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PREPARATION AND STRUCTURAL CHARACTERIZATION OF 14–16-MEMBERED PENDENT ARM MACROCYCLIC COMPLEXES OF TRANSITION METAL IONS

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Abstract—Template condensation reaction of ethylenediamine or propylenediamine, formaldehyde and benzidine in 1:2:1 molar ratio in methanol medium resulted in the formation of a new series of pendent arm hexaazamacrocyclic complexes of the type $[ML_1Cl_2]$ or $[ML_2Cl_2]$ (M^{II} = Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}). These polycrystalline compounds are soluble in DMSO and have been characterized by IR, ^1H NMR, EPR and electronic spectral studies, and conductivity and magnetic susceptibility measurements. An octahedral geometry is suggested for all the complexes, where two coordination sites are occupied by chloride ions and the other four by secondary amines.

Macrocyclic ligands containing multidentate centres have been the subject of considerable attention in recent years. It is now well established that multidentate macrocyclic ligands display unique and exciting chemistries in that they can stabilize unusual oxidation states of metal ions or they can function as receptors for substrates of widely differing physical and chemical properties.[1,2] Among the polyazamacrocycles, the tetraaza groups have been the most extensively studied. Pentaaza and higher polyazamacrocycles have begun to appear more frequently, particularly in view of the potential of the larger macrocycles to bind more than one metal ion.[3,4] Generally, macrocyclic ligands have been prepared either by conventional organic synthesis or by a template reaction involving cyclization in the presence of a metal ion. Recently, we have reported[5–8] the preparation of several transition metal macrocyclic complexes by the template condensation reaction. The size match selectively in macrocycles is very important.[9,10] The metal ion will form its most stable complexes with a number of a series of macrocycles where the match in size between the metal ion and the cavity in the ligand is closest.

Although the synthetic approaches to the preparation of various types of macrocycles have been thoroughly developed, relatively little work concerning the synthesis and characterization of macrocycles containing all nitrogen atoms in the fully saturated macrocyclic framework has been reported.[11] A large number of macrocyclic complexes have been prepared[12,13] by the template condensation reaction of primary diamines, formaldehyde and ammonia. Some reports[14,15] appeared in the literature for the synthesis of macrocyclic complexes obtained from polyamines and formaldehyde. Suh and Kang[11] successfully extended the synthesis of cyclam-like macrocycles by treating $[M(en)_2]^{2+}$ (M = Ni or Cu, en = ethylenediamine) with formaldehyde and a primary amine. Bernhardt and co-workers[16] have isolated various pendent arm macrocycles and studied their complexation properties. Here, we report a new series of pendent arm macrocyclic complexes $[ML_1Cl_2]$ and $[ML_2Cl_2]$ (M = Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}) obtained by the template condensation

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reaction of benzidine, formaldehyde and aliphatic primary diamines.

EXPERIMENTAL

Ethylenediamine, propylenediamine, formaldehyde and metal salts $FeCl_2$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and $ZnCl_2$ were obtained from Merck. The chemical benzidine is of SD's Fine Chemicals quality.

Synthesis of dichloro[1,8-*bis*(*biphenylamino*)-1,3,6,8,10,13-*hexaazacyclotetradecane*]*metal* (II), [ML_1Cl_2] (M = Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} *and* Zn^{II})

Ethylenediamine (0.65 cm^3, 10 mmol) was injected into a solution of metal chloride (5 mmol) dissolved in 30 cm^3 methanol with continuous stirring at room temperature. Formaldehyde (2 cm^3, 20 mmol) was then added dropwise with continuous stirring. To the reaction mixture benzedine (1.84 gm, 10 mmol) dissolved in the minimum quantity of methanol was added at room temperature, which changed the colour of the solution. The mother liquor was stirred overnight giving a solid material which was filtered, washed with methanol, vacuum dried and kept in a desiccator.

Synthesis of dichloro[1,9-*bis*(*biphenylamino*)-1,3,7,9,11,15-*hexaazacyclohexadecane*]*metal* (II), [ML_2Cl_2] (M = Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} *and* Zn^{II})

The procedure adopted for this synthesis was exactly analogous to that described above, but instead of ethylenediamine propylenediamine was added. The product thus obtained was filtered, washed with methanol and vacuum dried.

The elemental analyses for carbon, hydrogen and nitrogen were obtained from CDRI, Lucknow, India. ^1H NMR spectra in DMSO-d_6 using a Bruker AC 200 E spectrometer with Me_4Si as an internal standard were obtained from GNDU, Amritsar, India. The estimation of halogen was done gravimetrically[17] and the metals were estimated by titrating with standard EDTA solution.[18] 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 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 $25 \pm 0.01°C$.

