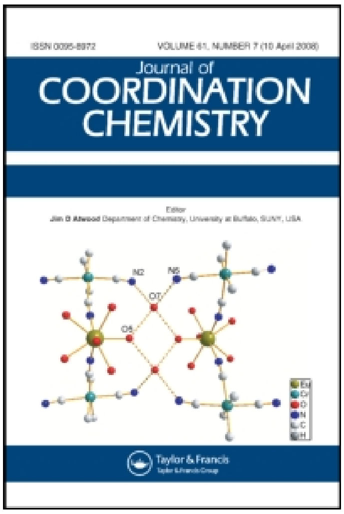

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Ramesh Bembi[a]; Randhir Singh[a]; Shabana Aftab[a]; Tapashi G. Roy[a]; Amrit K. Jhanjee[a]
[a] Department of Chemistry, University of Roorkee, Roorkee, U.P, India

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SYNTHESIS AND CHARACTERIZATION OF COPPER(II) AND NICKEL(II) COMPLEXES WITH 1,5,8,12-TETRAAZACYCLOHEPTADECANE AND 1,5,8,12-TETRAAZACYCLOOCTADECANE

RAMESH BEMBI, RANDHIR SINGH, SHABANA AFTAB, TAPASHI G. ROY
and
AMRIT K. JHANJEE
Department of Chemistry, University of Roorkee, Roorkee 247667, U.P., India

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Copper(II) and nickel(II) complexes with 1,5,8,12-tetraazacycloheptadecane and 1,5,8,12-tetraazacyclooctadecane have been synthesised. These complexes contain 8- and 9-membered chelate rings. The visible spectra of the copper(II) complexes show that the 5,6,5 chelate ring sequence is the most favourable geometry for coordination. The nickel(II) complex of 1,5,8,12-tetraazacycloheptadecane is square planar, but can be converted into corresponding octahedral complexes. The geometrical features of this macrocyclic ligand show that the 4-coordinate nickel(II) species is favoured over the 6-coordinate one.

Keywords: macrocycles; synthesis; stability; nickel(II); copper(II)

INTRODUCTION

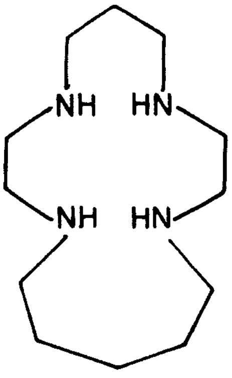
Stabilities of macrocyclic complexes have attracted significant attention during recent years.[1-7] In the case of tetraaza macrocycles, the cavity size and that of the chelate rings appear to be the most important factors in determining stability. In order to further investigate these aspects, we have recently carried out studies[8] on two new macrocycles, 1,4,8,11-tetraazacyclohexadecane, L^1, (with a 5,6,5,8 chelate ring sequence) and 1,4,8,11-tetraazacycloheptadecane, L^2, (with a 5,6,5,9 chelate ring sequence). These studies have now been extended to two other such macrocycles, 1,5,8,12-tetraazacycloheptadecane, L^3, (with 6,5,6,8 chelate ring sequence) and 1,5,8,12-tetraazacyclooctadecane, L^4, (with a 6,5,6,9 chelate ring sequence). The results of these studies show that in addition to the above mentioned two factors, the sequence in which the chelate rings occur has a marked influence on the stability of these complexes. It appears that the 5,6,5 chelate ring sequence is ideal for coordination in the case tetraaza macrocyclic complexes, since this holds the four nitrogen donors in a 'pre-oriented' configuration which is favourable for coordination.

EXPERIMENTAL

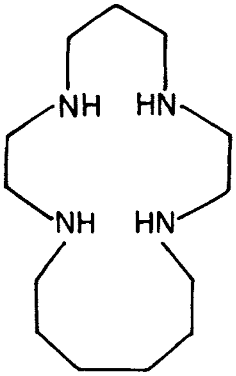
The ligands L^3 and L^4 were prepared by condensation of 3,2,3-tet with 1,5-pentanediol or 1,6-hexanediol by a method similar to one reported earlier.[8]

