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A NEW SYNTHETIC ROUTE FOR THE PREPARATION OF A NEW SERIES OF 14–22-MEMBERED TETRAOXOMACROCYCLIC TETRAAMINES AND THEIR TRANSITION METAL COMPLEXES

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Abstract—The condensation of aliphatic diamines $H_2N(CH_2)_nNH_2$ ($n = 2$–3) with dicarboxylic acids in the presence of DCC (dicyclohexylcarbodiimide) and DMAP [4-(dimethylamino)pyridine] gave new types of 14–22-membered tetraamide macrocyclic ligands L_1–L_{10} which were characterized by element analysis and mass, IR and ^1H NMR spectroscopic techniques. The complexes of these macrocylic moieties with some transition metal ions have also been synthesized. The mode of bonding and overall geometry of these complexes has been inferred through UV–vis, IR, ^1H NMR and ESR spectral techniques as well as molar conductance and magnetic moment data. An octahedral geometry around the metal ion is suggested for $[ML_1Cl_2]$–$[ML_{10}Cl_2]$, where M = Mn^{II}, Fe^{II} and Co^{II}, while a square planar, a distorted tetrahedral and a tetrahedral geometry is proposed for $[ML_1]Cl_2$–$[ML_{10}]Cl_2$ for M = Ni^{II}, Cu^{II} and Zn^{II}, respectively. Bonding parameters have been derived from the ESR hyperfine structure of copper and cobalt complexes.

Macrocylic compounds containing nitrogen and other heteroatoms as ring components have usually been prepared by use of either the metal template reaction or the high dilution technique. Recent studies[1] have established that DCC (dicyclohexylcarbodiimide) and DMAP [4-(dimethylamino)pyridine] can act as good condensing reagents for the condensation of primary amines and carboxylic acids. However, there is no report of the preparation of polyoxopolyaza macrocycles obtained from dicarboxylic acids and primary diamines. In this communication we report a new efficient route for the preparation of a new series of 14–22-membered tetraoxomacrocyclic tetraamines utilizing DCC and DMAP as the condensing reagents and their complexes.

An amide group offers two potential binding atoms, the oxygen and nitrogen, for complexation of metal ions. A number of complexes have been reported with amide group ligands which exhibit diverse coordinating behaviour with different metal ions.[2,3] The amide macrocyclic ligands are of particular interest in view of the application of their metal complexes in catalysing organic oxidation reactions[4,5] similar to the porphyrin analogues. A number of macrocyclic amides containing oxygen or sulphur atoms as ring components through cyclization via amonolysis of the dimethyl ester of α, ω-dicarboxylic acid with polyethylenepolyamines have been reported.[6] Generally, the macrocyclic polyamide ligand is prepared[6–8] by the reaction of polyamine with either the diester salt of a dicarboxylic acid or the dicarboxylic acid dichloride. As in our programme for the development of polyaza and mixed polyaza macrocycles, we have recently reported[9–13] the transition metal complexes of various macrocycles.

RESULTS AND DISCUSSION

A new series of tetraamide macrocyclic ligands, L_1–L_{10}, have been prepared by the condensation

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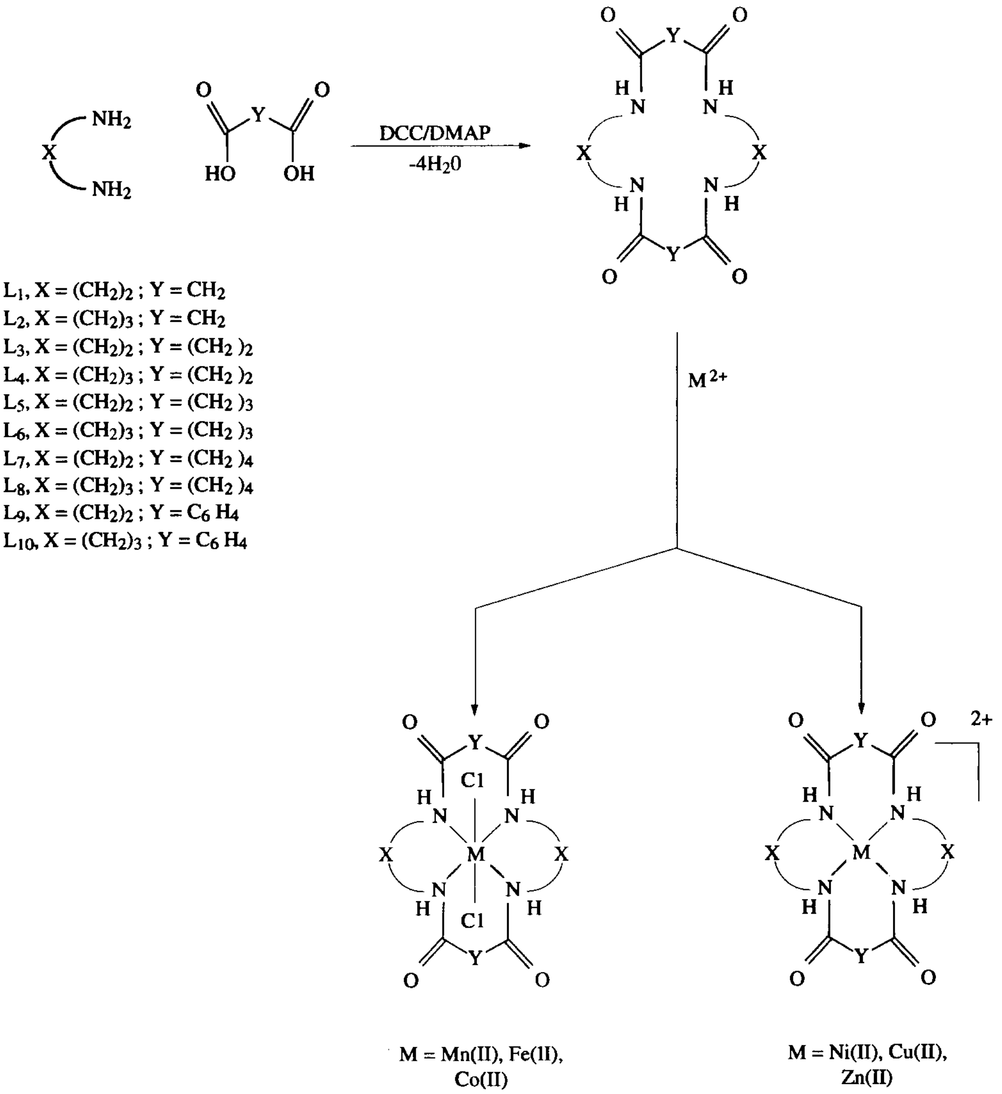
reaction of dicarboxylic acids with primary diamines using the condensing reagents DCC and DMAP, as shown in Scheme 1. The colour and crystalline habits of all these ligands show that they belong to the same class of compounds. However, an attempt to synthesize these macrocyclic ligands without the use of DCC and DMAP failed. In addition, the ligand corresponding to *o*-phenylenediamine could not be formed. Thus, the reaction seems to be the basis for new possibilities for the synthesis of macrocycles in the absence of any template or high dilution technique. The complexation behaviour of these macrocyclic ligands with transition metal ions has also been studied. All the ligands are freely soluble in H_2O, DMSO and THF and insoluble in benzene, dichloromethane, dioxane, chloroform and alcohol. However, we could not isolate any single crystal suitable for X-ray crystallographic studies.