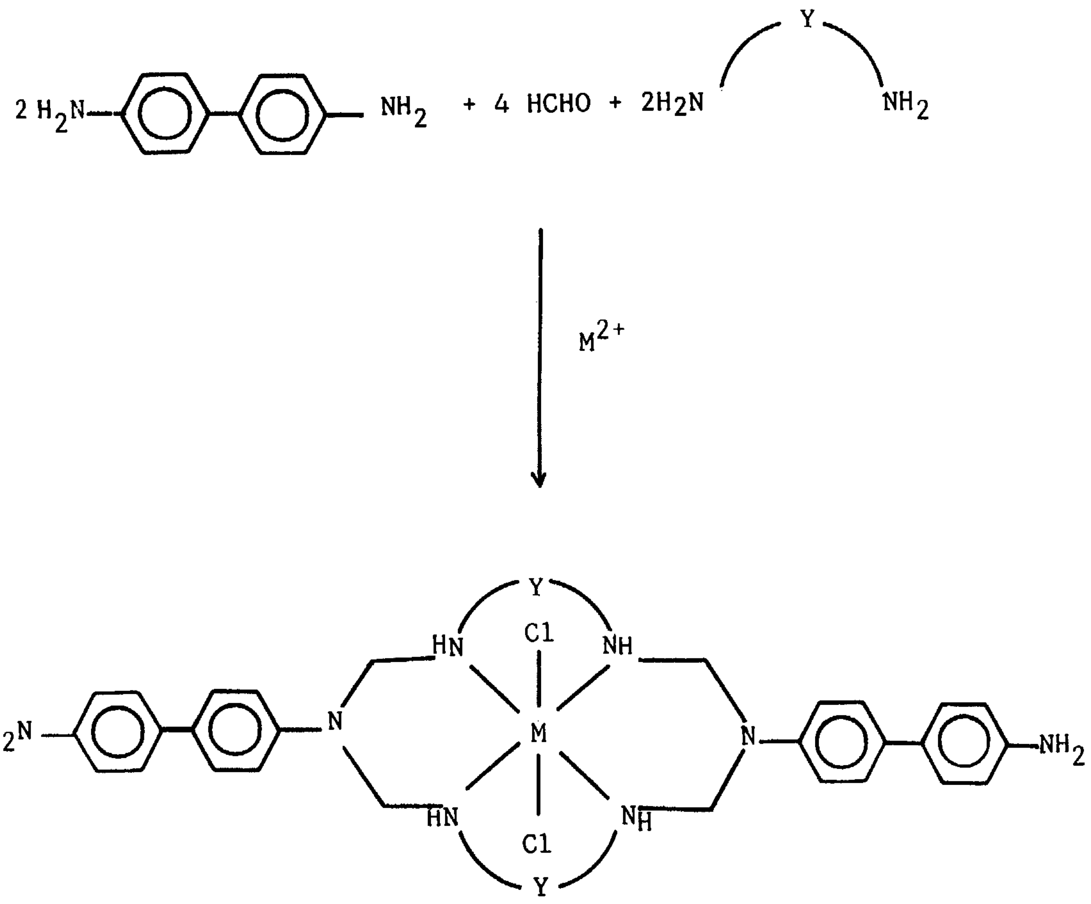
RESULTS AND DISCUSSION

Novel hexaazamacrocyclic complexes of the type [ML_1Cl_2] and [ML_2Cl_2] (M = Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}) were obtained by employing the metal template condensation reaction of ethylenediamine or propylenediamine, formaldehyde and benzidine in 1 : 2 : 1 molar ratio in methanol medium, thereby signifying the important role of the metal ion in the cyclization process. However, an attempt to synthesize the metal-free 14- and 16-membered hexaazamacrocyclic ligands L_1 or L_2 by the condensation reaction of aliphatic primary diamines, formaldehyde and benzidine did not prove to be successful.

The results of elemental analyses suggest that the proposed macrocyclic complexes have 1 : 1 metal to ligand stoichiometry, as shown in Scheme 1. All the compounds are found to be polycrystalline in nature, slightly soluble in DMF and MeCN and freely soluble in DMSO. The molar conductance values of all the compounds are in the range 11–22 $cm^2\ ohm^{-1}\ mol^{-1}$, which indicates[19] that they are non-electrolytes in DMSO (Table 1).