$[CuL](ClO_4)_2$

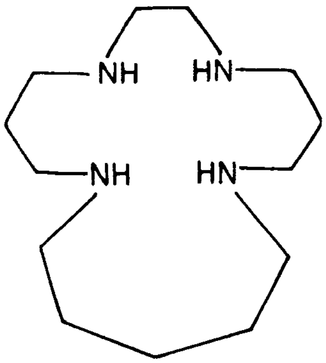
The ligand (20 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (20 mmol) were dissolved in 20 cm^3 of methanol and heated on a steam bath until the volume was reduced to *ca* 5 cm^3. To this solution was added 0.5g of $LiClO_4$ and the mixture allowed to stand for a few hours. The greenish blue product in the case of L^3 and the bright blue one in the case of L^4



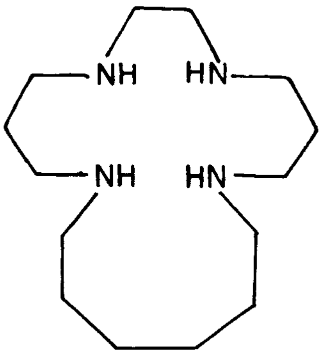
L^1



L^2



L^3



L^4

crystallized out during this period. The copper(II) complexes were filtered, washed with isopropanol then ether, and dried *in vacuo*.

$[NiL^3](ClO_4)_2$

The ligand L^3 (20 mmol) and $Ni(ClO_4)_2 \cdot 6H_2O$ (20 mmol) were dissolved in 20 cm^3 of methanol which had been acidified with a drop of $HClO_4$. The solution was heated on a steam bath until the volume was *ca* 5 cm^3. 0.5g of $LiClO_4$ was added and the solution cooled to room temperature. The orange coloured product which settled down was filtered, washed with isopropanol then ether, and dried *in vacuo*.

$[NiL^3Cl_2]$ and $[NiL^3(SCN)_2]$

$[NiL^3Cl_2](ClO_4)_2$(10 mmol) and KCl or KSCN (20 mmol) were dissolved in 100 cm^3 of methanol and stirred for 1 h. The precipitated $KClO_4$ was filtered and the filtrate slowly taken to dryness on a steam bath. The blue residue was extracted with chloroform and removed by filtration. The filtrate on evaporation gave the crude complex, which was recrystallized from acetonitrile to give green crystals of $[NiL^3Cl_2]$ and blue crystals of $[NiL^3(SCN)_2]$. Both complexes are highly hygroscopic and give orange coloured products very rapidly on exposure to moisture.

Conductance measurements were carried using a Systronics 302 conductivity bridge and a dip cell, at 25 ± 0.1°. Infrared spectra were measured in KBr pellets on a Beckmann IR 20 spectrophotometer. Electronic spectra were recorded on a Carl Zeiss Spectrocord recording spectrophotometer.

D.C. polarograms were recorded on a Cambridge pen-recording polarograph at 25 ± 0.1° using a dropping mercury electrode together with a saturated calomel electrode. 0.1M KCl or 0.1M $NaClO_4$ was used as the supporting electrolyte. A solution of 0.02% triton X-100 was used as supressor.

RESULTS AND DISCUSSION

The ligands are obtained with a yield of *ca* 40%. L^3 forms complexes with copper(II) and nickel(II) while for L^4 only a copper(II) was isolated. They do not give any complexes with cobalt(III). The non-complexation is probably due to the unsuitable geometrical orientation of the donor nitrogens by virtue of the 6,5,6,8 and 6,5,6,9 chelate ring sequence.

Copper(II) Complexes

L^3 gives a greenish blue copper(II) complex while L^4 gives a bright blue copper(II) complex. Conductance measurements show the two copper(II) complexes to be 2:1 electrolytes. The infrared spectra show a single νNH band (*ca* 3260 cm^{-1}) and characteristic perchlorate bands (*ca* 1100 cm^{-1} and 620 cm^{-1}). The perchlorate is ionic in the solid complexes, since there is no splitting of the perchlorate band around 1100 cm^{-1}.