Scheme 1.

The results of elemental analysis and molecular ion peaks in the mass spectra (Table 1) support the proposed macrocyclic framework. All mass spectra of the ligands showed molecular ion peaks for the 2:2 reaction product with no peaks above them. The molar conductivity values for all the complexes except nickel, copper and zinc in DMSO solutions suggest them to be non-electrolytes, while those of nickel, copper and zinc complexes suggest their 1 : 2 electrolytic nature.[14]

The IR spectra of the macrocyclic ligands (Table 2) show the absence of uncondensed functional groups (NH_2, OH), stretching modes of starting

Table 1. Melting point, yield, colour, elemental analysis and molar conductance values of the compounds

Compound	Melting point (°C)	Yield (%)	Colour	Found (calc.) (%)					m/z	Molar conductance (mol^{-1} cm^2 ohm^{-1})
				M	Cl	C	H	N		
L_1	198	40	Chalky white	—	—	46.7	6.2	21.8	257	—
						(46.8)	(6.3)	(21.8)		
L_2	210	36	Chalky white	—	—	50.8	7.0	19.5	283	—
						(50.7)	(7.0)	(19.7)		
L_3	218	29	Chalky white	—	—	50.5	7.6	19.1	285	—
						(50.7)	(7.0)	(19.7)		
L_4	205	35	Chalky white	—	—	53.8	7.6	17.8	311	—
						(53.8)	(7.7)	(17.9)		
L_5	228	42	Chalky white	—	—	53.8	7.6	17.6	311	—
						(53.8)	(7.7)	(17.9)		
L_6	235	42	Chalky white	—	—	56.6	8.2	16.5	339	—
						(56.4)	(8.3)	(16.4)		
L_7	118	38	Chalky white	—	—	56.5	8.2	16.3	341	—
						(56.4)	(8.3)	(16.4)		
L_8	232	41	Chalky white	—	—	58.6	8.6	15.2	369	—
						(58.3)	(8.6)	(15.3)		
L_9	211	45	Chalky white	—	—	63.1	5.2	14.7	370	—
						(63.7)	(5.3)	(14.5)		
L_{10}	198	43	Chalky white	—	—	64.7	5.8	13.7	409	—
						(64.5)	(5.8)	(13.6)		
$[FeL_1Cl_2]$	185	34	Red	14.6	18.4	31.1	4.5	14.2	—	15
				(14.5)	(18.4)	(31.1)	(4.2)	(14.6)		
$[NiL_1]Cl_2$	211	27	Light yellow	15.3	18.6	31.4	4.1	14.2	—	110
				(15.2)	(18.5)	(31.3)	(4.2)	(14.3)		
$[CuL_1]Cl_2$	188	42	Light green	16.3	18.4	30.6	4.3	14.2	—	121
				(16.1)	(18.2)	(30.5)	(4.1)	(14.3)		
$[ZnL_1]Cl_2$	143	22	White	16.8	18.0	30.4	4.2	14.3	—	117
				(16.6)	(18.2)	(30.2)	(4.1)	(14.5)		
$[FeL_2Cl_2]$	160	32	Red	13.8	17.0	34.8	4.8	13.5	—	17
				(13.6)	(17.3)	(35.0)	(4.8)	(13.6)		
$[NiL_2]Cl_2$	193	33	Light yellow	14.1	17.5	34.2	4.7	13.6	—	105
				(14.3)	(17.3)	(34.4)	(4.8)	(13.4)		
$[CuL_2]Cl_2$	168	37	Light green	15.0	17.3	34.4	4.7	13.3	—	126
				(15.2)	(17.0)	(34.2)	(4.6)	(13.0)		
$[ZnL_2]Cl_2$	158	33	White	15.1	16.9	34.0	4.9	13.4	—	115
				(15.3)	(16.6)	(33.9)	(4.7)	(13.3)		
$[MnL_3Cl_2]$	191	35	Light pink	13.6	17.3	35.4	5.0	13.5	—	17
				(13.4)	(17.3)	(35.1)	(4.9)	(13.6)		
$[FeL_3Cl_2]$	165	38	Red	13.0	17.5	34.8	4.8	13.3	—	19
				(13.6)	(17.3)	(35.0)	(4.8)	(13.6)		
$[NiL_3]Cl_2$	198	44	Light yellow	14.3	17.2	35.1	4.7	13.4	—	95
				(14.1)	(17.3)	(34.9)	(4.8)	(13.5)		
$[CuL_3]Cl_2$	176	31	Light green	15.3	17.1	34.6	4.5	13.5	—	130
				(15.0)	(16.9)	(34.5)	(4.7)	(13.3)		
$[ZnL_3]Cl_2$	137	44	White	15.6	16.7	34.4	4.6	13.3	—	119
				(15.5)	(16.9)	(34.5)	(4.7)	(13.4)		
$[MnL_4Cl_2]$	164	30	Light pink	13.2	17.5	34.8	4.8	13.3	—	16
				(13.4)	(17.3)	(35.1)	(4.9)	(13.6)		
$[FeL_4Cl_2]$	161	31	Reddish brown	12.6	16.0	35.5	5.5	12.5	—	17
				(12.7)	(16.2)	(35.6)	(5.5)	(12.9)		
$[NiL_4]Cl_2$	215	22	Light yellow	13.4	16.5	38.3	5.4	12.5	—	99
				(13.3)	(16.2)	(38.1)	(5.3)	(12.5)		
$[CuL_4]Cl_2$	185	28	Light green	14.1	15.7	37.0	5.4	12.7	—	119
				(14.3)	(15.9)	(36.7)	(5.3)	(12.5)		

