Pergamon

0277-5387(94)00395-5

Polyhedron Vol. 14, No. 10, pp. 1283–1288, 1995
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0277–5387/95 $9.50+0.00

TRANSITION METAL COMPLEXES OF 20–22-MEMBERED OCTAAZAMACROCYCLES: SYNTHESIS AND CHARACTERIZATION

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(*Received* 18 *July* 1994; *accepted* 26 *September* 1994)

Abstract—A series of binuclear octaazamacrocyclic complexes $[M_2L_1X_4]$–$[M_2L_2X_4]$ ($M = Ni^{II}$, Co^{II} and Zn^{II}; X = Cl or NO_3) and $[Cu_2L_1]X_4$–$[Cu_2L_2]X_4$ (X = Cl or NO_3) have been synthesized by template condensation reaction of aliphatic primary diamines with 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione in methanol. The overall geometry and stereochemistry of these complexes have been elucidated by IR, ^1H NMR, EPR and electronic spectral studies, and magnetic susceptibility and conductance values. An octahedral geometry around the metal ion is suggested for nickel, cobalt and zinc complexes, whilst a square planar geometry is proposed for copper complexes.

Metal ions are known to affect the steric course of reactions; the template syntheses of macrocyclic ligands are among the best examples. The design and synthesis of binculeating ligands and their metal complexes has been the subject of much recent interest.[1–3] The formation of rings will become disadvantageous with the increasing ring members owing to an increase in ring strain and a decrease in the probability of ring closure. There is considerable current interest[4–7] in the complexes of higher polydentate macrocyclic ligands because of the variety of geometrical forms available and the possible encapsulation of the metal ion. Several macrocyclic ligands derived from hydrazine precursors have been reported,[8–10] and most of the studies involved deal with mononuclear complexes. However, less work has been reported for higher membered polyazamacrocyclic complexes. Goedken and Peng[11] have reported the synthesis of 14-membered octaazamacrocyclic complexes by the template condensation reaction of butane-2,3-dione dihydrazone with formaldehyde. Recently, several reports[12–14] have appeared concerning the chemistry of binuclear macrocyclic complexes, especially structural, magnetism correlation and bioinorganic modelling studies. We have recently reported[15–18] the synthesis and characterization of polyaza and dithiadiaza macrocyclic complexes. Here, we wish to report the synthesis and characterization of octaazamacrocyclic complexes $[M_2L_1X_4]$–$[M_2L_2X_4]$ ($M = Co^{II}$, Ni^{II} and Zn^{II}) and $[Cu_2L_1]X_4$–$[Cu_2L_2]X_4$ (X = Cl or NO_3) obtained by the template condensation reaction of 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione with primary diamines, a system not reported hitherto.

EXPERIMENTAL

The metal salts, $MX_2 \cdot 6H_2O$ (M = Co and Ni; X = Cl or NO_3), $CuX_2 \cdot 2H_2O$ (X = Cl or NO_3), $ZnCl_2$ and $Zn(NO_3)_2 \cdot 6H_2O$ (all BDH) were commercially pure samples. The chemicals biacetyl (Aldrich), hydrazine hydrate (BDH), 1,2-diaminoethane and 1,3-diaminopropane (both Merck) were used as received. The diketone 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione was prepared by the literature method.[19]

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Synthesis of tetrachloro/nitrato(2,3,6,7,12,13,16,17-*octamethyl*-1,4,5,8,11,14,15,18-*octaazacycloeicosane*-1,3,5,7,11,13,15,17-*octaene*) *dimetal*(II), $[M_2L_1X_4]$ ($M = Co^{II}$, Ni^{II} *and* Zn^{II}; $X = Cl$ *or* NO_3)

To an ice-cold solution of metal salt (0.02 mol) in methanol (50 cm^3) was added 1,2-diaminoethane (0.02 mol) dissolved in methanol (50 cm^3), followed by the addition of 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione (0.02 mol) in methanol (50 cm^3). The resulting mixture was stirred continuously for *ca* 5 h. The resultant polycrystalline solid product was filtered and recrystallized from ethanol.

