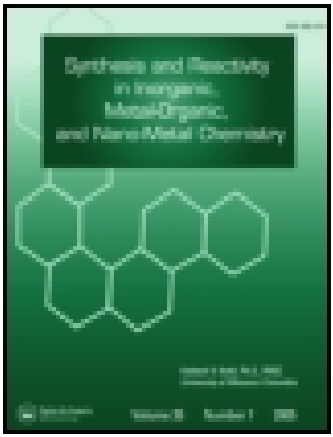

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Synthesis and Spectroscopic Studies of Bis(Macrocyclic) Dimetal(II) Complexes Based on 14-18 Membered Pentaaza Units

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SYNTHESIS AND SPECTROSCOPIC STUDIES OF BIS(MACROCYCLIC) DIMETAL(II) COMPLEXES BASED ON 14-18 MEMBERED PENTAAZA UNITS

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ABSTRACT

Bis(macrocyclic) binuclear transition metal complexes $[M_2LCl_4]$ [M = Fe(II), Co(II), Ni(II), Cu(II) and Zn(II); L = L^1-L^6, have been synthesised by the template condensation reaction of ethylenediamine or 1,3-diaminopropane with formaldehyde, benzidine and acetylacetone or dibenzoyl methane or phthalaldehyde in 4:4:1:2:2 molar ratio. All prepared complexes have been characterized by elemental analyses, IR, ^1H NMR, EPR and UV/VIS and conductivity data as well as magnetic susceptibility measurements. An octahedral geometry is suggested for all complexes.

INTRODUCTION

Recently, a series of investigations has centered on the synthesis of macrocyclic ligands which are able to

encapsulate two metal ions. Many researchers have prepared numerous binuclear marocyclic complexes where one of the metals exhibits coordinative saturation and the other acts as a coordinatively unsaturated site[1,2]. Such types of complexes have been largely employed for the study of redox behaviour accompanying dioxygen binding to metals. The preparation of bis(macrocyclic) N-donor ligands with binucleating properties towards transition metals has attracted much interest and a variety of systems have been reported[3-6]. Fenton has reviewed[7] this class of compounds emphasizing their relevance to bioinorganic systems. Recent studies on dimetallic bis-cyclam compound reveal that many of these compounds can be used for the electrocatalytic reduction[8-10] of O_2, CO_2 or H_2O. Experiments proved that bis-cyclams are better electrocatalysts than those of the corresponding mononuclear species. Several articles have been reported in recent years on the coordination chemistry of bis(macrocyclic) molecules in which two potentially coordinating tetraaza subunits are linked together by bridging the amine nitrogens or carbon atoms of the ligand's backbone[11-14]. In such compounds each ring may coordinate a metal ion and the two metal centers may display independent or cooperative behaviour depending upon the length of the bridge joining the two subunits.

Our interest was to generate a rare situation where the macrocyclic rings are held far from each other such that the two proximate metal centers act as independently as possible, especially with regard to the magnetic behaviour.

We have recently reported the synthesis and characterization of various mononuclear cyclam[15], dioxo cyclam[16,17] and other related[18-20] polyazamacrocyclic systems. In this paper we report the synthesis of a new series of bis(marocyclic) complexes where both tetraaza units are bridged through the nitrogen of the benzidine moiety.

EXPERIMENTAL

The metal salts $FeCl_2$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, ethylenediamine, 1,3-diaminopropane and formaldehyde were purchased from E.Merck. Benzidine was purchased from SD's Fine Chemicals.

Synthesis of Tetrachloro[1,1'-biphenylbis(1,3,6,10,13-pentaazacyclotetradecane-7,9-dimethyl-6,9-diene)]dimetal(II) and Tetrachloro[1,1'-biphenylbis(1,3,7,11,15-pentaazacyclohexadecane-8,10-dimethyl-7,10-diene)]dimetal(II), $[M_2L^1Cl_4]$ and $[M_2L^2Cl_4]$ [M = Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)].

