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Complexation properties of a heteroditopic cryptand towards $\mathrm{Cu^{II}}$ and $\mathrm{Ni^{II}}$, crystal structures of the cryptand and its nickel(II) cascade complex†

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The crystal structure of the heteroditopic cryptand (L) formed by Schiff-base condensation of tris(2-aminoethyl)amine and 2,2′,2″-nitrilotris(ethyleneoxy)tris(benzaldehyde) followed by reduction with $\mathrm{NaBH_4}$ has been determined. The molecule has an *endo-endo* conformation with a pseudo-three-fold symmetry axis passing through the two bridgehead nitrogens. This symmetry is maintained in chloroform solution as indicated by its ^{1}H NMR spectrum. The cryptand accepts a metal ion ($\mathrm{Cu^{II}}$, $\mathrm{Zn^{II}}$ or $\mathrm{Ni^{II}}$) inside the cavity forming mononuclear cryptates of general formula $\mathrm{[ML][ClO_4]_2}$. The metal ion occupies the $\mathrm{N_4}$ end of the cavity. The light blue $\mathrm{CuN_4}$ chromophore thus formed exhibits an axial EPR spectrum with very small $A_{\parallel}$ value (63×10^{-4} cm^{-1}) and a low-energy ligand-field band. Nickel(II) initially forms a blue $\mathrm{[NiL][ClO_4]_2}$ complex which on dissolving in moist MeCN solution crystallizes as purple rectangular parallelopipeds with the formulation $\mathrm{[NiL(H_2O)(MeCN)][ClO_4]_2{\cdot}H_2O{\cdot}2MeCN}$. The crystal structure of this complex has also been determined. The $\mathrm{Ni^{II}}$ ion is octahedrally co-ordinated with the equatorial sites occupied by the three secondary amino N atoms of the cryptand and the N atom of the bound MeCN. The axial sites are occupied by the bridgehead N and the O atom of the water molecule which enters the cavity forming a cascade complex.

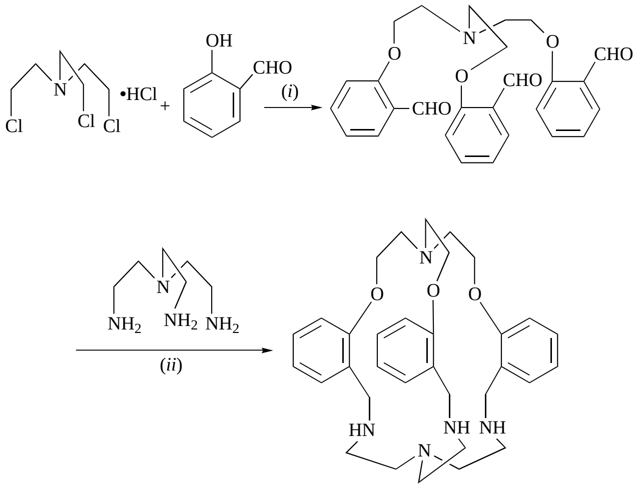
The synthesis of macropolycyclic compounds with recognition site(s) for transition-metal ions is a subject of considerable current interest[1–10] due to their use in many research areas. It has been observed, that macrobicyclic cryptands incorporating nitrogen donors readily accept transition-metal ion(s) inside their cavities forming cryptates. We have been involved [11–13] in synthesizing heteroditopic cryptands through [1 + 1] Schiff-base condensation of tripodal triamines with tripodal trialdehydes. Only one end of the cavity of such a cryptand is recognized by transition-metal ions leaving the other end vacant. Such cryptates are useful in homogeneous catalysis,[14] or in stabilizing metal–ligand bonds which are otherwise unstable.[13] Besides, they are well suited for studying chelation-enhanced fluorescence,[15] and for making ordered structures like vesicles,[16] *etc*. It is, therefore, important to probe the metal-binding abilities of the heteroditopic cryptands. Here we describe an improved synthesis of a heteroditopic cryptand (L) and its complexing properties towards $\mathrm{Cu^{II}}$ and $\mathrm{Ni^{II}}$. The structures of L and of the nickel(II) cryptate, $\mathrm{[NiL(H_2O)(MeCN)][ClO_4]_2{\cdot}H_2O{\cdot}2MeCN}$, are also described. The latter provides the first example of a water molecule bonded to the metal ion inside the cavity in a cascade fashion. A copper(II) ion bonded to a water molecule inside the cavity of an oxaaza macrobicycle has been reported previously.[17]

Experimental

Reagent-grade chemicals (Aldrich) were used as provided. All the solvents (SD Fine Chemicals, India) were purified prior to use. Spectroscopic and microanalytical data for the complexes were collected as described[18] earlier.

