow {}^4T_{1g}(F)(\nu_2)$, and $^4A_{2g} \rightarrow {}^4T_{1g}(P)(\nu_3)$. The ν_2/ν_1 ratio is in the range of 0.70-1.36, which is close to the value of 1.38 obtained for pure octahedral chromium(III) complexes.[30−32] The manganese(III) complexes show bands at around 14,880-14,990, 16,830-16,985, and 18,350-18,860 cm^{-1} assigned to $^5B_{1g} \rightarrow {}^5A_{1g}$, $^5B_{1g} \rightarrow {}^5B_{2g}$ and $^5B_{1g} \rightarrow {}^5E_g$ transitions, respectively, suggesting spin–free manganese(III) complexes with octahedral geometry. The high energy bands in the regions 23,340-24,500 and 34,015-34,245 cm^{-1} may be assigned to the charge transfer and intraligand, respectively.[33] The electronic spectra of iron(III) complexes show several bands at 14,500-16,850, 19,360-20,100, and 25,200-26,900 cm^{-1}, which may be assigned to transitions $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$, and $^6A_{1g} \rightarrow {}^4A_{1g}$, ^4E_g. Although d–d transitions are forbidden in high-spin iron(III) complexes, the high intensity bands at 25,200-26,900 cm^{-1} may be ascribed to the borrowing of intensity from a low lying charge transfer ligand band.[34] The calculated values of 10 Dq, interelectronic repulsion parameters (B and C), and nephelauxetic ratios (β) for the iron(III) complexes are found to correspond well to earlier reports for high-spin octahedral stereochemistry around iron(III) ions. The magnetic moment and the ligand field parameters indicate that it is of the spin–free octahedral type. In all the macrocyclic cobalt(III) complexes, the electronic spectra show bands in the regions 6500-6590(ν_1), 16,500-17,100(ν_2), 20,000-23,000(ν_3), and 24,200-25,700(ν_4) cm^{-1}, which may be assigned to transitions, $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. Assignment of 2 higher energy bands is difficult

Table 1. The analytical, physical, and electrical conductivity data of the ligands and their complexes.