To a stirred methanolic solution (10 mL) of benzidine (0.2 g, 0.01 mol) in a two-necked round-bottomed flask was added simultaneously formaldehyde (0.125 g, 0.04 mol) and ethylenediamine (0.25 g, 0.04 mol) or 1,3-diaminopropane (0.3 g, 0.04 mol) followed by addition of a methanolic solution (30 mL) of metal salt (0.02 mol). The resulting mixutre was stirred for about 2 h and finally acetylacetone (0.2 g, 0.02 mol) was added to the reaction vessel. A change in colour of the solution was observed. The reaction mixture was then refluxed for about 7 h. The resulting precipitate was filtered, washed with methanol, and dried in vacuo.

Synthesis of Tetrachloro[1,1'-biphenylbis(1,3,6,10,13-pentaazacyclotetradecane-7,9-diphenyl-6,9-diene)]dimetal(II) and Tetrachloro[1,1'-biphenylbis(1,3,7,11,15-pentaazacyclohexadecane-8,10-diphenyl-7,10-diene)]dimetal(II), $[M_2L^3Cl_4]$ and $[M_2L^4Cl_4]$ [M = Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)].

The compounds were prepared by adopting the same procedure as stated above. Here, instead of acetylacetone, dibenzoylmethane (0.45 g, 0.02 mol) was added.

Synthesis of Tetrachloro[1,1'-biphenylbis(1,3,6,11,14-pentaazacyclopentadecane-8,9-phenyl-6,10-diene)]dimetal(II) and Tetrachloro[1,1'-biphenylbis(1,3,7,12,16-pentaazacycloheptadecane-9,10-phenyl-7,11-diene)]dimetal(II), $[M_2L^5Cl_4]$ and $[M_2L^6Cl_4]$ [M = Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)].

The procedure adopted was the same as discussed in the first preparation except that here phthalaldehyde (0.275 g, 0.02 mol) was added in the final step.

Measurements

The elemental analyses were obtained from the Microanalytical Laboratory of CDRI Lucknow. ^1H NMR spectra in DMSO-d_6 were obtained at GNDU, Amritsar, India, using a Bruker AC 200 E spectrometer with Me_4Si as an internal standard. The determination of chloride was done gravimetrically[21] and the metals were determined by titrating with standard EDTA solution[22]. The IR spectra (4000-200 cm^{-1}) were recorded as KBr discs on an IR 408 Shimadzu spectrophotometer. The electronic spectra of compounds in

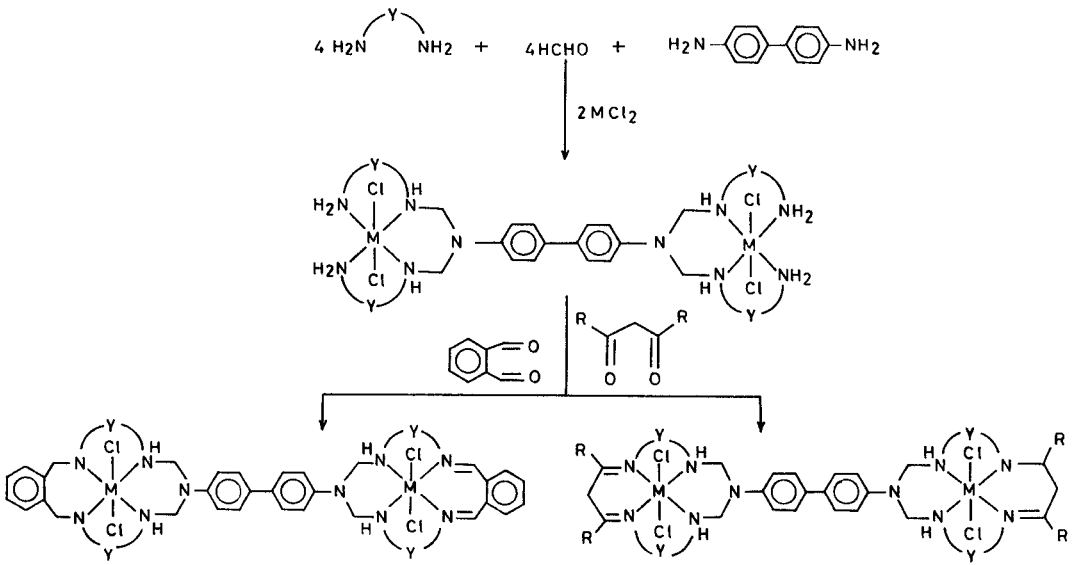
DMSO were recorded on a Pye-Unicam 8800 spectrophotometer. EPR spectra of the solid complexes at room temperature were recorded on a Jeol JES RE2X EPR spectrometer. Magnetic susceptibility measurements were carried out using a Faraday balance at 25°C. The electrical conductivities of 10^{-3} M solutions in DMSO were obtained on a Systronic type 302 conductivity bridge equilibrated at 25±0.05°C.