Preparations

Cryptand L. The synthesis of L by tripod–tripod Schiff-base condensation in the presence of $\mathrm{Cs^I/Rb^I}$ as the templating metal ion has been reported[11] by us. An improved method on the multigram scale without involving any templating metal ion is described here. In a typical experiment, the tripodal trialdehyde (Scheme 1) (3.68 g, 8 mmol) dissolved in a mixture of dry MeOH (500 cm^3) and dry tetrahydrofuran (thf) (50 cm^3) was cooled to 5 °C. To this was added a solution of tris(2-aminoethyl)amine (1.17 g, 8 mmol) in MeOH (300 cm^3) over a period of 12 h with constant stirring while maintaining the temperature at 5 °C. After the addition was complete the light yellow solution was allowed to warm to room temperature and kept for another 4 h. The Schiff base formed was not isolated but immediately treated with an excess of solid $\mathrm{NaBH_4}$ (≈1.6 g) and refluxed for 2 h. After complete removal of the solvent the white solid left was shaken with water (40 cm^3) and the desired cryptand (L) was extracted with $\mathrm{CHCl_3}$ (4×50 cm^3). The organic layer after drying over anhydrous $\mathrm{Na_2SO_4}$ was completely evaporated to obtain L as a colourless solid in 65% yield, m.p. 144 °C (uncorrected). NMR ($\mathrm{CDCl_3}$): ^{1}H (80 MHz), δ 2.5 (m, 12 H), 3.2 (t, 6 H), 3.6 (s, 6 H), 4.1 (t, 6 H) and 7.1 (m, 12 H);



L

Scheme 1 (*i*) NaOH, EtOH, reflux; (*ii*) 5 °C, MeOH + thf, $\mathrm{NaBH_4}$ *in situ*

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† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

^{13}C (20.1 MHz), δ 47.06, 48.60, 54.37, 55.30, 67.55, 111.29, 120.63, 127.16, 128.70, 131.33 and 156.35. FAB mass spectrum: *m/z* 560 (L^+) (Found: C, 70.25; H, 8.3; N, 12.4. $C_{33}H_{45}N_5O_3$ requires C, 70.8; H, 8.1; N, 12.5%). Colourless X-ray-quality crystals of L were grown by slow evaporation of an acetonitrile solution at room temperature.

$[CuL][ClO_4]_2$ 1. A solution of $[Cu(H_2O)_6][ClO_4]_2$ (0.18 g, 0.5 mmol) in MeOH (15 cm^3) was added to a stirred solution of L (0.28 g, 0.5 mmol) dissolved in MeOH (15 cm^3) at room temperature. A blue solid precipitated immediately and was filtered off, washed with MeOH and dried *in vacuo*. Yield 82% (Found: C, 48.15; H, 5.45; N, 8.6. $C_{33}H_{45}Cl_2CuN_5O_{11}$ requires C, 48.2; H, 5.5; N, 8.5%). FAB mass spectrum: *m/z* 723 (**1** − ClO_4^-) and 623 (**1** − $2ClO_4^-$).

$[NiL][ClO_4]_2$ 2. This complex was prepared as above by treating $[Ni(H_2O)_6][ClO_4]_2$ with L in warm (40 °C) MeOH. It was isolated as a blue solid in 68% yield upon partial evaporation of the solvent and dried *in vacuo* (Found: C, 48.65; H, 5.5; N, 8.4. $C_{33}H_{45}Cl_2N_5NiO_{11}$ requires C, 48.5; H, 5.55; N, 8.55%). FAB mass spectrum: *m/z* 717 (**2** − ClO_4^-) and 617 (**2** − $2ClO_4^-$). When the light blue solid was dissolved in moist MeCN the solution gradually changed to purple overnight. X-Ray-quality crystals (**2a**) were grown upon slow evaporation of this purple solution at 5 °C.