The electronic spectra show a single d → d band, as do other square-planar copper(II) tetraaza macrocyclic complexes. The copper(II) complexes generally have square-planar or tetragonally distorted octahedral structures, for which broad bands are observed due to the overlap of the $a_{1g} \rightarrow b_{1g}$, $b_{2g} \rightarrow b_{1g}$ and $b_{2g} \rightarrow b_{1g}$ transitions in the visible region.[9] The $b_{2g} \rightarrow b_{1g}$ transition is equal to the difference in the energies of the d_{xy} and $d_{x^2-y^2}$ states and thus gives an approximate value of $10Dq_{xy}$. It has been further shown that this value of $10Dq_{xy}$ is proportional to the strength of the metal nitrogen in-plane interactions.[10] On this basis, the order of field strength[11] in terms of the ring size of the macrocycle is 14 > 13 > 15 > 16. The 14-membered cavity (with a 5,6,5,6 chelate ring sequence) is the best-fit case. In the larger rings, the structure is probably planar with longer Cu-N bonds, while in the case of 13-membered and smaller rings, the metal sits

TABLE I
Analytical[a] and conductivity data for the complexes.

Complex	C(%)	H(%)	N(%)	Λ_M (ohm^{-1} cm^2 mol^{-1})
		(a)		
$[CuL^3](ClO_4)_2$	30.8(30.9)	6.0(6.0)	11.2(11.1)	166[b]
$[CuL^4](ClO_4)_2$	32.3(32.4)	6.2(6.2)	10.9(10.8)	175[b]
$[NiL^3](ClO_4)_2$	31.2(31.2)	5.9(6.1)	11.2(11.2)	171[b]
$[NiL^3Cl_2]$	41.9(42.0)	8.0(8.1)	14.9(15.1)	0.1[c]
$[NiL^3(SCN)_2]$	43.3(43.2)	7.4(7.3)	20.1(20.2)	0.1[c]

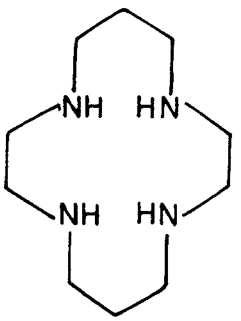
[a] Calculated percentages are given in parentheses. [b] In water. [c] In dichloromethane.

Table II
Spectral and enthalpy data[a] for some copper(II)-tetraazamacrocyclic complexes, $[CuL]^{2+}$

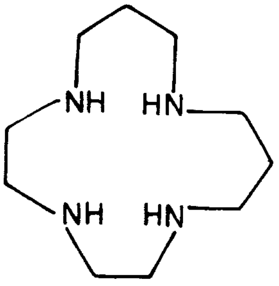
Macrocycle	$\nu(\varepsilon)^b$	$-\Delta H$ (kJ mol^{-1})	Chelate Ring Sequence	Ref.
L^1	18.587(90)		5.6.5.8	8
L^2	17.600(213)		5.6.5.9	8
L^3	17.460(261)		6.5.6.8	this work
L^4	16.100(110)		6.5.6.9	this work
L^5	19.900(100)	135.6	5.6.5.6	14
L^6	18.200(172)	116.3	5.6.6.5	14
L^8	17.600(213)	87.5	5.5.5.7	14
L^9	17.390(205)	95.0	5.5.5.6	18
L^{10}	19.685(92)		5.6.5.6	19
L^{11}	17.094(130)	110.9	6.6.6.5	11
L^{12}	16.529(104)	83.6	6.6.6.6	11
L^{13}	18.519(285)	107.1	5.6.5.5	11

[a] Enthalpy change, $-\Delta H$, refers to the reaction $M^{2+}_{(aq)} + L_{(aq)} \rightleftharpoons ML^{2+}_{(aq)}$ at 25° with $I = 0.5$ mol dm^{-3}. [b] Maxima (cm^{-1}) with extinction coefficients (M^{-1} cm^{-1}) in parentheses.

atop the N_4-arrangement resulting in weaker Cu-N interactions.[10,12,13] A comparison of the spectral data for a variety of copper(II) complexes with saturated tetraazamacrocycles (Table II) shows that besides the cavity size, the sequence of the chelate rings and their sizes play dominant roles in deciding the strength of the Cu-N interaction. Cyclam, L^5, (5,6,5,6) forms the most stable copper(II) complex, since it is able to dispose its donor nitrogens closest to the metal ion-preferred sites at the corners of the equatorial square in tetragonal geometry. In the case of isocyclam, L^6, (5,5,6,6) there is a loss of Cu-N bond strength although it has a 14-membered cavity. The introduction of bulky chelate rings (7-, 8- and 9-membered) also leads to a weaker Cu-N interaction.[14] In spite of the 8- and 9-membered chelate rings in L^1 and L^2, the strength of Cu-N interaction is quite high by virtue of the 5,6,,5 chelate ring sequence. It is intriguing to note that the extinction coefficients of the complexes with this 5,6,5 sequence are quite similar. The sequence places the nitrogen donors in a pre-oriented geometry favourable for coordination. The values of $\Delta H_{(aq)}$[14] also show trends similar to the ν(d → d) values. The values show that the 5,6,5 sequence enjoys an enthalpic advantage over other chelate ring sequences.