Table 1. Continued

Compound	Melting point (°C)	Yield (%)	Colour	Found (calc.) (%)					*m/z*	Molar conductance (mol^{-1} cm^2 ohm^{-1})
				M	Cl	C	H	N		
$[ZnL_4]Cl_2$	166	37	White	14.6	15.5	36.8	5.7	12.9	—	122
				(14.8)	(15.9)	(36.6)	(5.3)	(12.6)		
$[FeL_5Cl_2]$	155	28	Reddish brown	12.5	16.3	35.6	5.5	12.5	—	22
				(12.7)	(16.2)	(35.5)	(5.5)	(12.7)		
$[CoL_5Cl_2]$	177	38	Reddish brown	13.1	15.5	38.4	5.3	13.0	—	15
				(12.8)	(15.8)	(38.1)	(5.4)	(12.8)		
$[CuL_5]Cl_2$	169	25	Light green	13.9	16.0	36.5	5.5	12.5	—	115
				(14.2)	(15.8)	(36.7)	(5.4)	(12.6)		
$[FeL_6Cl_2]$	168	31	Reddish brown	11.8	15.3	40.8	6.1	11.5	—	19
				(12.0)	(15.2)	(41.1)	(6.0)	(12.0)		
$[CoL_6Cl_2]$	191	40	Reddish brown	12.8	15.4	41.2	5.5	11.9	—	18
				(12.6)	(15.3)	(41.0)	(5.6)	(11.5)		
$[CuL_6]Cl_2$	188	39	Light green	14.2	14.1	40.8	5.6	11.4	—	113
				(13.9)	(14.5)	(40.4)	(5.8)	(11.8)		
$[FeL_7Cl_2]$	158	27	Red	11.8	15.2	40.9	6.0	12.5	—	16
				(12.0)	(15.2)	(41.1)	(6.0)	(12.0)		
$[CoL_7Cl_2]$	163	31	Reddish brown	12.5	15.1	41.4	5.4	11.6	—	23
				(12.6)	(15.3)	(41.0)	(5.6)	(11.5)		
$[CuL_7]Cl_2$	191	48	Light green	14.1	14.2	40.1	5.9	12.0	—	117
				(13.9)	(14.5)	(40.4)	(5.8)	(11.8)		
$[FeL_8Cl_2]$	171	33	Red	11.0	14.5	43.5	6.6	11.7	—	17
				(11.3)	(14.3)	(43.6)	(6.5)	(11.3)		
$[CoL_8Cl_2]$	156	37	Reddish brown	11.8	14.1	42.9	6.5	11.3	—	17
				(11.8)	(14.2)	(43.4)	(6.4)	(11.2)		
$[CuL_8]Cl_2$	154	28	Light green	12.4	13.8	42.5	6.4	10.9	—	112
				(12.6)	(14.1)	(43.0)	(6.4)	(11.1)		
$[MnL_9Cl_2]$	175	28	Light pink	11.2	13.8	47.0	3.8	9.9	—	17
				(10.9)	(14.0)	(47.4)	(3.9)	(10.1)		
$[FeL_9Cl_2]$	164	26	Reddish brown	10.8	13.7	47.2	3.9	10.9	—	16
				(11.0)	(14.0)	(47.3)	(3.9)	(11.0)		
$[NiL_9]Cl_2$	205	38	Light yellow	11.6	14.1	46.7	4.0	11.1	—	108
				(11.4)	(13.9)	(46.5)	(3.9)	(10.9)		
$[CuL_9]Cl_2$	142	34	Light green	12.4	14.0	46.3	3.9	11.0	—	107
				(12.2)	(13.7)	(46.5)	(3.7)	(10.8)		
$[ZnL_9]Cl_2$	148	25	White	12.5	13.5	46.2	3.9	10.7	—	118
				(12.6)	(13.8)	(46.4)	(3.9)	(10.8)		
$[FeL_{10}Cl_2]$	158	29	Red	10.4	13.7	49.8	4.5	10.4	—	18
				(10.5)	(13.3)	(49.3)	(4.5)	(10.5)		
$[NiL_{10}]Cl_2$	209	24	Light yellow	11.1	13.7	48.4	4.4	10.5	—	98
				(10.9)	(13.3)	(48.9)	(4.4)	(10.6)		
$[CuL_{10}]Cl_2$	156	42	Light green	11.3	13.0	48.5	4.4	10.5	—	123
				(11.6)	(13.3)	(48.7)	(4.4)	(10.3)		
$[ZnL_{10}]Cl_2$	144	38	White	12.1	13.0	48.3	4.5	10.2	—	121
				(11.9)	(12.9)	(48.5)	(4.9)	(10.3)		

materials and the appearance of four new bands in the regions 1680–1710, 1530–1570, 1240–1260 and 650–675 cm^{-1}, characteristic[10] of amide groups. A single sharp band observed for the ligands in the region 3250–3290 cm^{-1} may be assigned[15] to ν(N—H) of the secondary amino group.