Compounds Empirical Formula	Molar Conductance $\Omega^{-1}mol^{-1}cm^2$	m/e	Colour	Yield %	Decomp. temp	Analyses Found (Calcd.)%					F.w.
						C	H	N	Cl	M	
MDDD $C_8H_{12}N_2O_2$	-	168	Yellow	60	39	57.0 (57.1)	7.2 (7.1)	16.3 (16.6)	-	-	168
PDDD $C_{26}H_{20}N_2O_2$	-	392	White	70	45	79.3 (79.5)	5.0 (5.1)	7.2 (7.1)	-	-	392
$[Cr_2(MDE)Cl_4]Cl_2$ $C_{20}H_{40}Cl_6Cr_2N_8$	180	638	Brown	55	230	33.6 (33.9)	5.5 (5.7)	15.6 (15.8)	29.8 (29.7)	14.5 (14.7)	709
$[Cr_2(MDP)Cl_4]Cl_2$ $C_{22}H_{44}Cl_6Cr_2N_8$	185	666	Green	55	228	35.6 (35.8)	6.2 (6.0)	15.0 (15.2)	28.6 (28.8)	14.3 (14.1)	737
$[Cr_2(MDOP)Cl_4]Cl_2$ $C_{28}H_{40}Cl_6Cr_2N_8$	220	734	Magenta	55	298	41.5 (41.7)	5.2 (5.0)	13.6 (13.9)	26.2 (26.4)	12.6 (12.9)	805
$[Cr_2(PDE)Cl_4]Cl_2$ $C_{60}H_{56}Cl_6Cr_2N_8$	210	1134	Brown	55	268	59.6 (59.7)	4.5 (4.6)	9.5 (9.5)	17.5 (17.6)	8.4 (8.6)	1205
$[Cr_2(PDP)Cl_4]Cl_2$ $C_{62}H_{60}Cl_6Cr_2N_8$	200	1162	Brown	55	253	60.0 (60.3)	4.6 (4.9)	9.2 (9.0)	17.0 (17.2)	8.1 (8.4)	1233
$[Cr_2(PDOP)Cl_4]Cl_2$ $C_{68}H_{56}Cl_6Cr_2N_8$	190	1235	Brown	55	246	62.6 (62.7)	4.4 (4.3)	8.8 (8.6)	16.2 (16.3)	7.8 (7.9)	1306
$[Mn_2(MDE)(AcO)_4](AcO)_2$ $C_{32}H_{58}Mn_2N_8O_{12}$	180	796	Brown	60	290	44.6 (44.8)	6.9 (6.8)	13.3 (13.0)	-	12.9 (12.8)	856
$[Mn_2(MDP)(AcO)_4](AcO)_2$ $C_{34}H_{62}Mn_2N_8O_{12}$	185	824	Brown	60	298	46.0 (46.1)	7.2 (7.0)	12.9 (12.6)	-	12.4 (12.4)	884
$[Mn_2(MDOP)(AcO)_4](AcO)_2$ $C_{40}H_{58}Mn_2N_8O_{12}$	201	892	Brown	60	268	50.2 (50.4)	6.0 (6.1)	11.5 (11.7)	-	11.4 (11.5)	952
$[Mn_2(PDE)(AcO)_4](AcO)_2$ $C_{72}H_{74}Mn_2N_8O_{12}$	210	1293	Brown	60	240	63.6 (63.9)	5.6 (5.5)	8.0 (8.2)	-	8.3 (8.1)	1353
$[Mn_2(PDP)(AcO)_4](AcO)_2$ $C_{74}H_{78}Mn_2N_8O_{12}$	220	1321	Brown	60	269	64.2 (64.3)	5.2 (5.6)	8.0 (8.1)	-	7.6 (7.9)	1381
$[Mn_2(PDOP)(AcO)_4](AcO)_2$ $C_{80}H_{74}Mn_2N_8O_{12}$	180	1389	Brown	60	269	66.3 (66.3)	5.0 (5.1)	7.5 (7.7)	-	7.4 (7.5)	1449
$[Fe_2(MDE)Cl_4]Cl_2$ $C_{20}H_{40}Cl_6Fe_2N_8$	190	646	Brown	55	248	33.2 (33.5)	5.5 (5.6)	15.6 (15.6)	29.5 (29.6)	15.3 (15.5)	717

Table 1. Continued.