L5



L6

TABLE III
Relative abundance of 4-coordinate and 6-coordinate nickel(II)-macrocyclic complexes at 25° in aqueous solution

Macrocycle	%4-Coordinate Species	% 6-Coordinate Species	Ref.
L^1	75	25	8
L^2	40	60	8
L^3	100		this work
L^7	75	25	16
L^8	61	39	16
L^{13}	87	13	16
L^{14}	44	56	16

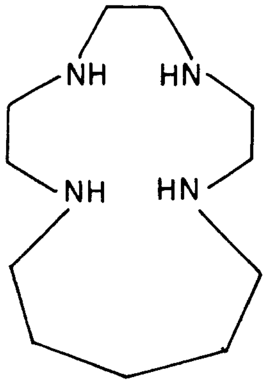
Nickel(II) Complexes

The yellow complex $[NiL^3](ClO_4)_2$ is a 2:1 electrolyte. The infrared spectra show a single νNH band at 3200 cm^{-1} and perchlorate bands at 1100 cm^{-1} and 620 cm^{-1}. The visible spectra show a single broad d → d band at 20,900 cm^{-1} ($\varepsilon = 90$) which is typical of square planar nickel(II) complexes.

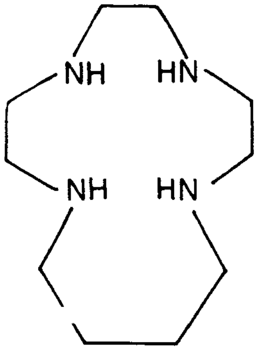
The complex $[NiL^3](ClO_4)_2$ does not show any octahedral -planar equilibrium which is in contrast to behaviour observed with $[NiL^1](ClO_4)_2$ and $[NiL^2](ClO_4)_2$.[8] The 13-membered ring in tetraaza macrocycles provides the best-fit cavity for nickel(II).[15] With larger cavities an elongation of the Ni-N bonds occurs. Since the Ni-N bonds are longer in the case of paramagnetic 6-coordinate complexes as compared to corresponding diamagnetic 4-coordinate complexes, a larger macrocyclic ligand facilitates the formation of 6-coordinate complexes. Therefore, the relative amount of 6-coordinate species in equilibrium with the 4-coordinate species in solution (Table III) increases with an increase in the ring size of the macrocycle.[16] In the case of nickel(II) complexes with macrocycles giving 8-membered chelate rings, the 4-coordinate species is especially favoured by virtue of the structural features of the ligand.[8,16]

X-ray analysis[17] of a nickel(II) complex of L^7 shows that the skeletal structure is extremely distorted. All the carbons of the 8-membered chelate ring lie on one side of the NiN_4 plane. As a result, the methylene protons adjacent to the nitrogens sterically hinder coordination at the axial sites in both *cis* and *trans*-configurations, thus favouring the 4-coordinate species. Molecular models of $[NiL^3](ClO_4)_2$ show that in this complex the N(1) proton (I) is equatorial while others are axial with a severely distorted macrocyclic ring. All the carbon atoms of the 8-membered chelate ring lie on one side of the NiN_4 plane, while the carbons of the two 6-membered chelate rings lie on the opposite side of the NiN_4 plane. The central five membered ring has an almost eclipsed conformation. The methylene protons of the 6- and 8-membered chelate rings strongly shield the apical coordination sites of the nickel(II) ion and hinder coordination of other molecules, thereby giving only 4-coordinate species.

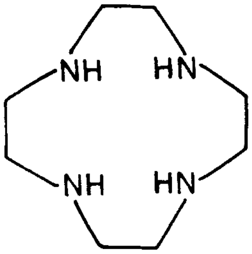
$[NiL^3](ClO_4)_2$ forms the two 6-coordinate complexes $[NiL^3Cl_2]$ and $[NiL^3(SCN)_2]$ when solutions of their corresponding four coordinate complexes, $[NiL^3]Cl_2$ and $[NiL^3](SCN)_2$ are slowly heated to dryness. Spectral data for these complexes are given in Table IV. Molecular models show that both complexes have highly distorted geometries. They are highly hygroscopic and rapidly revert to yellow 4-coordinate planar species on exposure to moisture.