The major change noticed for the IR spectra of their corresponding metal complexes is the slight negative shift (40–60 cm^{-1}) in ν(N—H) which appeared in the region 3190–3240 cm^{-1} and thus can be ascribed[16] to coordinated ν(N—H). The appearance of a new medium intensity band in the

Table 2. IR spectroscopic data (cm^{-1}) of the compounds

			Amide bands						
Compound	ν(N—H)	ν(C—H)	I	II	III	IV	δ(CH)	ν(C—N)	ν(M—N)
L_1	3250	2915	1710	1530	1250	660	1430	1150	—
L_2	3270	2910	1720	1530	1260	670	1410	1180	—
L_3	3280	2915	1710	1540	1250	650	1450	1160	—
L_4	3275	2900	1720	1550	1260	670	1405	1140	—
L_5	3290	2915	1680	1570	1250	670	1420	1155	—
L_6	3285	2905	1705	1560	1255	675	1430	1140	—
L_7	3290	2910	1700	1570	1240	650	1450	1155	—
L_8	3270	2920	1710	1550	1255	670	1430	1150	—
L_9	3280	2890	1700	1570	1250	660	1450	1160	—
L_{10}	3275	2910	1715	1560	1260	670	1420	1150	—
$[FeL_1Cl_2]$	3190	2930	1710	1525	1250	655	1415	1135	415
$[NiL_1]Cl_2$	3200	2890	1715	1530	1260	645	1420	1130	420
$[CuL_1]Cl_2$	3225	2930	1700	1525	1265	660	1415	1125	430
$[ZnL_1]Cl_2$	3195	2920	1695	1535	1250	645	1410	1120	435
$[FeL_2Cl_2]$	3230	2890	1700	1530	1240	660	1415	1190	440
$[NiL_2]Cl_2$	3210	2880	1710	1525	1250	670	1400	1180	420
$[CuL_2]Cl_2$	3220	2920	1725	1535	1240	660	1420	1175	430
$[ZnL_2]Cl_2$	3240	2910	1720	1520	1260	650	1415	1170	415
$[MnL_3Cl_2]$	3220	2880	1710	1525	1240	650	1435	1160	430
$[FeL_3Cl_2]$	3235	2910	1715	1535	1250	660	1430	1160	440
$[NiL_3]Cl_2$	3230	2930	1720	1535	1240	670	1450	1150	420
$[CuL_3]Cl_2$	3200	2890	1720	1525	1260	650	1460	1160	430
$[ZnL_3]Cl_2$	3210	2920	1700	1520	1250	670	1455	1170	450
$[MnL_4Cl_2]$	3320	2895	1705	1540	1250	650	1420	1145	495
$[FeL_4Cl_2]$	3215	2930	1706	1535	1260	660	1410	1150	435
$[NiL_4]Cl_2$	3230	2940	1715	1540	1240	655	1430	1150	430
$[CuL_4]Cl_2$	3240	2900	1720	1530	1260	660	1440	1155	440
$[ZnL_4]Cl_2$	3220	2890	1725	1550	1250	670	1430	1150	450
$[FeL_5Cl_2]$	3205	2880	1710	1540	1240	650	1420	1130	430
$[CoL_5Cl_2]$	3230	2875	1690	1560	1245	640	1430	1150	420
$[CuL_5]Cl_2$	3235	2940	1715	1570	1230	660	1410	1155	435
$[FeL_6Cl_2]$	3230	2890	1700	1550	1250	670	1430	1140	440
$[CoL_6Cl_2]$	3225	2870	1710	1540	1255	675	1425	1145	430
$[CuL_6]Cl_2$	3240	2930	1690	1555	1260	680	1450	1130	450
$[FeL_7Cl_2]$	3195	2890	1700	1550	1255	650	1440	1140	425
$[CoL_7Cl_2]$	3230	2915	1710	1540	1240	640	1460	1135	420
$[CuL_7]Cl_2$	3190	2880	1715	1560	1255	655	1450	1145	460
$[FeL_8Cl_2]$	3215	2890	1705	1515	1250	670	1425	1130	460
$[CoL_8Cl_2]$	3210	2920	1700	1510	1260	660	1450	1155	440
$[CuL_8]Cl_2$	3235	2930	1720	1525	1270	680	1440	1150	425
$[MnL_9Cl_2]$	3215	2895	1710	1540	1250	660	1450	1130	420
$[FeL_9Cl_2]$	3210	2890	1710	1530	1245	650	1440	1140	430
$[NiL_9]Cl_2$	3215	2910	1700	1545	1240	640	1450	1140	415
$[CuL_9]Cl_2$	3210	2915	1715	1540	1240	660	1455	1150	430
$[ZnL_9]Cl_2$	3230	2900	1705	1550	1250	670	1450	1125	440
$[FeL_{10}Cl_2]$	3210	2890	1710	1540	1245	650	1400	1150	430
$[NiL_{10}]Cl_2$	3200	2880	1700	1530	1240	640	1420	1140	440
$[CuL_{10}]Cl_2$	3215	2910	1720	1530	1230	640	1430	1150	440
$[ZnL_{10}]Cl_2$	3235	2915	1715	1520	1235	650	1420	1160	445

region 415–460 cm^{-1} assignable to $\nu(\mathrm{M—N})$ vibration further confirms the involvement of nitrogen in coordination. However, the amide I band is found to be unaffected on coordination and thus rules out the coordination through amide oxygen. This has been further supported by the absence of any band attributable to $\nu(\mathrm{M—O})$ vibration.

The ^1H NMR spectra of all the macrocyclic ligands do not show any signal corresponding to primary amino and alcoholic protons. All the macrocyclic ligands show a multiplet (Table 3) in the region 8.41–8.60 ppm, which can be assigned[17] to amide (HN—CO, 4H) protons. Another multiplet appeared in the region 3.35–3.67 ppm, corresponding[18] to the methylene protons ($\mathrm{CO—N—CH_2}$, 8H) which are adjacent to the nitrogen atoms. However, a multiplet in the region 1.98–2.18 ppm for the ligands L_2, L_4, L_6, L_8 and L_{10} is assigned as the middle methylene protons ($\mathrm{C—CH_2—C}$, 4H) of the 1,3-diaminopropane moiety. Singlets in the region 2.30–3.18 and 3.30–3.35 ppm and a multiplet in the region 3.23–3.25 ppm were observed for the respective ligands L_1, L_2, L_3, L_4 and L_5, L_6, assignable[11,18] to the methylene protons of a dicarboxylic acid moiety [($\mathrm{CO—CH_2—CO}$, 4H), ($\mathrm{CO—(CH_2)_2—CO}$, 8H) and ($\mathrm{CO—(CH_2)_3—CO}$, 12H)]. However, the ^1H NMR spectra of L_7 and L_8 gave two multiplets in the regions 3.30–3.34 and 1.98–2.26 ppm, which may be assigned to methylene protons of an adipic acid moiety ($\mathrm{CH_2—C—C—CH_2}$, 8H) and $\mathrm{C—(CH_2)_2—C}$ (8H), respectively. The ^1H NMR spectra of all the macrocyclic zinc(II) complexes (Table 3) have also been recorded and the main change compared with that of the ligands is the shift of the signals towards lower field, which is an indication of the coordination of the macrocycles.