Compounds Empirical Formula	Molar Conductance $\Omega^{-1}mol^{-1}cm^2$	m/e	Colour	Yield %	Decomp. temp	Analyses Found (Calcd.)%					F.w.
						C	H	N	Cl	M	
$[Fe_2(MDP)Cl_4]Cl_2$ $C_{28}H_{40}Cl_6Fe_2N_8$	195	674	Brown	55	259	35.2 (35.4)	5.8 (5.9)	15.3 (15.0)	28.2 (28.5)	14.6 (14.9)	745
$[Fe_2(MDOP)Cl_4]Cl_2$ $C_{28}H_{40}Cl_6Fe_2N_8$	198	742	Brown	55	298	41.1 (41.3)	4.6 (4.9)	13.5 (13.7)	26.3 (26.1)	13.4 (13.7)	813
$[Fe_2(PDE)Cl_4]Cl_2$ $C_{60}H_{56}Cl_6Fe_2N_8$	190	1142	Brown	55	255	59.0 (59.3)	4.4 (4.6)	9.3 (9.2)	17.5 (17.5)	9.2 (9.2)	1213
$[Fe_2(PDP)Cl_4]Cl_2$ $C_{62}H_{60}Cl_6Fe_2N_8$	180	1170	Brown	55	260	59.6 (59.9)	4.6 (4.8)	9.2 (9.0)	17.3 (17.1)	9.2 (9.0)	1241
$[Fe_2(PDOP)Cl_4]Cl_2$ $C_{68}H_{56}Cl_6Fe_2N_8$	210	1238	Brown	55	262	62.0 (62.3)	4.2 (4.3)	8.2 (8.5)	16.0 (16.2)	8.7 (8.5)	1309
$[Co_2(MDE)Cl_4]Cl_2$ $C_{20}H_{40}Cl_6Co_2N_8$	190	652	Brown	55	254	33.2 (33.2)	5.2 (5.5)	15.2 (15.4)	29.6 (29.4)	16.4 (16.3)	723
$[Co_2(MDP)Cl_4]Cl_2$ $C_{28}H_{40}Cl_6Co_2N_8$	200	680	Brown	55	213	35.0 (35.1)	5.8 (5.9)	14.7 (14.9)	28.1 (28.3)	15.4 (15.6)	751
$[Co_2(MDOP)Cl_4]Cl_2$ $C_{28}H_{40}Cl_6Co_2N_8$	210	748	Coffee	55	219	41.2 (41.0)	4.6 (4.9)	13.4 (13.6)	25.6 (25.9)	14.0 (14.3)	819
$[Co_2(PDE)Cl_4]Cl_2$ $C_{60}H_{56}Cl_6Co_2N_8$	205	1139	Brown	55	220	59.0 (59.0)	4.6 (4.6)	9.1 (9.1)	17.4 (17.4)	9.6 (9.6)	1210
$[Co_2(PDP)Cl_4]Cl_2$ $C_{62}H_{60}Cl_6Co_2N_8$	220	1176	Black	55	227	59.3 (59.6)	4.6 (4.8)	8.8 (8.9)	17.3 (17.0)	9.2 (9.4)	1247
$[Co_2(PDOP)Cl_4]Cl_2$ $C_{68}H_{56}Cl_6Co_2N_8$	190	1239	Black	55	226	62.0 (62.0)	4.2 (4.2)	8.5 (8.5)	16.1 (16.1)	8.9 (8.9)	1310
$[Ru_2(MDE)Cl_4]Cl_2$ $C_{20}H_{40}Cl_6Ru_2N_8$	195	734	Brown	50	289	29.5 (29.7)	5.2 (5.0)	13.8 (13.9)	26.2 (26.3)	25.0 (25.2)	805
$[Ru_2(MDP)Cl_4]Cl_2$ $C_{22}H_{44}Cl_6Ru_2N_8$	200	762	Brown	52	300	31.5 (31.6)	5.3 (5.3)	13.2 (13.4)	25.0 (25.1)	24.6 (24.4)	833
$[Ru_2(MDOP)Cl_4]Cl_2$ $C_{28}H_{40}Cl_6Ru_2N_8$	205	832	Black	58	315	37.1 (37.2)	4.5 (4.4)	12.2 (12.4)	23.3 (23.2)	22.5 (22.6)	901
$[Ru_2(PDE)Cl_4]Cl_2$ $C_{60}H_{56}Cl_6Ru_2N_8$	210	1231	Brown	50	345	55.4 (55.3)	4.1 (4.3)	8.8 (8.6)	16.2 (16.1)	15.7 (15.6)	1302
$[Ru_2(PDP)Cl_4]Cl_2$ $C_{62}H_{60}Cl_6Ru_2N_8$	220	1259	Black	51	322	55.7 (55.9)	4.6 (4.5)	8.3 (8.4)	15.5 (15.7)	15.0 (15.3)	1330
$[Ru_2(PDOP)Cl_4]Cl_2$ $C_{68}H_{56}C_6Ru_2N_8$	190	1327	Black	54	352	58.2 (58.3)	4.1 (4.0)	8.2 (8.0)	15.1 (15.0)	14.6 (14.5)	1398

due to the overlap of intraligand and charge transfer bands in this region of the spectrum, but ν_2 is more difficult to assign because this weak-spin forbidden band is often at the onset of the higher energy, more intense bands.[35] In most of the ruthenium(III) complexes, the UV-Vis spectra show only charge transfer bands. In a d^5 system, ruthenium(III), which is a relatively strong oxidizing agent, charges transfer bands of the type $L\pi y \rightarrow t_{2g}$ are prominent in the low energy region and obscure the weaker bands due to d-d transition.[36] The binuclear ruthenium(III) complexes show 3 bands in the region 14,400-14,910, 17,600-18,110, and 22,830-23,010 cm^{-1}, which may be assigned to $^2T_{2g} \rightarrow ^4T_{1g}$, $^2T_{2g} \rightarrow ^4T_{2g}$ and $^2T_{2g} \rightarrow ^2A_{2g}$, $^2T_{1g}$ transitions with charge transfer bands, respectively. The electronic spectra of these complexes are further rationalized in terms of different ligand field parameters. The ligand field parameters are comparable with those reported for other ruthenium(III) derivatives involving nitrogen donor molecules.