RESULTS AND DISCUSSION

A new series of bis(macrocyclic) complexes, $[M_2LCl_4]$ [M = Fe(II), Co(II), Ni(II), Cu(II) and Zn(II); L = L^1-L^6], has been synthesized by the template reaction of primary diamines, formaldehyde and benzidine followed by the addition of diketones or phthalaldehyde in 4:4:1:2:2 molar ratio (Scheme 1). All the formed complexes are polycrystalline in nature and stable to air. Melting points and colours of all the complexes are shown in Table I. Elemental analyses (Table I) agree well with the bis(macrocyclic) complexes shown in Scheme 1. The molar conductance values in DMSO (10^{-3} M) are indicative[23] of the non-electrolytic nature of all these complexes.

IR Spectra

The prominent IR spectral results are presented in Table II. In all the complexes, a single sharp band in the 3210-3270 cm^{-1} region belongs to the coordinated N-H stretching vibration of a secondary amine moiety. A medium to strong band observed in the region 1560-1600 cm^{-1} is due to the coordinated ν(C=N) vibrations and is consistent[24]



Scheme 1

Table I. Colour, Melting Points, Molar Conductances, Elemental Analyses, μ_{eff}(B.M) and Electronic Spectral Data of the Compounds.

Compounds	F.W.	Colour	Melting point (°C)	Yield (%)	Λm $cm^2\,\Omega^{-1}\,mol^{-1}$	Found (Calc) % C	H	N	M	Cl	μeff (B.M.)	Electronic spectral data λ max (cm^{-1})
$[Fe_2L^1Cl_4]$ $Fe_2C_{34}H_{52}N_{10}Cl_4$	853.7	Brick red	341	65	11	47.5 (47.8)	5.8 (6.1)	16.1 (16.4)	13.3 (13.2)	16.1 (16.5)	5.60	11,600
$[Co_2L^1Cl_4]$ $Co_2C_{34}H_{52}N_{10}Cl_4$	859.8	Orange	238	68	20	47.2 (47.5)	5.6 (6.0)	15.5 (15.9)	13.3 (13.7)	16.4 (16.5)	4.05	22,300 14,200
$[Ni_2L^1Cl_4]$ $Ni_2C_{34}H_{52}N_{10}Cl_4$	859.4	Brown	320	70	13	47.0 (47.3)	5.8 (6.0)	15.8 (16.1)	13.0 (13.4)	16.1 (16.4)	3.11	27,600 20,500 11,250
$[Cu_2L^1Cl_4]$ $Cu_2C_{34}H_{52}N_{10}Cl_4$	869.0	Dark brown	295	73	24	47.5 (47.9)	5.6 (5.9)	16.1 (16.0)	14.2 (14.6)	16.5 (16.3)	1.70	20,500 16,350
$[Zn_2L^1Cl_4]$ $Zn_2C_{34}H_{52}N_{10}Cl_4$	872.0	White	311	70	13	46.0 (46.3)	5.5 (5.9)	15.6 (15.9)	15.1 (15.5)	16.0 (16.2)	-	-
$[Fe_2L^2Cl_4]$ $Fe_2C_{38}H_{60}N_{10}Cl_4$	909.7	Red	278	65	15	50.0 (50.1)	6.2 (6.6)	15.0 (15.4)	12.2 (12.3)	15.1 (15.5)	5.41	11,400
$[Co_2L^2Cl_4]$ $Co_2C_{38}H_{60}N_{10}Cl_4$	915.7	Yellowish brown	262	70	18	49.2 (49.6)	6.4 (6.5)	15.1 (15.3)	12.5 (12.7)	15.2 (15.5)	4.23	21,900 13,800
$[Ni_2L^2Cl_4]$ $Ni_2C_{38}H_{60}N_{10}Cl_4$	915.4	Grey	296	72	10	49.5 (49.8)	6.4 (6.6)	15.0 (15.3)	12.6 (12.8)	15.3 (15.5)	3.10	27,800 20,000 11,150
$[Cu_2L^2Cl_4]$ $Cu_2C_{38}H_{60}N_{10}Cl_4$	925.0	Green	319	75	20	49.0 (49.3)	6.1 (6.4)	14.8 (15.1)	13.5 (13.7)	15.1 (15.3)	1.61	20,100 16,200