The X-band ESR spectra of the polycrystalline copper(II) macrocyclic complexes at room temperature exhibit an axial type of signal. The complexes of L_2, L_3, L_4, L_9 and L_{10} showed hyperfine splitting and their $g_{\parallel}$, $g_{\perp}$, g_0, $A_{\parallel}$, $A_{\perp}$ and A_0 values have been calculated, while all other complexes gave a single broad signal with two g values (Table 4). The absence of hyperfine splitting in these complexes may be due to the strong dipolar and exchange interactions between copper(II) ions in the unit cell.[19] The tetraamide macrocyclic copper(II) complexes studied here show $g_{\parallel}$ and $g_{\perp}$ values in the 2.171–2.201 and 2.037–2.048 regions, respectively, which support[20] the contention that $d_{x^2-y^2}$ may be the ground state. However, the $A_{\parallel}$ and $A_{\perp}$ values for the complexes of L_2, L_3, L_4, L_9 and L_{10} appeared in the 82.96–100.50 and 12.00–25.62 G range, respectively. All the complexes gave the same spectral pattern and thus the ring size of the macrocyclic ligand has little effect on the ESR spectral parameters. The g values are related[10,21] by the expression $G = (g_{\parallel}-2)/(g_{\perp}-2)$, which measures the exchange interaction between copper centres in the polycrystalline solid. In the present case the axial symmetry parameter, G, lies in the range 4.14–5.32, which indicates that the exchange interaction is very small.

The isotropic nuclear hyperfine constant, A_0, of these complexes is much lower than those of planar species, which is an indication of the distortion of the copper environments from planar to pseudo-tetrahedral.[13] Furthermore, the tendency for $g_{\parallel}$ to increase and $A_{\parallel}$ values to decrease is again suggestive[22,23] of the above proposed geometry. The quotient $g_{\parallel}/A_{\parallel}$ is found to be in the range 218–265 cm, clearly suggesting[24] the presence of tetrahedral distortion in these complexes. All the compounds that were studied show $g_{\parallel} < 2.3$, which indicates[25] that the present complexes possess considerable covalent character.

ESR spectra of powders of cobalt(II) complexes of L_5, L_6, L_7 and L_8 at room temperature show the low-spin formulations of cobalt complexes. All the spectra exhibit hyperfine structures due to the nuclear spin $I = 7/2$ of Co^{2+} is clearly seen and their $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ values have been calculated (Table 4). The observed ESR spectra show eight clear strong signals with a few weak lines at the high field side. The strong lines at $g = 2.20$–2.24 may be due to the perpendicular components. The weak lines seem to be due to the parallel components of Co^{2+}. All the parallel components could not be identified, as the starting lines are overlapped by the strong perpendicular components. The $g_{\parallel}$ values are found to be in the region 1.83–1.86 and the $A_{\parallel}$ and $A_{\perp}$ values appeared in the ranges 135–150 and 78–89 G, respectively. The observed spectra and the existence of $g_{\perp}$ values in a higher region than the $g_{\parallel}$ values and the appearance of A values ($A_{\parallel} > A_{\perp}$) are comparable[26] with the spectra of low spin ($S = 1/2$) octahedral cobalt complexes having d_{z^2} as the ground state.

The electronic spectra (Table 4) of manganese complexes gave two bands in the regions 22,300–22,500 and 18,550–18,900 cm^{-1}, which may be assigned to $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4T_{1g}$ transitions, respectively, suggesting[27] an octahedral environment around the Mn^{2+} ion. However, the spectra of iron complexes exhibit a weak intensity band in the 11,300–11,700 cm^{-1} region, which may reasonably be assigned to the $^5T_{2g} \rightarrow {}^5E_g$ transition, consistent[27] with an octahedral geometry around the metal ion. Magnetic susceptibility measurements (Table 4) of cobalt complexes reveal[28,29] that the complexes are low-spin. The electronic spectra of

Table 3. ^{1}H NMR spectral data[a] of the compounds

Compound	HN—CO	CO—N—CH$_2$	C—CH$_2$—C	CO—(CH$_2$)$_x$—CO[b]	C—(CH$_2$)$_2$—C	CH$_2$—C—C—CH$_2$	Ring protons
L$_1$	8.41 (m)	3.35 (m)	—	2.80 (s)	—	—	—
L$_2$	8.51 (m)	3.56 (m)	1.99 (m)	3.18 (s)	—	—	—
L$_3$	8.56 (m)	3.67 (m)	—	3.30 (s)	—	—	—
L$_4$	8.52 (m)	3.55 (m)	2.03 (m)	3.35 (s)	—	—	—
L$_5$	8.58 (m)	3.51 (m)	2.16 (m)	3.25 (m)	—	—	—
L$_6$	8.51 (m)	3.62 (m)	2.18,1.98 (m)	3.23 (m)	—	—	—
L$_7$	8.60 (m)	3.58 (m)	—	—	2.26 (m)	3.30 (m)	—
L$_8$	8.55 (m)	3.61 (m)	1.98 (m)	—	2.22 (m)	3.34 (m)	—
L$_9$	8.54 (m)	3.50 (m)	—	—	—	—	6.92 (m)
L$_{10}$	8.52 (m)	3.55 (m)	2.18 (m)	—	—	—	7.11 (m)
[ZnL$_1$]Cl$_2$	8.56 (m)	3.38 (m)	—	2.89 (s)	—	—	—
[ZnL$_2$]Cl$_2$	8.55 (m)	3.58 (m)	2.21 (m)	3.30 (s)	—	—	—
[ZnL$_3$]Cl$_2$	8.58 (m)	3.69 (m)	—	3.35 (s)	—	—	—
[ZnL$_4$]Cl$_2$	8.56 (m)	3.58 (m)	2.02 (m)	3.40 (s)	—	—	—
[ZnL$_9$]Cl$_2$	8.58 (m)	3.54 (m)	—	—	—	—	6.95 (m)
[ZnL$_{10}$]Cl$_2$	8.56 (m)	3.61 (m)	—	—	—	—	7.20 (m)