The preliminary identification of the macrocyclic complexes has been inferred from the IR spectra. The main bands and their assignments are listed in Table 2. The IR spectra of all the macrocyclic complexes do not show any peaks corresponding to a carbonyl group; instead, a new single, sharp, medium intensity band appeared in the region 3250–3210 cm^{-1}, which can be attributed[11] to the N—H stretching mode of the coordinated secondary amines. This strongly suggests that the proposed ligand framework is formed. However, the appearance of a doublet at 3380–3350 cm^{-1} in all the macrocyclic complexes may be due to the N—H stretching frequency of the primary amino groups of the benzidine moiety. The IR absorption bands in the 2950–2880 and 1450–1410 cm^{-1} regions observed in all the complexes may reasonably be assigned to the C—H stretching and C—H bending vibrational modes, respectively. The bands corresponding to phenyl group vibration and N—H deformation appeared at their expected positions (Table 2). The presence of a sharp band at 420–380 cm^{-1} in all the macrocyclic complexes is due to the M—N stretching vibrations.[20] However, a medium band in the frequency region 280–250 cm^{-1} has been assigned as an M—Cl stretching vibration.

The ^1H NMR spectra of all the Zn^{II} macrocyclic complexes show two broad signals in the regions 6.05–6.11 and 3.98–4.14 ppm and can be assigned



Scheme 1. M = Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} ; L_1, Y = $(CH_2)_2$; L_2, Y = $(CH_2)_3$.

Table 1. Colour, melting point, molar conductance and analytical data of the compounds

Compounds	Colour	M.p. (°C)	Λ_m (cm^2 ohm^{-1} mol^{-1})	Found (Calc.) (%)				
				C	H	N	M	Cl
$[FeL_1Cl_2]$	Light brown	210	11	57.9	5.9	16.8	8.2	10.6
				(57.9)	(6.3)	(7.8)	(8.4)	(10.7)
$[CoL_1Cl_2]$	Brown	238	22	57.6	5.9	16.3	8.6	(10.6)
				(57.7)	(6.0)	(16.8)	(8.9)	(10.7)
$[NiL_1Cl_2]$	Brown	216	15	57.7	5.9	16.7	8.7	10.6
				(57.7)	(6.0)	(16.8)	(8.7)	(10.7)
$[CuL_1Cl_2]$	Black	350	17	57.2	5.9	16.6	9.5	10.5
				(57.3)	(6.0)	(16.7)	(9.5)	(10.6)
$[ZnL_1Cl_2]$	White	225	13	57.1	5.9	16.6	9.6	10.5
				(57.1)	(6.0)	(16.7)	(9.7)	(10.6)
$[FeL_2Cl_2]$	Brown	220	20	59.0	6.4	16.2	8.0	10.2
				(59.7)	(6.4)	(16.2)	(8.1)	(10.3)
$[CoL_2Cl_2]$	Black	245	19	58.9	6.3	16.1	8.5	10.2
				(58.8)	(6.3)	(16.1)	(8.5)	(10.2)
$[NiL_2Cl_2]$	Grey	198	13	58.8	6.4	16.2	8.4	10.2
				(58.8)	(6.3)	(16.2)	(8.5)	(10.2)
$[CuL_2Cl_2]$	Bluish black	295	14	58.2	6.2	16.0	9.1	10.1
				(58.4)	(6.3)	(16.3)	(9.1)	(10.2)
$[ZnL_2Cl_2]$	Whitish cream	214	21	58.2	6.3	16.0	9.3	10.1
				(58.3)	(6.3)	(16.0)	(9.3)	(10.1)

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

Compounds	ν(NH/NH_2)	ν(C—H)	ν(C—N)	δ(N—H)	ν(M—N)	ν(M—Cl)	Ring vibrations
[FeL_1Cl_2]	3220 3390	2900	1180	1610	380	250	1410 1030 720
[CoL_1Cl_2]	3230 3380	2920	1180	1650	420	260	1430 1050 760
[NiL_1Cl_2]	3210 3370	2900	1200	1650	390	280	1410 1060 740
[CuL_1Cl_2]	3250 3350	2950	1210	1610	380	250	1420 1020 780
[ZnL_1Cl_2]	3240 3380	2930	1220	1630	350	300	1440 1060 730
[FeL_2Cl_2]	3230 3390	2920	1190	1600	370	260	1420 1040 730
[CoL_2Cl_2]	3220 3400	2950	1220	1640	400	280	1440 1060 780
[NiL_2Cl_2]	3180 3390	2940	1200	1620	360	250	1400 1080 750
[CuL_2Cl_2]	3240 3390	2900	1220	1600	370	250	1410 1030 750
[ZnL_2Cl_2]	3230 3400	2930	1210	1620	360	290	1430 1050 740

to the secondary amino proton (C—NH—C, 4H) and primary amino protons (C_6H_4—NH_2, 4H) of ethylenediamine or propylenediamine and benzidine moieties, respectively.[21,22] Two other multiplets observed at 2.41–2.51 and 2.96–3.18 ppm can be attributed to the methylene protons (N—CH_2—CH_2—N, 8H and N—CH_2—N, 8H) of primary amines and the aldehyde moiety. The ^1H NMR spectra of [ZnL_2Cl_2] gave a multiplet at 2.51 ppm, corresponding to the middle methylene protons (C—CH_2—C, 4H) of the propylenediamine moiety.[6] All the compounds gave a broad multiplet in the region 7.08–7.20 ppm, which is assigned[23] to the aromatic ring protons (C_6H_4, 16H). However, no band could be identified which may correspond to aldehyde protons, indicating that the proposed macrocyclic skeleton has been formed.