(continued)

Table I. Continued

$[Zn_2L^2Cl_4]$ $Zn_2C_{38}H_{60}N_{10}Cl_4$	928.8	Cream	171	68	16	48.3 (48.6)	6.0 (6.4)	14.7 (14.9)	15.0 (15.2)	14.2 (14.6)	-	-
$[Fe_2L^3Cl_4]$ $Fe_2C_{54}H_{60}N_{10}Cl_4$	1101.7	Redish brown	272	62	19	58.4 (58.8)	5.0 (5.4)	12.2 (12.7)	10.0 (10.2)	12.3 (12.7)	5.39	11,800
$[Co_2L^3Cl_4]$ $Co_2C_{54}H_{60}N_{10}Cl_4$	1107.8	Brown	220	70	21	58.1 (58.5)	5.2 (5.4)	12.2 (12.6)	10.2 (10.6)	12.4 (12.8)	4.11	21,600 14,300
$[Ni_2L^3Cl_4]$ $Ni_2C_{54}H_{60}N_{10}Cl_4$	1107.4	Dark grey	286	70	12	58.1 (58.4)	5.0 (5.4)	12.3 (12.6)	10.1 (10.5)	12.3 (12.6)	3.05	27,850 20,600 11,150
$[Cu_2L^3Cl_4]$ $Cu_2C_{54}H_{60}N_{10}Cl_4$	1117.0	Light green	252	65	22	57.7 (58.0)	5.0 (5.3)	12.1 (12.5)	11.2 (11.4)	12.5 (12.7)	1.60	19,800 16,400
$[Zn_2L^3Cl_4]$ $Zn_2C_{54}H_{60}N_{10}Cl_4$	1120.8	White	211	65	16	57.2 (57.5)	5.0 (5.3)	12.0 (12.4)	12.0 (12.2)	12.2 (12.6)	-	-
$[Fe_2L^4Cl_4]$ $Fe_2C_{58}H_{68}N_{10}Cl_4$	1157.7	Red	265	60	17	63.3 (63.6)	5.0 (5.3)	12.0 (12.4)	11.8 (12.2)	12.2 (12.6)	5.45	11,500
$[Co_2L^4Cl_4]$ $Co_2C_{58}H_{68}N_{10}Cl_4$	1163.8	Pink	226	68	21	63.0 (63.4)	4.8 (5.2)	10.5 (10.9)	8.9 (9.2)	10.7 (11.1)	4.20	22,000 14,100
$[Ni_2L^4Cl_4]$ $Ni_2C_{58}H_{68}N_{10}Cl_4$	1163.4	Grey	263	68	15	63.2 (63.5)	5.0 (5.3)	10.2 (10.6)	8.8 (9.2)	10.5 (10.9)	3.15	27,700 20,200 11,200
$[Cu_2L^4Cl_4]$ $Cu_2C_{58}H_{68}N_{10}Cl_4$	1173.0	Bluish green	275	75	19	62.5 (62.9)	4.8 (5.2)	10.5 (10.8)	9.6 (9.8)	10.7 (11.0)	1.59	19,900 16,200
$[Zn_2L^4Cl_4]$ $Zn_2C_{58}H_{68}N_{10}Cl_4$	1176.8	Light violet	220	68	12	62.0 (62.4)	4.9 (5.1)	10.6 (10.7)	10.0 (10.4)	10.3 (10.7)	-	-