[a] Chemical shift (δ/ppm) with multiplicities in parentheses. s = singlet, m = multiplet.

[b] CO—(CH$_2$)$_x$—CO, where x = 1, 2, 3 or 4.

Table 4. μ_{eff}, ligand field band (cm^{-1}) observed in the electronic spectra and ESR parameters[a] for the complexes

Compound	μ_{eff} (B.M.)	Band position (cm^{-1})	ESR data							
			$g_{\parallel}$	$g_{\perp}$	g_0	$A_{\parallel}$	$A_{\perp}$	A_0	G	$g_{\parallel}/A_{\parallel}$
[FeL$_1$Cl$_2$]	5.2	11,500, 31,000	—	—	—	—	—	—	—	—
[NiL$_1$]Cl$_2$	—	15,400, 19,700, 31,500	—	—	—	—	—	—	—	—
[CuL$_1$]Cl$_2$	1.8	13,300, 18,900, 32,200	2.188	2.038	2.088	—	—	—	4.94	—
[FeL$_2$Cl$_2$]	5.4	11,400, 30,500	—	—	—	—	—	—	—	—
[NiL$_2$]Cl$_2$	—	15,200, 19,900, 30,800	—	—	—	—	—	—	—	—
[CuL$_2$]Cl$_2$	1.9	13,700, 19,500	2.171	2.040	2.083	91.00	19.58	43.38	4.27	238
[MnL$_3$Cl$_2$]	5.8	22,300, 18,900, 31,500	—	—	—	—	—	—	—	—
[FeL$_3$Cl$_2$]	5.4	11,700, 32,000	—	—	—	—	—	—	—	—
[NiL$_3$]Cl$_2$	—	15,700, 19,400, 31,200	—	—	—	—	—	—	—	—
[CuL$_3$]Cl$_2$	1.8	13,200, 20,000	2.189	2.043	2.091	88.56	16.54	40.52	4.39	247
[MnL$_4$Cl$_2$]	5.7	22,500, 18,550, 32,000	—	—	—	—	—	—	—	—
[FeL$_4$Cl$_2$]	5.6	11,300, 31,500	—	—	—	—	—	—	—	—
[NiL$_4$]Cl$_2$	—	15,500, 20,100, 31,300	—	—	—	—	—	—	—	—
[CuL$_4$]Cl$_2$	1.7	14,100, 19,900, 31,800	2.199	2.048	2.098	82.96	25.62	44.73	4.14	265
[FeL$_5$Cl$_2$]	5.3	11,550, 31,000	—	—	—	—	—	—	—	—
[CoL$_5$Cl$_2$]	1.9	13,400	1.83	2.20	—	150.85	89.0	—	—	—
[CuL$_5$]Cl$_2$	1.8	14,000, 20,300, 30,500	1.185	2.040	2.088	—	—	—	4.62	—
[FeL$_6$Cl$_2$]	5.3	11,400, 32,500	—	—	—	—	—	—	—	—
[CoL$_6$Cl$_2$]	2.1	14,800	1.86	2.22	—	145.35	78.85	—	—	—
[CuL$_6$]Cl$_2$	1.9	14,100, 19,500, 30,000	2.183	2.042	2.089	—	—	—	4.62	—
[FeL$_7$Cl$_2$]	5.5	11,650, 30,100	—	—	—	—	—	—	—	—
[CoL$_7$Cl$_2$]	2.0	14,000	1.84	2.23	—	135.10	82.75	—	—	—
[CuL$_7$]Cl$_2$	1.7	13,800, 19,300, 31,400	2.191	2.039	2.089	—	—	—	4.89	—
[FeL$_8$Cl$_2$]	5.6	11,700, 31,000	—	—	—	—	—	—	—	—
[CoL$_8$Cl$_2$]	1.9	14,600	1.86	2.24	—	143.50	80.55	—	—	—
[CuL$_8$]Cl$_2$	1.9	13,900, 20,200, 31,500	2.197	2.037	2.090	—	—	—	5.32	—
[MnL$_9$Cl$_2$]	5.8	22,450, 18,700, 30,500	—	—	—	—	—	—	—	—
[FeL$_9$Cl$_2$]	5.4	11,400, 30,750	—	—	—	—	—	—	—	—
[NiL$_9$]Cl$_2$	—	15,700, 20,000, 31,700	—	—	—	—	—	—	—	—
[CuL$_9$]Cl$_2$	1.9	13,600, 19,000, 31,100	2.198	2.046	2.096	100.50	12.00	41.50	4.30	218
[FeL$_{10}$Cl$_2$]	5.3	11.400, 31.400	—	—	—	—	—	—	—	—
[NiL$_{10}$]Cl$_2$	—	15,400, 20,100, 31,400	—	—	—	—	—	—	—	—
[CuL$_{10}$]Cl$_2$	1.8	13,700, 20,200, 30,900	2.201	2.042	2.093	90.50	12.60	38.56	4.78	243

[a] $g_0 = 1/3(g_{\parallel}+2g_{\perp})$; $A_0 = 1/3(A_{\parallel}+2A_{\perp})$

the cobalt complexes show a band around 14,000 cm^{-1}, which is consistent[29] with the low-spin octahedral complexes of cobalt(II). This band may correspond to the $^2E_g \rightarrow {}^2T_{1g}$ transition, further confirming the ESR data. However, the band below 900 nm could not be recorded because it is beyond the range of the instrument used. The magnetic moment measurements for the nickel complexes suggest their square planar geometry. This has been further confirmed by the appearance of two bands in their electronic spectra centred in the 15,200–15,700 and 19,400–20,100 cm^{-1} regions, which may reasonably be assigned[27] to the $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions, respectively. The copper complexes gave two bands in their electronic spectra in the regions 13,200–14,100 and 18,800–20,300 cm^{-1}, which are in close agreement[13,27] with those expected for a pseudotetrahedral structure. The band appearing around 32,000 cm^{-1} may be due to a charge-transfer transition.