Table 2. Magnetic moments and electronic spectral bands of macrocyclic complexes.

Complexes	μ_B	Bands Observed ^{a} (cm^{-1})	Assignments	ν_2/ν_1	Dq	B	C	β
[Cr$_2$(MDE)Cl$_4$]Cl$_2$	3.88	16,560 23,520 30,800	$^4A_{2g} \rightarrow ^4T_{2g}$(F) $^4A_{2g} \rightarrow ^4T_{1g}$(F) $^4A_{2g} \rightarrow ^4T_{1g}$(P)	0.70	1656	617	2703	0.67
[Cr$_2$(MDP)Cl$_4$]Cl$_2$	3.92	17,600 21,000 32,630	-do-	0.83	1760	718	2873	0.78
[Cr$_2$(MDOP)Cl$_4$]Cl$_2$	3.96	16,896 22,165 31,568	-do-	0.76	1689	689	2757	0.75
[Cr$_2$(PDE)Cl$_4$]Cl$_2$	3.93	16,798 22,864 31,894	-do-	1.36	1679	685	2741	0.74
[Cr$_2$(PDP)Cl$_4$]Cl$_2$	3.89	17,000 22,980 32,200	-do-	1.35	1700	693	2775	0.75
[Cr$_2$(PDOP)Cl$_4$]Cl$_2$	3.88	17,450 21,860 31,560	-do-	1.25	1745	712	2848	0.76
[Mn$_2$(MDE)(AcO)$_4$](AcO)$_2$	4.88	14,880 16,840 18,600	$^5B_{1g} \rightarrow ^5A_{1g}$ $^5B_{1g} \rightarrow ^5B_{2g}$ $^5B_{1g} \rightarrow ^5E_g$	1.13	1488	607	2428	0.62
[Mn$_2$(MDP)(AcO)$_4$](AcO)$_2$	4.80	14,960 16,830 18,860	-do-	1.12	1496	610	2442	0.63
[Mn$_2$(MDOP)(AcO)$_4$](AcO)$_2$	4.90	14,890 16,985 18,350	-do-	1.14	1489	607	2431	0.63
[Mn$_2$(PDE)(AcO)$_4$](AcO)$_2$	4.82	14,990 16,900 18,550	-do-	1.12	1499	611	2447	0.63
[Mn$_2$(PDP)(AcO)$_4$](AcO)$_2$	4.86	14,920 16,935 18,800	-do-	1.13	1492	608	2435	0.63
[Mn$_2$(PDOP)(AcO)$_4$](AcO)$_2$	4.93	14,980 16,880 18,400	-do-	1.13	1498	611	2445	0.63
[Fe$_2$(MDE)Cl$_4$]Cl$_2$	4.92	14,500 20,100 25,200	$^6A_{1g} \rightarrow ^4T_{1g}$ $^6A_{1g} \rightarrow ^4T_{2g}$ $^6A_{1g} \rightarrow ^4T_{1g}$, ^4E_g	1.39	664	604	2416	0.60

Table 2. Continued.