$[Fe_2L^5Cl_4]$ $Fe_2C_{40}H_{48}N_{10}Cl_4$	921.7	Dark red	241	65	17	51.9 (52.1)	4.7 (5.1)	14.8 (15.2)	11.6 (12.0)	15.0 (15.4)	5.50	11,400
$[Co_2L^5Cl_4]$ $Co_2C_{40}H_{48}N_{10}Cl_4$	928.8	Orange brown	252	70	15	51.4 (51.7)	4.8 (5.1)	14.6 (15.0)	12.2 (12.6)	15.0 (15.3)	4.15	22,100 14,300
$[Ni_2L^5Cl_4]$ $Ni_2C_{40}H_{48}N_{10}Cl_4$	928.4	Green	278	72	23	51.6 (51.8)	4.9 (5.2)	14.5 (14.9)	12.2 (12.6)	15.0 (15.3)	3.25	27,650 20,100 11,150
$[Cu_2L^5Cl_4]$ $Cu_2C_{40}H_{48}N_{10}Cl_4$	938.0	Grey	238	75	20	49.6 (50.0)	4.7 (5.1)	14.6 (14.9)	13.3 (13.5)	14.6 (15.0)	1.65	20,300 16,400
$[Zn_2L^5Cl_4]$ $Zn_2C_{40}H_{48}N_{10}Cl_4$	940.8	Light cream	205	70	15	49.8 (50.1)	4.4 (5.0)	14.6 (14.8)	14.3 (14.5)	14.4 (14.8)	-	-
$[Fe_2L^6Cl_4]$ $Fe_2C_{44}H_{56}N_{10}Cl_4$	977.7	Red	297	60	11	53.7 (53.9)	5.2 (5.6)	14.0 (14.3)	11.3 (11.4)	14.1 (14.5)	5.56	11,700
$[Co_2L^6Cl_4]$ $Co_2C_{44}H_{56}N_{10}Cl_4$	983.8	Dark pink	275	65	19	53.4 (53.6)	5.5 (5.7)	14.0 (14.2)	11.6 (11.9)	14.2 (14.4)	4.18	22,200 14,000
$[Ni_2L^6Cl_4]$ $Ni_2C_{44}H_{56}N_{10}Cl_4$	983.4	Green	265	70	15	53.5 (53.7)	5.3 (5.6)	14.0 (14.2)	11.5 (11.9)	14.2 (14.5)	3.09	27,800 20,300 11,250
$[Cu_2L^6Cl_4]$ $Cu_2C_{44}H_{56}N_{10}Cl_4$	993.0	Grey	250	72	12	52.6 (53.0)	5.4 (5.6)	13.7 (14.0)	12.6 (12.8)	14.0 (14.3)	1.60	20,100 16,350
$[Zn_2L^6Cl_4]$ $Zn_2C_{44}H_{56}N_{10}Cl_4$	996.8	White	228	68	21	52.4 (52.6)	5.2 (5.5)	13.5 (13.9)	13.4 (13.6)	13.8 (14.1)	-	-

Table II. IR Spectral Data (cm^{-1}) and EPR Spectral Parameters of the Complexes

Compounds	ν(N-H)	ν(C=N)	ν(C-H)	ν(C-N)	δ(N-H)	δ(C-H)	ν(M-N)	ν(M-Cl)	Ring vibrations	EPR data		
										$g_{\parallel}$	$g_{\perp}$	G
$[Fe_2L^1Cl_4]$	3210	1560	2850	1175	1610	1420	460	300	1400, 1030 720	-	-	-
$[Co_2L^1Cl_4]$	3225	1590	2890	1190	1640	1430	475	290	1410, 1050 760	-	-	-
$[Ni_2L^1Cl_4]$	3240	1575	2960	1180	1630	1460	510	285	1420, 1060 740	-	-	-
$[Cu_2L^1Cl_4]$	3270	1580	2915	1175	1625	1435	500	310	1410, 1025 780	2.141	2.058	2.43
$[Zn_2L^1Cl_4]$	3255	1570	2880	1200	1610	1450	480	305	1405, 1035 750	-	-	-
$[Fe_2L^2Cl_4]$	3220	1570	2865	1180	1630	1425	500	310	1410, 1040 735	-	-	-
$[Co_2L^2Cl_4]$	3230	1585	2860	1185	1625	1440	470	280	1400, 1020 720	-	-	-
$[Ni_2L^2Cl_4]$	3265	1560	2850	1220	1620	1460	490	290	1430, 1040 750	-	-	-
$[Cu_2L^2Cl_4]$	3270	1585	2910	1210	1640	1430	470	300	1410, 1020 730	2.134	2.061	2.23
$[Zn_2L^2Cl_4]$	3245	1590	2920	1190	1630	1440	480	310	1415, 1030 725	-	-	-
$[Fe_2L^3Cl_4]$	3215	1580	2930	1185	1610	1440	510	300	1420, 1040 760	-	-	-
$[Co_2L^3Cl_4]$	3240	1560	2870	1195	1620	1460	505	290	1410, 1060 720	-	-	-
$[Ni_2L^3Cl_4]$	3255	1565	2890	1200	1635	1435	465	285	1400, 1035 725	-	-	-
$[Cu_2L^3Cl_4]$	3210	1585	2915	1215	1615	1425	480	295	1415, 1025 740	2.138	2.060	2.30