EXPERIMENTAL

Materials and methods

The metal salts $MnCl_2 \cdot 4H_2O$, $FeCl_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and $ZnCl_2$ (all BDH) were commercially available pure samples. The dicarboxylic acids malonic, succinic, glutaric, adipic and phthalic acids, DCC and DMAP (all Fluka) were used as purchased. The primary diamines 1,2-diaminoethane and 1,3-diaminopropane were purchased from Merck and were used without further purification. All solvents were dried before use.

Synthesis of 2,4,9,11-*tetraoxo*-1,4,8,12-*tetraazacyclotetradecane* (L_1)

DCC (2.29 g, 11.10 mmol) and a catalytic amount of DMAP in dichloromethane (50 cm^3) at 0°C were kept in a magnetically stirred two-necked 250 cm^3 round-bottomed flask. To this stirred solution was added simultaneously 1,2-diaminoethane (0.34 cm^3, 5.10 mmol) and malonic acid (0.53 g, 5.10 mmol) in dichloromethane (50 cm^3). The resultant reaction mixture was stirred for 8 h. The solid product thus obtained was filtered off and washed several times with dichloromethane. The product was obtained as a chalky white solid after recrystallization from methanol and was dried *in vacuo*.

Synthesis of 2,4,10,12-*tetraoxo*-1,5,9,13-*tetraazacyclohexadecane* (L_2)

This compound was prepared by adopting the same procedure described above. Instead of 1,2-diaminoethane here 1,3-diaminopropane (0.43 cm^3, 5.10 mmol) was added.

Synthesis of 2,5,10,13-*tetraoxo*-1,6,9,14-*tetraazacyclohexadecane* (L_3)

This preparation was exactly analogous to the previous ones. Here the diamine and diacid employed were 1,2-diaminoethane (0.34 cm^3, 5.10 mmol) and succinic acid (0.60 g, 5.10 mmol), respectively.

Synthesis of 2,5,11,14-*tetraoxo*-1,6,10,15-*tetraazacyclooctadecane* (L_4)

This compound was prepared by adopting the above mentioned method using 1,3-diaminopropane (0.43 cm^3, 5.10 mmol) and succinic acid (0.60 g, 5.10 mmol).

Synthesis of 2,6,11,15-*tetraoxo*-1,7,10,16-*tetraazacyclooctadecane* (L_5)

This preparation was exactly analogous to the previous ones except that 1,2-diaminoethane (0.34 cm^3, 5.10 mmol) and glutaric acid (0.67 g, 5.10 mmol) were introduced.

Synthesis of 2,6,12,16-*tetraoxo*-1,7,11,17-*tetraazacycloeicosane* (L_6)

The procedure used for the preparation of this compound was the same as detailed above. The diamine and diacid used were 1,3-diaminopropane (0.43 cm^3, 5.10 mmol) and glutaric acid (0.67 g, 5.10 mmol), respectively.

Synthesis of 2,7,12,17-*tetraoxo*-1,8,11,18-*tetraazacycloeicosane* (L_7)

This compound was prepared by using 1,2-diaminoethane (0.34 cm^3, 5.10 mmol) and adipic acid (0.75 g, 5.10 mmol). The rest of the procedure is the same as mentioned above.

Synthesis of 2,7,13,18-*tetraoxo*-1,8,12,19-*tetraazacyclobicosane* (L_8)

This preparation was exactly analogous to the previous one except that 1,3-diaminopropane (0.43 cm^3, 5.10 mmol) and adipic acid (0.75 g, 5.10 mmol) were introduced.

Synthesis of 3,4 : 11,12-*dibenzo*-2,5,10,13-*tetraoxo*-1,6,9,14-*tetraazacyclohexadecane* (L_9)

This compound was prepared by adopting the above mentioned method using 1,2-diaminoethane (0.34 cm^3, 5.10 mmol) and phthalic acid (0.85 g, 5.10 mmol).

Synthesis of 3,4 : 12,13-*dibenzo*-2,5,11,14-*tetraoxo*-1,6,10,15-*tetraazacyclooctadecane* (L_{10})

This preparation was similar to the method described previously. Here, 1,3-diaminopropane (0.43 cm^3, 5.10 mmol) and phthalic acid (0.85 g, 5.10 mmol) were employed.

The purities of all these compounds (L_1–L_{10}) were checked through TLC by dissolving them in DMF using petrol–ether (2 : 3, v/v) as eluents. Only one spot was observed in each case after developing in an iodine chamber, indicating that the compounds were pure.

Synthesis of dichloro(2,4,9,11-*tetraoxo*-1,5,8,12-*tetraazacyclotetradecane*)*metal*(II), $[ML_1Cl_2]$ ($M = Fe^{II}$) *and* (2,4,9,11-*tetraoxo*-1,5,8,12-*tetraazacyclotetradecane*)*metal*(II) chloride, $[ML_1]Cl_2$ ($M = Ni^{II}$, Cu^{II} *and* Zn^{II})

To a stirred solution of metal(II) chloride (1 mmol) in THF (50 cm^3) was added a solution of ligand L_1 (1.10 mmol) in THF at room temperature.

The mixture was stirred continuously for 7 h. The solid product obtained was filtered off, washed with ether and dried *in vacuo*.