Complexes	μ_B	Bands Observed [a] (cm^{-1})	Assignments	ν_2/ν_1	Dq	B	C	β
[Fe$_2$(MDP)Cl$_4$]Cl$_2$	4.98	15,560 20,100 25,860	-do-	1.29	713	648	2592	0.63
[Fe$_2$(MDOP)Cl$_4$]Cl$_2$	5.20	16,750 19,860 26,900	-do-	1.19	767	697	2788	0.69
[Fe$_2$(PDE)Cl$_4$]Cl$_2$	5.22	15,555 19,800 26,500	-do-	1.27	712	648	2592	0.64
[Fe$_2$(PDP)Cl$_4$]Cl$_2$	5.10	15,890 19,900 26,468	-do-	1.25	662	728	2912	0.71
[Fe$_2$(PDOP)Cl$_4$]Cl$_2$	5.02	15,890 20,000 25,700	-do-	1.26	728	662	2648	0.65
[Co$_2$(MDE)Cl$_4$]Cl$_2$	Dia.	6500 16,500 20,000 25,600	$^1A_{1g} \rightarrow {}^3T_{1g}$ $^1A_{1g} \rightarrow {}^3T_{2g}$ $^1A_{1g} \rightarrow {}^1T_{1g}$ $^1A_{1g} \rightarrow {}^1T_{2g}$	1.2	2105	526	3157	0.49
[Co$_2$(MDP)Cl$_4$]Cl$_2$	Dia.	6585 16,600 21,450 24,700	-do-	1.20	2257	564	3386	0.53
[Co$_2$(MDOP)Cl$_4$]Cl$_2$	Dia.	6585 16,600 21,450 24,600	-do-	1.29	2257	564	3384	0.53
[Co$_2$(PDE)Cl$_4$]Cl$_2$	Dia.	6580 16,900 21,420 25,700	-do-	1.27	2254	563	3382	0.53
[Co$_2$(PDP)Cl$_4$]Cl$_2$	Dia.	6590 17,000 22,450 24,200	-do-	1.32	2263	590	3544	0.55
[Co$_2$(PDOP)Cl$_4$]Cl$_2$	Dia.	6555 16,550 23,000 24,250	-do-	1.39	2421	605	3631	0.57
[Ru$_2$(MDE)Cl$_4$]Cl$_2$	1.85	14,400 17,650 22,850	$^2T_{2g} \rightarrow {}^4T_{1g}$ $^2T_{2g} \rightarrow {}^4T_{2g}$ $^2T_{2g} \rightarrow {}^2A_{2g},\ {}^2T_{1g}$	1.23	2607	406	2410	0.65
[Ru$_2$(MDP)Cl$_4$]Cl$_2$	2.13	14,910 17,600 23,010	-do-	1.18	2604	336	2363	0.53
[Ru$_2$(MDOP)Cl$_4$]Cl$_2$	1.82	14,850 18,110 22,830	-do-	1.22	2589	407	2252	0.65
[Ru$_2$(PDE)Cl$_4$]Cl$_2$	1.96	14,600 18,000 22,900	-do-	1.23	2609	425	2341	0.68
[Ru$_2$(PDP)Cl$_4$]Cl$_2$	2.11	14,840 17,980 23,000	-do-	1.21	2611	392	2327	0.62
[Ru$_2$(PDOP)Cl$_4$]Cl$_2$	2.10	14,450 17,600 22,910	-do-	1.22	2612	393	2426	0.63

[a] in DMF

Infrared Spectra

Infrared spectra were obtained for binuclear macrocyclic chromium(III), manganese(III), iron(III), cobalt(III), and ruthenium(III) complexes. Salient features of the infrared spectra of these complexes are summarized in Table 3. The characteristic IR bands for the ligand MDDD and PDDD, when compared with those of its complexes, provide meaningful information regarding the bonding sites of the ligand molecule.[37,38] All the complexes have a characteristic, single sharp absorption band in the 1580-1630 cm^{-1} region, which is attributed to the coordinated ν(C=N) moiety.[39,40] Characteristic bands that free carbonyl or free amine were not observed. The above information strongly suggests that the proposed ligand is formed. The complexes gave bands at 2055–2080 cm^{-1} arising from the ν_{asym}(N-N) mode of the coordinated azine. Bands appearing in the regions 2870-2930 and 1410-1450 cm^{-1} in all the complexes may be due to ν(C-H) and δ(C-H), respectively. The range observed may be indicative of different stereoisomers and/or specific hydrogen

Table 3. Selected IR bands (cm^{-1}) of ligands and their macrocyclic complexes.