Synthesis of tetrachloro/nitrato(2,3,6,7,13,14,17,18-*octamethyl*-1,4,5,8,12,15,16,19-*octaazacyclodocosane*-1,3,5,7,12,14,16,18-*octaene*) *dimetal*(II), $[M_2L_2X_4]$ ($M = Co^{II}$, Ni^{II} *and* Zn^{II}; $X = Cl$ *or* NO_3)

These complexes were prepared by similar procedures to those discussed above but using 1,3-diaminopropane.

Synthesis of 2,3,6,7,12,13,16,17-*octamethyl*-1,4,5,8,11,14,15,18-*octaazacycloeicosane*-1,3,5,7,11,13,15,17-*octaene metal*(II) *chloride or nitrate*, $[Cu_2L_1]X_4$ ($X = Cl$ *or* NO_3) *and* 2,3,6,7,13,14,17,18-*octamethyl*-1,4,5,8,12,15,16,19-*octaazacyclodocosane*-1,3,5,7,12,14,16,18-*octaene dimetal*(II) *chloride/nitrate*, $[Cu_2L_2]X_4$ ($X = Cl$ *or* NO_3)

These complexes were also synthesized by a similar method as discussed above, except that the metal ion employed was copper(II).

The purities of all these compounds were checked by TLC by dissolving the appropriate complex in DMF and using ethyl acetate (80%)–methanol (15%)–acetic acid (5%) as eluant. Only one spot was observed in each case after developing in an iodine chamber, indicating that the compounds were pure.

The elemental analyses were obtained from the Microanalytical Laboratory of CDRI, Lucknow, India. ^{1}H 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[20] and gravimetrically,[21] respectively. The IR spectra (4000–400 cm^{-1}) were recorded as KBr discs on a Pye-Unicam SP3-300 spectrophotometer. The electronic spectra of the compounds in DMSO were recorded on a Pye-Unicam 8800 spectrophotometer at room temperature. EPR spectra 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 Systronics type 302 conductivity bridge equilibrated at 25 ± 0.01°C.

RESULTS AND DISCUSSION

A new series of octaazamacrocyclic complexes $[M_2L_1X_4]$–$[M_2L_2X_4]$ ($M = Co^{II}$, Ni^{II} and Zn^{II}; $X = Cl$ or NO_3) and $[Cu_2L_1]X_4$–$[Cu_2L_2]X_4$ ($X = Cl$ or NO_3) have been prepared by the metal ion controlled synthesis of 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione with aliphatic diamines. However, an attempt to synthesize the corresponding metal-free macrocyclic ligands did not prove successful and the reaction did not produce the ligand. In addition, the ligands corresponding to *o*-phenylenediamine could not be formed. All the complexes are polycrystalline solids and the elemental analysis results (Table 1) agree well with the binuclear structure shown in Scheme 1.

The molar conductance values (Table 1) in DMSO for cobalt, nickel and zinc complexes are suggestive of their non-electrolytic nature, while those of copper complexes show their electrolytic nature.[22]

The IR spectra of all the complexes exhibit a single sharp absorption band in the 1590–1620 cm^{-1} region, attributed[17] to the coordinated ν(C═N). No bands characteristic of free carbonyl or free amine were observed. The above information strongly suggests that the proposed ligand framework is formed. However, a medium intensity band in the 410–450 cm^{-1} region may reasonably be assigned to the M—N stretching vibration. Bands appearing in the regions 2880–2920 and 1410–1440 cm^{-1} in all the complexes may be due to ν(C—H) and δ(C—H), respectively. The spectra of nitrato complexes gave additional bands around 1230, 1040 and 870 cm^{-1}, which are consistent with the monodentate nature of this group. Bands appearing in the nitro and chloro complexes in the regions 230–240 and 270–300 cm^{-1} are assignable[23] to ν(M—O) and ν(M—Cl), respectively.