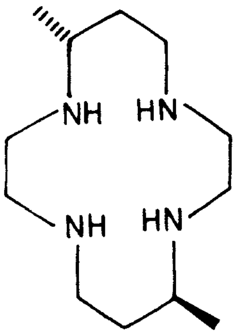
L^7



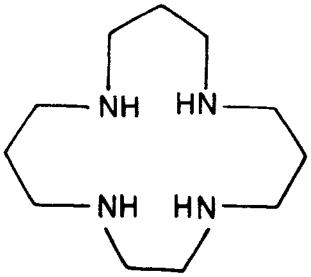
L^8



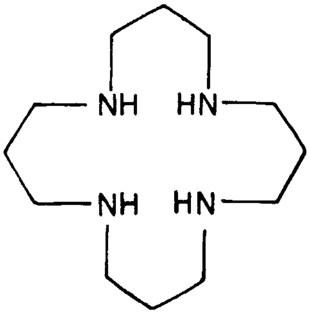
L^9



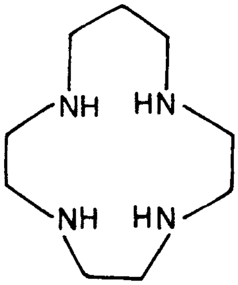
L^{10}



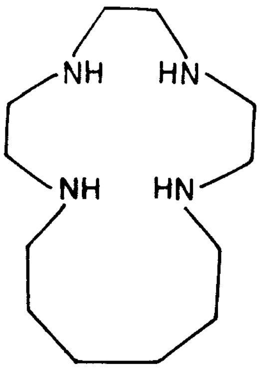
L^{11}



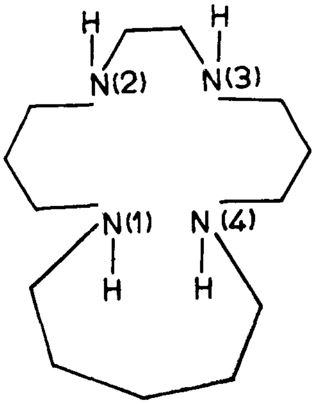
L^{12}



L^{13}



L^{14}



(I)

TABLE IV

Spectral data for the nickel(II)-tetraazamacrocyclic complexes.

Complex	Infrared Spectra (cm^{-1})			Electronic Spectra[a]
	νNH	νClO$_4$	ν(SCN)	
[NiL^3](ClO$_4$)$_2$	3260	1100, 620		20,900(90)
[NiL^{3}Cl$_2$]	3240			25,316(61), 15,625(27); 12,422(18); 11,628(19).
[NiL^3(SCN)$_2$]	3220		2040	28,169(61), 17,094(31); 12,500(16); 11,494(25)

[a] Absorbance maximum (cm^{-1}) is given with extinction coefficient (M^{-1} cm^{-1}) in parentheses.

Polarographic Studies

The copper(II) complexes show a single, diffusion controlled, one electron transfer, reversible wave due to the Cu(II)/Cu(I) couple. The half wave potentials decrease with increasing ring size (Table V). This variation is in the same order as corresponding ligand field strengths.[11] The nickel(II) complexes did not show any well defined wave.

TABLE V

D.C. Polarographic half-wave potentials for the copper(II)-macrocyclic complexes.

Complex	$E_{1/2}$ (-V) *vs* SCE	
	A[a]	B[a]
[CuL^1](ClO$_4$)$_2$	0.61	0.55
[CuL^2](ClO$_4$)$_2$	0.44	0.54
[CuL^3](ClO$_4$)$_2$	0.50	0.47
[CuL^4](ClO$_4$)$_2$	0.26	0.27
[CuL^6](ClO$_4$)$_2$	0.80	0.72
[CuL^{10}](ClO$_4$)$_2$	0.74	0.78

[a] Supporting electrolyte: A: 0.1M KCl, B: 0.1M NaClO$_4$.

ACKNOWLEDGEMENTS

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