Compounds	ν(C=N)	ν_{asym}(N-N)	ν(C-H)	δ(C-H)	ν(M-N)	ν(M-Cl)
MDDD	1650s	2010s	2850s	1470w	-	-
PDDD	1670s	2015s	2855s	1468w	-	-
[Cr$_2$(MDE)Cl$_4$]Cl$_2$	1580s	2055s	2870m	1410m	450m	350m
[Cr$_2$(MDP)Cl$_4$]Cl$_2$	1582s	2060s	2877m	1415m	445m	350w
[Cr$_2$(MDOP)Cl$_4$]Cl$_2$	1590s	2055s	2890m	1417m	445m	355w
[Cr$_2$(PDE)Cl$_4$]Cl$_2$	1580s	2060s	2888m	1416m	430m	350w
[Cr$_2$(PDP)Cl$_4$]Cl$_2$	1585s	2060s	2880m	1420m	430m	352w
[Cr$_2$(PDOP)Cl$_4$]Cl$_2$	1580s	2055m	2876m	1412m	425m	356w
[Mn$_2$(MDE)(AcO)$_4$](AcO)$_2$	1600s	2065m	2905m	1430m	430m	355w
[Mn$_2$(MDP)(AcO)$_4$](AcO)$_2$	1605s	2065m	2915m	1440m	440s	356w
[Mn$_2$(MDOP)(AcO)$_4$](AcO)$_2$	1615s	2070m	2910w	1435w	435m	358w
[Mn$_2$(PDE)(AcO)$_4$](AcO)$_2$	1600s	2065m	2912w	1438w	425s	350w
[Mn$_2$(PDP)(AcO)$_4$](AcO)$_2$	1608m	2065s	2908w	1436w	430m	359w
[Mn$_2$(PDOP)(AcO)$_4$](AcO)$_2$	1612m	2070s	2915w	1440w	420s	356m
[Fe$_2$(MDE)Cl$_4$]Cl$_2$	1590s	2070s	2890m	1420w	410m	370m
[Fe$_2$(MDP)Cl$_4$]Cl$_2$	1596s	2060s	2892s	1430w	415w	370m
[Fe$_2$(MDOP)Cl$_4$]Cl$_2$	1592s	2060s	2895m	1425w	425m	360w
[Fe$_2$(PDE)Cl$_4$]Cl$_2$	1590s	2065s	2900w	1430m	430m	365w
[Fe$_2$(PDP)Cl$_4$]Cl$_2$	1595s	2060s	2890w	1426w	450w	365w
[Fe$_2$(PDOP)Cl$_4$]Cl$_2$	1598s	2063s	2895s	1422m	425w	365w
[Co$_2$(MDE)Cl$_4$]Cl$_2$	1615s	2070s	2916s	1440w	440w	370w
[Co$_2$(MDP)Cl$_4$]Cl$_2$	1630s	2075s	2920s	1450s	460m	370w
[Co$_2$(MDOP)Cl$_4$]Cl$_2$	1625s	2080s	2925m	1445s	445m	370m
[Co$_2$(PDE)Cl$_4$]Cl$_2$	1628s	2075s	2930m	1445m	435m	365m
[Co$_2$(PDP)Cl$_4$]Cl$_2$	1618s	2077s	2920m	1448m	460m	370m
[Co$_2$(PDOP)Cl$_4$]Cl$_2$	1630s	2080s	2925m	1447m	430s	370m
[Ru$_2$(MDE)Cl$_4$]Cl$_2$	1590s	2070s	2890m	1420w	460m	370m
[Ru$_2$(MDP)Cl$_4$]Cl$_2$	1596s	2060s	2892s	1430w	455w	370m
[Ru$_2$(MDOP)Cl$_4$]Cl$_2$	1592s	2055s	2885m	1425w	455m	365w
[Ru$_2$(PDE)Cl$_4$]Cl$_2$	1590s	2075s	2910w	1430m	445m	366w
[Ru$_2$(PDP)Cl$_4$]Cl$_2$	1595s	2060s	2880w	1426w	460w	365w
[Ru$_2$(PDOP)Cl$_4$]Cl$_2$	1598s	2055s	2895s	1422m	450w	360w

bonding interactions. The presence of M–N bonds is shown by the appearance of M–N stretching vibrations at 410-460 cm^{-1}. Bands appearing in the range 350-370 cm^{-1} are attributable to ν(M-Cl) vibrations[41].