The EPR spectra (Table 2) of polycrystalline dicopper(II) macrocyclic complexes have been recorded at room temperature and all the complexes gave the same type of spectrum. However, none of the complexes gave hyperfine splitting, which may be due to the strong dipolar and exchange interactions between copper(II) ions in the unit cell, and a single broad signal was observed.

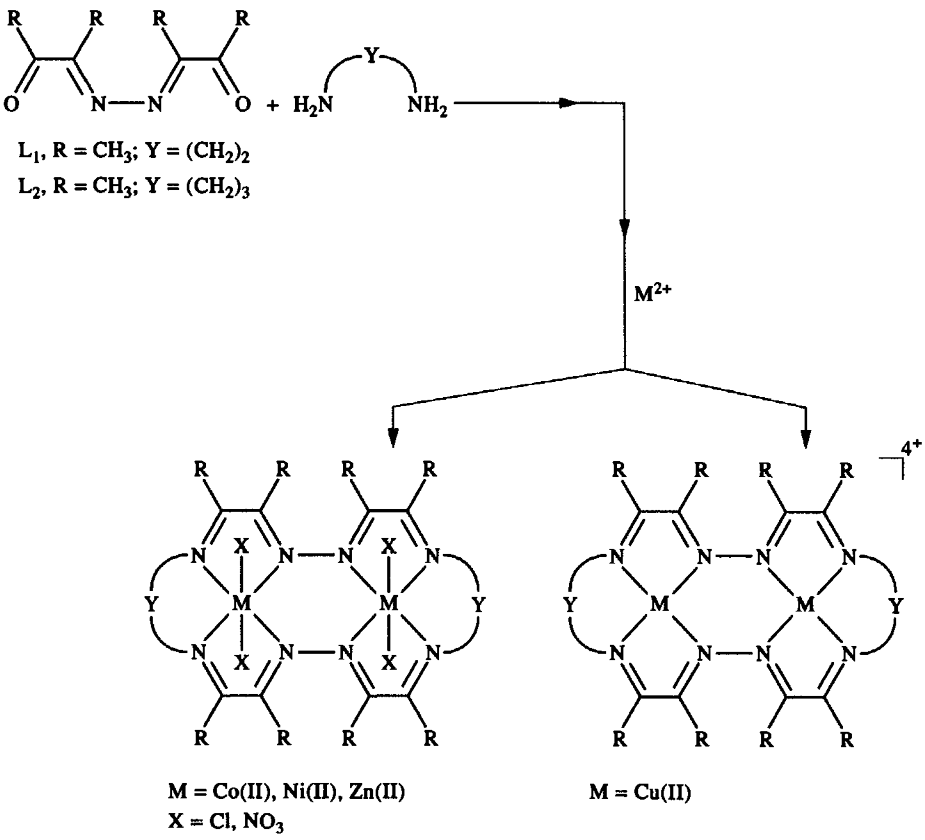
The EPR spectra of the present complexes gave

Table 1. Yield, colour, melting point, elemental analysis and molar conductivity values for the compounds