Synthesis of dichloro(2,4,10,12-*tetraoxo*-1,5,9,13-*tetraazacyclohexadecane*)*metal*(II), $[ML_2Cl_2]$ (M = Fe^{II}) *and* (2,4,10,12-*tetraoxo*-1,5,9,13-*tetraazacyclohexadecane*)*metal*(II) *chloride*, $[ML_2]Cl_2$ (M = Ni^{II}, Cu^{II} *and* Zn^{II})

These complexes were prepared by using the same method adopted for $[ML_1Cl_2]$. Instead of L_1, here a solution of L_2 (1.10 mmol) in THF was added to the metal salt solution (1 mmol).

Synthesis of dichloro(2,5,10,13-*tetraoxo*-1,6,9,14-*tetraazacyclohexadecane*)*metal*(II), $[ML_3Cl_2]$ (M = Mn^{II} *and* Fe^{II}) *and* (2,5,10,13-*tetraoxo*-1,6,9,14-*tetraazacyclohexadecane*)*metal*(II), $[ML_3]Cl_2$ (M = Ni^{II}, Cu^{II} *and* Zn^{II})

These preparations were carried out using the same procedure discussed above for the preparation of $[ML_1Cl_2]$. Here, instead of ligand L_1, L_3 (1.10 mmol) in THF was added.

Synthesis of dichloro(2,5,11,14-*tetraoxo*-1,6,10,15-*tetraazacyclooctadecane*)*metal*(II). $[ML_4Cl_2]$ (M = Mn^{II} *and* Fe^{II}) *and* (2,5,11,14-*tetraoxo*-1,6,10,15-*tetraazacyclooctadecane*)*metal*(II) *chloride*, $[ML_4]Cl_2$ (M = Ni^{II}, Cu^{II} *and* Zn^{II})

These complexes were also synthesized by the method which is adopted for the preparation of $[ML_1Cl_2]$. Here, the ligand employed for complexation was L_4 (1.10 mmol).

Synthesis of dichloro(2,6,11,15-*tetraoxo*-1,7,10,16-*tetraazacyclooctadecane*)*metal*(II), $[ML_5Cl_2]$ (M = Fe^{II} *and* Co^{II}) *and* (2,6,11,15-*tetraoxo*-1,7,10,16-*tetraazacyclooctadecane*)*metal*(II) *chloride*, $[ML_5]Cl_2$ (M = Cu^{II})

These complexes were prepared from the above mentioned procedure using the ligands L_5 (1.10 mmol).

Synthesis of dichloro(2,6,12,16-*tetraoxo*-1,7,11,17-*tetraazacycloeicosane*)*metal*(II), $[ML_6Cl_2]$ (M = Fe^{II}*and* Co^{II}) *and* (2,6,12,16-*tetraoxo*-1,7,11,17-*tetraazacycloeicosane*)*metal*(II) *chloride*, $[ML_6]Cl_2$ (M = Cu^{II})

This preparation was exactly analogous to that above, except the ligand L_6 (1.10 mmol) was added.

Synthesis of dichloro(2,7,12,17-*tetraoxo*-1,8,11,18-*tetraazacycloeicosane*)*metal*(II), $[ML_7Cl_2]$ (M = Fe^{II} *and* Co^{II}) *and* (2,7,12,17-*tetraoxo*-1,8,11,18-*tetraazacycloeicosane*)*metal*(II) *chloride*, $[ML_7]Cl_2$ (M = Cu^{II})

This preparation was analogous to the above, except that ligand L_7 (1.10 mmol) was introduced.

Synthesis of dichloro(2,7,13,18-*tetraoxo*-1,8,12,19-*tetraazacyclobicosane*)*metal*(II), $[ML_8Cl_2]$ (M = Fe^{II} *and* Co^{II}) *and* (2,7,13,18-*tetraoxo*-1,8,12,19-*tetraazacyclobicosane*)*metal*(II) *chloride*, $[ML_8]Cl_2$ (M = Cu^{II})

The procedure used for the preparation of these complexes was the same as detailed above, except the ligand L_8 (1.10 mmol) was used.

Synthesis of dichloro(3,4 : 11,12-*dibenzo*-2,5,10,13 - *tetraoxo* - 1,6,9,14 - *tetraazacyclohexadecane*) *metal*(II), $[ML_9Cl_2]$ (M = Mn^{II} *and* Fe^{II}) *and* (3,4 : 11,12-*dibenzo*-2,5,10,13-*tetraoxo*-1,6,9,14-*tetraazacyclohexadecane*)*metal*(II) *chloride*, $[ML_9]Cl_2$ (M = Ni^{II}, Cu^{II} *and* Zn^{II})

These complexes were prepared by adopting the same procedure discussed above. Here, the ligand added was L_9 (1.10 mmol).

Synthesis of dichloro(3,4 : 12,13-*dibenzo*-2,5,11,14-*tetraoxo* - 1,6,10,15 - *tetraazacyclooctadecane*) *metal*(II), $[ML_{10}Cl_2]$ (M = Fe^{II}) *and* (3,4 : 12,13-*dibenzo* - 2,5,11,14 - *tetraoxo* - 1,6,10,15 - *tetraazacyclooctadecane*)*metal*(II) *chloride*, $[ML_{10}]Cl_2$ (M = Ni^{II}, Cu^{II} *and* Zn^{II})

These complexes were also prepared using the above method with the ligand L_{10} (1.10 mmol).

The elemental analyses were obtained from the Microanalytical Laboratory of CDRI, Lucknow, India. ^1H NMR spectra in DMSO-d_6 using a Bruker AC 200E NMR spectrometer with Me_4Si as an internal standard were obtained from GNDU, Amritsar, India. Metals and chlorides were determined volumetrically[30] and gravimetrically,[31] respectively. The IR spectra (4000–400 cm^{-1}), were recorded as KBr discs on a Pye-Unicam SP3-300 spectrophotometer. The electronic spectra of compounds in DMSO were recorded on a Pye-Unicam 8800 spectrophotometer at room temperature. ESR spectra were recorded on a Jeol JES RE2X ESR spectrometer. Magnetic susceptibility measurements were carried out using a Faraday balance at 25°C. The electrical conductivities of 10^{-3} M solutions in DMSO were obtained on a systronics type 302 conductivity bridge equilibrated at $25 \pm 0.01^\circ$C.

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