$[Zn_2L^3Cl_4]$	3270	1580	2950	1190	1640	1460	495	300	1430, 1060 740	-	-	-
$[Fe_2L^4Cl_4]$	3235	1560	2930	1190	1625	1455	460	305	1400, 1020 720	-	-	-
$[Co_2L^4Cl_4]$	3240	1570	2855	1215	1640	1435	500	290	1405, 1040 750	-	-	-
$[Ni_2L^4Cl_4]$	3250	1590	2950	1180	1610	1440	510	280	1400, 1025 740	-	-	-
$[Cu_2L^4Cl_4]$	3210	1565	2900	1175	1620	1430	490	295	1400, 1030 720	2.135	2.061	2.21
$[Zn_2L^4Cl_4]$	3225	1580	2890	1210	1630	1420	480	300	1410, 1040 750	-	-	-
$[Fe_2L^5Cl_4]$	3220	1565	2875	1220	1615	1460	475	310	1405, 1070 760	-	-	-
$[Co_2L^5Cl_4]$	3235	1575	2915	1180	1640	1450	480	280	1420, 1025 735	-	-	-
$[Ni_2L^5Cl_4]$	3265	1585	2940	1195	1630	1425	500	290	1400, 1020 740	-	-	-
$[Cu_2L^5Cl_4]$	3260	1590	2925	1200	1640	1440	500	310	1415, 1050 760	2.139	2.058	2.39
$[Zn_2L^5Cl_4]$	3245	1560	2880	1220	1610	1420	490	290	1400, 1040 750	-	-	-
$[Fe_2L^6Cl_4]$	3225	1570	2870	1190	1615	1460	400	310	1420, 1060 730	-	-	-
$[Co_2L^6Cl_4]$	3260	1585	2875	1210	1635	1450	460	300	1410, 1035 725	-	-	-
$[Ni_2L^6Cl_4]$	3250	1565	2945	1200	1620	1450	485	290	1405, 1030 730	-	-	-
$[Cu_2L^6Cl_4]$	3260	1570	2930	1195	1640	1430	480	300	1410, 1020 720	2.145	2.059	2.45
$[Zn_2L^6Cl_4]$	3230	1580	2910	1205	1620	1440	500	310	1425, 1030 740	-	-	-

with that of analogous compounds. Along with these results, the most important feature is that the IR spectra of the complexes show no bands assignable to primary amine or carbonyl group stretching vibrations, consistent with the proposed structures shown in Scheme I. Another band at 1610-1640 cm^{-1} is assignable to δ(N-H) vibrations. The bands corresponding to phenyl group vibrations are observed in their expected positions (Table II). The IR spectra of all complexes gave bands around 1175 cm^{-1} which can be assigned to ν(C-N). All complexes show absorption bands in position (Table II). The IR spectra of all complexes the 2850-2960 and 1420-1460 cm^{-1} regions which may correspond to ν(C-H) and δ(C-H) vibration, respectively. A medium intensity band at 300 cm^{-1} can be attributed[21] to the M-Cl stretching vibration. Finally, the band around 460-510 cm^{-1} can be ascribed[26] to the ν(M-N) vibration.