Compound	Yield (%)	Melting point (°C)	Colour	Found (Calc.) (%)					Molar conductivity ($cm^2\ ohm^{-1}\ mol^{-1}$)
				M	Cl	C	H	N	
$[Co_2L_1Cl_4]$	38	278	Bright green	18.2	21.8	37.6	4.9	17.3	19
				(18.3)	(22.1)	(37.3)	(5.0)	(17.4)	
$[Co_2L_1(NO_3)_4]$	30	255	Bright green	15.4	—	31.8	4.3	22.2	18
				(15.7)		(32.0)	(4.3)	(22.4)	
$[Co_2L_2Cl_4]$	43	180	Dark green	17.3	20.9	39.3	5.4	16.5	21
				(17.5)	(21.1)	(39.3)	(5.3)	(16.7)	
$[Co_2L_2(NO_3)_4]$	40	195	Dark green	14.9	—	34.1	4.5	21.6	16
				(15.1)		(33.9)	(4.6)	(21.6)	
$[Ni_2L_1Cl_4]$	45	160	Olive green	18.3	21.8	37.4	4.9	17.3	24
				(18.2)	(22.1)	(37.3)	(5.0)	(17.4)	
$[Ni_2L_1(NO_3)_4]$	35	215	Olive green	15.7	—	31.8	4.3	22.6	17
				(15.6)		(32.0)	(4.3)	(22.4)	
$[Ni_2L_2Cl_4]$	42	235	Yellowish green	17.7	21.4	39.1	5.2	16.8	20
				(17.5)	(21.2)	(39.2)	(5.4)	(16.7)	
$[Ni_2L_2(NO_3)_4]$	38	260	Yellowish green	14.8	—	33.8	4.5	21.6	24
				(15.1)		(34.0)	(4.6)	(21.6)	
$[Cu_2L_1]Cl_4$	48	190	Dark green	19.5	21.8	36.5	5.0	17.3	115
				(19.4)	(21.7)	(36.7)	(4.9)	(17.2)	
$[Cu_2L_1](NO_3)_4$	41	175	Dark green	16.8	—	31.7	4.3	22.3	98
				(16.7)		(31.6)	(4.2)	(22.1)	
$[Cu_2L_2]Cl_4$	33	214	Light green	18.5	21.0	38.7	5.3	16.5	109
				(18.6)	(20.8)	(38.8)	(5.3)	(16.4)	
$[Cu_2L_2](NO_3)_4$	38	190	Light green	15.8	—	33.6	4.5	21.5	119
				(16.1)		(33.5)	(4.6)	(21.4)	
$[Zn_2L_1Cl_4]$	42	140	Colourless	20.0	21.5	36.4	5.0	17.0	17
				(19.9)	(21.6)	(36.5)	(4.9)	(17.1)	
$[Zn_2L_1(NO_3)_4]$	35	156	Colourless	16.9	—	31.4	4.2	21.8	16
				(17.1)		(31.5)	(4.2)	(22.0)	
$[Zn_2L_2Cl_4]$	48	193	Colourless	19.4	20.3	38.5	5.4	16.5	21
				(19.1)	(20.7)	(38.5)	(5.3)	(16.4)	
$[Zn_2L_2(NO_3)_4]$	42	170	Colourless	16.7	—	33.5	4.7	21.3	20
				(16.5)		(33.4)	(4.6)	(21.2)	

$g_{\parallel}$ and $g_{\perp}$ values in the regions 2.02–2.23 and 2.09–2.10, respectively, which indicate[24] essentially a $d_{x^2-y^2}$ ground state for the copper(II) ion. Proctor and co-workers have postulated[25] that the magnitude of the ratio $G = (g_{\parallel}-2)/g_{\perp}-2)$ indicates the possibility of exchange interaction in the copper(II) complexes. In the present case, the value appeared in the range 2.00–2.55, which indicates ($G < 4$) considerable exchange interaction in the solid complexes. It has been reported[26] that the $g_{\parallel}$ value in a copper(II) complex can be used as a measure of the covalent character of the metal–ligand bond. If this value is greater than 2.3 the environment is essentially ionic and values less than this limit are indicative of a covalent environment. The present complexes show considerable covalent character.

The ^1H NMR spectra of all the macrocyclic zinc(II) complexes have been recorded do not show any signal attributable to amino protons, suggesting that the proposed macrocyclic skeleton has been



Scheme 1.

formed by the condensation reaction. The ^{1}H NMR spectra of all the macrocyclic complexes show a singlet in the 2.20–2.38 ppm range due to the methyl protons[16] (C—CH$_3$, 24H) of the 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione moiety. However, the ^{1}H NMR spectra of the complexes [Zn$_2$L$_1$X$_4$] show a singlet at 3.09–3.13 ppm region and a multiplet for the complexes [Zn$_2$L$_2$X$_4$] at 3.10–3.14 ppm region corresponding to the methylene protons[27] adjacent to the nitrogen (N—CH$_2$, 8H), while the middle methylene protons (C—CH$_2$—C, 4H) of the propane chain of the complexes [Zn$_2$L$_2$X$_2$] show a multiplet in the region 2.08–2.13 ppm.