Proton Magnetic Resonance Spectra

The proton magnetic resonance spectra of the ligands and their cobalt(III) complexes were recorded in a DMSO-d$_6$ solution. Comparing the spectra of the ligands and their complexes the following conclusions can be derived:

(a) The complexes do not show any signal attributable to amino protons, suggesting that the proposed macrocyclic skeleton has been formed by the condensation reactions.

(b) The complexes derived from 3,6–dimethyl–4,5–diazaocta–3,5–diene–2,7–dione moiety show a singlet in the δ2.21–2.39 ppm range due to the methyl protons (C–CH$_3$, 24H), whereas the complexes derived from 3,6–diphenyl–4,5-diazaocta–3,5–diene–2,7–dione moiety show a singlet peak at δ7.22–8.20 ppm range due to the phenyl (C–C$_6$H$_5$, 40H).

(c) In addition, the complexes show a singlet at the δ3.08-3.14 ppm region and multiplet at the δ3.12-3.14 ppm region, corresponding to methylene protons adjacent to the nitrogen (N-CH$_2$, 8H) derived from ethylenediamine and propylenediamine, respectively, whereas the middle methylene protons (C-CH$_2$-C, 4H) of the propylenediamine chain of the complexes show a multiplet in the region δ2.08-2.16 ppm.

Thermal Studies

Complexes are stable up to 200 °C, indicating the absence of any water molecules. The presence of chloride ions outside and inside the coordination sphere is confirmed by dynamic TGA studies. Complexes register a weight loss of 3.3% at 261 °C compared with the theoretical value of 3.54%, which corresponds to the loss of a half molecule of chlorine. A small exothermic peak at 390 °C in the DTA corroborated the formation of the transient intermediate as it is immediately transformed into subsequent product in TG. We tried to isolate the intermediates formed at 392 and 428 °C with the temperature arrest technique, but were unsuccessful. After 430 °C the complex starts to decompose and mass loss of 38% at 441 °C corresponds to the loss of one ligand. The total mass loss up to 552 °C is found to be 90.3%, which shows the formation of metal oxides. The high mass residue ($\sim$8%) is attributed to carbonaceous matter. Thus, the decomposition pattern obtained from the TGA curve confirms the proposed formulation of the complexes.

Thus, the spectral studies and thermogravimetric analysis suggest structure (2) for the complexes.
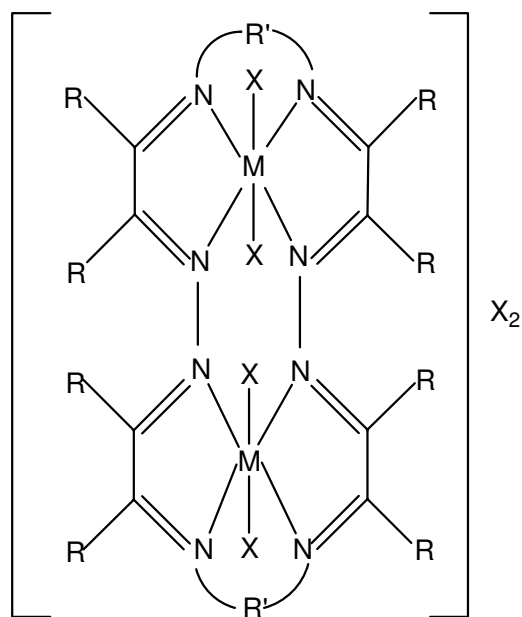
M = Cr(III), Mn(III), Fe(III), Co(III), or Ru(III)
R = CH_3 or C_6H_5; R' = $(CH_2)_2$, $(CH_2)_3$, or o-C_6H_4
X = Cl or AcO

(2)

Conclusion

The present study utilized octaazamacrocyclic binuclear chromium(III), manganese(III), iron(III), cobalt(III), and ruthenium(III) complexes formed by template synthesis. The structure of $[M_2LCl_4]Cl_2$ and $[Mn_2L(AcO)_4](AcO)_2$ revealed that the nitrogen donor sets of 2 ligand fragments form a distorted octahedral configuration of metal ions. A particular feature of this series of complexes is that the electronic properties of the central metal may be tuned by introducing different diamines into the ligand framework. Emphasis was given in this work to electronic and structural effects arising from the incorporation of a diamine group between the azine chelate.

Acknowledgment

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