EPR Spectra

The room temperature EPR spectra of the copper(II) bis(macrocyclic) complexes show a broad band with two g values. The absence of hyperfine splitting in these complexes may be due to the strong dipolar and exchange interactions between the copper(II) ions in the unit cell[27]. The $g_{\parallel}$ and $g_{\perp}$ values have been calculated from the spectra which appeared in the regions 2.135-2.145 and 2.058-2.061, respectively. The observed g values indicate the presence of unpaired electron density in the $d_{x^2-y^2}$ orbital as $g_{\parallel} > g_{\perp}$, a phenomenon reported[28] in many other complexes. All the

complexes show the same spectral pattern which suggest that the change in macrocyclic ring size has little effect on the EPR spectral parameters. Proctor and coworkers[29] have shown that the magnitude of the ratio $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$ implies the possibility of exchange interaction in the copper complexes. When $G > 4$, the exchange interaction is negligible. In the present complexes the values range from 2.21-2.45 which indicate a considerable exchange interaction in these complexes. It has been reported[30] that $g_{\parallel}$ is a sensitive function indicating covalency. For an ionic environment, $g_{\parallel}$ is greater than 2.3 and for a covalent environment, $g_{\parallel}$ is less than 2.3. In the present complexes $g_{\parallel} < 2.3$ which is indicative of the covalent nature of the complex.

^{1}H NMR Spectra

The ^{1}H NMR spectra of all bis(macrocyclic) zinc complexes recorded in DMSO-d_6 show two multiplets in the regions 6.28-6.43 and 3.35-3.50 ppm which correspond[26,31] to the secondary amino protons and methylene protons of the aldehyde moiety (C-NH-C, 4H and N-CH_2-N, 8H), respectively. Two more multiplets observed for all the complexes in the 2.38-2.48 and 2.62-2.74 ppm regions may be due to the two non-equivalent methylene protons (N-CH_2-C, 8H and C-CH_2N=, 8H) of the amine moiety[18]. All complexes show a multiplet in the region 7.13-7.53 ppm which is assigned[24] to aromatic ring protons. The ^{1}H NMR spectra of $[Zn_2L^5Cl_4]$ and $[Zn_2L^6Cl_4]$ show a singlet in the 8.34-8.40 ppm range which can be assigned[32] to the four equivalent carboximine protons

(CH=N, 4H). Furthermore, another sharp singlet seen for the complexes $[Zn_2L^1Cl_4]$ and $[Zn_2L^2Cl_4]$ in the range 2.14-2.18 ppm may be attributed[14] to the imine methyl (CH_3-C=N, 12H) protons. The ^1H NMR spectra of the compounds $[Zn_2L^2Cl_4]$, $[Zn_2L^4Cl_4]$ and $[Zn_2L^6Cl_4]$ show an additional multiplet in the region 1.88-1.95 ppm assignable to the middle methylene protons of the 1,3-diaminopropane moiety. We did not find any signals which are assignable to the protons of uncondensed moieties, supporting the macrocyclic structure shown in Scheme 1.

Electronic Spectra and Magnetic Moments

The electronic spectra (Table I) of the iron complexes gave a weak intensity band in the 11,400-11,800 cm^{-1} region which may reasonably be assigned[16,33] to the $^5T_{2g} \longrightarrow {}^5E_g$ transition, consistent with an octahedral geometry around the metal ion. The electronic spectra of the cobalt complexes gave two ligand field bands in the regions 13,800-14,300 and 21,600-22,300 cm^{-1} which can be ascribed[18,33] to the $^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transitions, respectively, corresponding to an octahedral geometry of the cobalt ion. The band below 11,100 cm^{-1} could not be recorded as it is beyond the range of the instrument used. The broad band in the range 11,150-11,250 cm^{-1} and two distinct bands in the 20,000-20,800 and 27,600-27,850 cm^{-1} regions of the spectra of nickel complexes, may be attributable[33] to the $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$ transitions,

respectively. The electronic spectra of the copper complexes exhibit two bands in the regions 19,800-20,500 and 16,200-16,400 cm^{-1} assignable to the $^2B_{1g} \longrightarrow {}^2E_g$ and $^2B_{1g} \longrightarrow {}^2B_{2g}$ transitions, respectively, corresponding[20,33] to a distorted octahedral geometry of the copper ion. The magnetic moment values further support the proposed geometry. All the complexes exhibit a high-intensity band around 33,300 cm^{-1} due to the charge transfer transition (metal to ligand, or ligand to metal). The electronic absorption bands of all bis(macrocyclic) binuclear complexes, in comparison with those of similar mononuclear complexes reported[20] earlier, do not show appreciable differences. Furthermore, the magnetic moment values of the present complexes agree well with the mononuclear complexes reported[20] earlier. This similarity in electronic, spectral and magnetic moment data gives significant confirmation of the non-interacting metal centers in the present complexes.

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