The μ_{eff} values (Table 2) are normal, which suggest the absence of any strong interaction between the electrons of the two metal centres. The electronic spectra of dicobalt(II) complexes exhibit two ligand field bands (Table 2), which are assignable[28] to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively, corresponding to the octahedral geometry around the cobalt(II) ion. However, the electronic spectra of dinickel(II) complexes show two bands which may be attributed[29] to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively, which corresponds to spin-free octahedral geometry around the nickel(II) ion. The dicopper(II) complexes gave a broad band around 16,000 cm^{-1} along with two shoulders, which may be ascribed[28] to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively, suggesting a square planar geometry of the copper ion.

Acknowledgements—Dr Saji P. Varkey is grateful to the CSIR, New Delhi for financial support. Mr Omar S. M. Nasman is grateful to El-Azhar University and the Islamic University, Gaza for financial and mutual support for this work. We thank Dr Istiaque Ahmad (GNDU, Amritsar) for providing IR and ^{1}H NMR facilities. Dr Alex Punnoose is gratefully acknowledged for EPR spectra.

Table 2. μ_{eff} and ligand field bands observed in the electronic spectra and EPR spectral data for the compounds

Compounds	μ_{eff} (μ_B)	Band position (cm^{-1})	Assignments	EPR data		
				$g_\parallel$	$g_\perp$	G
[$Co_2L_1Cl_4$]	4.55	14,100	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	—	—	—
		21,700	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$			
[$Co_2L_1(NO_3)_4$]	4.61	13,900	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	—	—	—
		22,100	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$			
[$Co_2L_2Cl_4$]	4.50	14,500	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	—	—	—
		21,900	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$			
[$Co_2L_2(NO_3)_4$]	4.63	14,200	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	—	—	—
		21,500	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$			
[$Ni_2L_1Cl_4$]	3.10	11,400	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	—	—	—
		17,300	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$			
[$Ni_2L_1(NO_3)_4$]	2.99	11,300	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	—	—	—
		17,250	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$			
[$Ni_2L_2Cl_4$]	3.10	11,200	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	—	—	—
		17,500	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$			
[$Ni_2L_2(NO_3)_4$]	3.13	11,350	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	—	—	—
		17,250	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$			
[Cu_2L_1]Cl_4	1.75	16,050	$^2B_{1g} \rightarrow {}^2A_{1g}$	2.23	2.09	2.55
		21,500	$^2B_{1g} \rightarrow {}^2E_g$			
		12,600	$^2B_{1g} \rightarrow {}^2B_{2g}$			
[Cu_2L_1]$(NO_3)_4$	1.73	16,000	$^2B_{1g} \rightarrow {}^2A_{1g}$	2.20	2.10	2.00
		22,000	$^2B_{1g} \rightarrow {}^2E_g$			
		12,800	$^2B_{1g} \rightarrow {}^2B_{2g}$			
[Cu_2L_2]Cl_4	1.80	16,100	$^2B_{1g} \rightarrow {}^2A_{1g}$	2.22	2.09	2.44
		22,200	$^2B_{1g} \rightarrow {}^2E_g$			
		11,900	$^2B_{1g} \rightarrow {}^2B_{2g}$			
[Cu_2L_2]$(NO_3)_4$	1.71	16,000	$^2B_{1g} \rightarrow {}^2A_{1g}$	2.23	2.10	2.30
		21,900	$^2B_{1g} \rightarrow {}^2E_g$			
		12,500	$^2B_{1g} \rightarrow {}^2B_{2g}$			

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