The EPR spectra of the polycrystalline copper(II) macrocyclic complexes were recorded at room temperature and their $g_\parallel$ and $g_\perp$ values have been calculated. All the complexes gave only a single broad signal with two g values. The absence of hyperfine splitting in these compounds may be due to the strong dipolar and exchange interactions between copper(II) ions in the unit cell.[24] In a $d_{x^2-y^2}$ ground state, the EPR spectrum should give $g_\parallel > g_\perp > 2.02$[25] in most cases, whilst a d_z^2 ground state usually gives a spectrum with $g_\perp > g_\parallel \sim 2.02$. The present macrocyclic complexes [CuL_1Cl_2] and [CuL_2Cl_2] studied here show $g_\parallel$ and $g_\perp$ values in the 2.149–2.155 and 2.050–2.058 ranges, respectively, which suggests that the ground state may be $d_{x^2-y^2}$. In axial symmetry, the g values are related[26] by the expression $G = (g_\parallel - 2)/(g_\perp - 2)$, which measures the exchange interaction between copper centres in the polycrystalline solid. The calculated G values for the present complexes appeared in the range 2.54–3.06, which suggests the existence of a considerable exchange interaction in these solid complexes. All the complexes show $g_\parallel < 2.3$. It should be noted[27] that for an ionic environment $g_\parallel > 2.3$, while for a covalent environment $g_\parallel < 2.3$, indi-

Table 3. Magnetic moment values, electronic spectral data and assignments

Compounds	μ_{eff} (B.M.)	Band position (cm^{-1})	Assignments
[FeL$_1$Cl$_2$]	5.39	11,500	$^5T_{2g} \rightarrow {}^5E_g$
[CoL$_1$Cl$_2$]	4.05	22,100	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
		17,200	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
[NiL$_1$Cl$_2$]	3.12	27,500	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
		20,000	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
		11,000	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
[CuL$_1$Cl$_2$]	1.70	19,400	$^2B_{1g} \rightarrow {}^2E_{2g}$
		16,300	$^2B_{1g} \rightarrow {}^2B_{2g}$
[FeL$_2$Cl$_2$]	5.41	11,700	$^5T_{2g} \rightarrow {}^5E_g$
[CoL$_2$Cl$_2$]	4.22	22,300	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
		17,300	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
[NiL$_2$Cl$_2$]	3.09	27,300	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
		20,100	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
		11,200	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
[CuL$_2$Cl$_2$]	1.66	19,200	$^2B_{1g} \rightarrow {}^2E_g$
		16,400	$^2B_{1g} \rightarrow {}^2B_{2g}$

cating that the present complexes exhibit considerable covalent character.

The electronic spectra of iron(II) complexes exhibit a weak intensity band in the 11,500–11,700 cm^{-1} region, which may reasonably be assigned to the $^5T_{2g} \rightarrow {}^5E_g$ transition, consistent[28] with an octahedral geometry around the iron(II) ion. The observed magnetic moment values for the macrocyclic cobalt(II) complexes appeared in the range expected for three unpaired electrons (Table 3). The electronic spectra (Table 3) of cobalt(II) complexes gave two bands in the regions 22,100–22,310 and 17,200–17,300 cm^{-1}, which may be ascribed[20,28] to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transitions, respectively, consistent with an octahedral geometry around the cobalt(II) ion. The macrocyclic complexes of nickel(II) show magnetic moments of 3.12 B.M., which corresponds to a spin-free complex, and the electronic spectrum shows three distinct bands, consistent[28] with the spectral features of octahedral nickel(II) complexes. The broad band around 11,000–11,200 cm^{-1} and two intense bands around 20,000–20,100 and 27,300–27,500 cm^{-1} may reasonably be assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively.

The electronic spectra of macrocyclic copper(II) complexes show a broad band maximum (Table 3) in the region 19,200–19,400 cm^{-1} with a shoulder in the region 16,300–16,400 cm^{-1}, which can unambiguously be assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively, corresponding[28] to a distorted octahedral geometry around the copper(II) ion. The magnetic moment values further confirm the above proposed geometry. Strikingly, all the macrocyclic complexes exhibit strong absorption around 30,000 cm^{-1}, which may be due to a charge-transfer band.

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