$[CuL(N_3)][ClO_4]$ 3. Complex **1** (0.21 g, 0.25 mmol) was dissolved in MeCN (20 cm^3) and stirred with a solution of NaN_3 (0.16 g, 0.25 mmol) in water (2 cm^3). The solution immediately changed to dark green which on evaporation afforded a green solid in 75% yield (Found: C, 50.95; H, 5.7; N, 14.45. $C_{33}H_{45}ClCuN_8O_7$ requires C, 51.85; H, 5.95; N, 14.65%). FAB mass spectrum: *m/z* 723 (**3** − N_3^-) and 623 (**3** − N_3^- − ClO_4^-).

$[NiL(N_3)][ClO_4]$ 4. This complex was prepared by treating **2** with NaN_3 in 1:1 molar ratio as in the case of **3**. The solution immediately changed to purple and a purple solid precipitated gradually and was filtered off and dried *in vacuo*. Yield 65% (Found: C, 52.3; H, 5.75; N, 14.4. $C_{33}H_{45}ClN_8NiO_7$ requires C, 52.15; H, 5.95; N, 14.75%). FAB mass spectrum: *m/z* 717 (**4** − N_3^-) and 617 (**4** − N_3^- − ClO_4^-).

CAUTION: Care should be taken while treating organic compounds with metal perchlorates as potentially explosive mixtures may be formed.

X-Ray crystallography

Crystallographic data for compounds L and **2a** are listed in Table 1. In the case of L a crystal of suitable size was mounted on a glass fibre with epoxy cement. For **2a** a crystal was sealed inside a Lindemann capillary containing a small amount of the mother-liquor. Cell parameters and reflection intensities were measured at 298 K on an Enraf-Nonius CAD4-mach diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods and completed by Fourier-difference syntheses. All non-hydrogen atoms were anisotropically refined by full-matrix least-squares calculations based on *F*. In each case a few H atoms could be located in the subsequent Fourier-difference maps while others were added at calculated positions. For **2a** the H atoms of the water molecule inside the cavity could be located in the Fourier-difference map. Hydrogen atoms were given a fixed U_{eq} (0.2 for L, 0.1 $Å^2$ for **2a**). Their positions or thermal parameters were not refined. Computations were made with the XTAL 3.2 program package[19] on a 486-DX personal computer (IBM compatible, PCL, India). Selected bond lengths and angles for both structures are collected in Table 2.

Table 1 Crystallographic and refinement data for L and complex **2a***

	L	**2a**
Formula	$C_{33}H_{45}N_5O_3$	$(C_{35}H_{50}Cl_2N_6NiO_{12})\cdot H_2O\cdot 2CH_3CN$
M	559.758	976.558
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
a/Å	10.133(2)	13.937(4)
b/Å	11.972(3)	14.547(3)
c/Å	13.433(3)	22.951(7)
α/°	106.69(2)	
β/°	90.93(2)	
γ/°	91.38(2)	
$U/Å^3$	1560(1)	4653(2)
Z	2	4
$D_c/g\ cm^{-3}$	1.192	1.394
μ/mm^{-1}	0.08	0.61
Crystal size/mm	0.20 × 0.30 × 0.30	0.20 × 0.20 × 0.15
Transmission (maximum, minimum)	0.9771, 0.9658	0.8745, 0.8360
hkl Ranges	0–15, −14 to ≤14, −30 to 30	0–16, 0–17, 0–27
Total reflections measured	5808	4589
No. unique reflections	5467	4563
No. reflections used [$I > 2\sigma(I)$]	2987	2935
No. variables	370	560
R	0.060	0.060
R′	0.054	0.052
Goodness of fit	2.968	2.625
Largest and mean shift/e.s.d.	0.001, 0.0006	0.003, 0.0006
Minimum, maximum peak in Fourier map/e $Å^{-3}$	−0.42, +0.45	−0.46, +0.53

* Details in common: θ–2θ scans, range 0.80 + 0.35 tan θ; 2θ range 2–50°; $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$, $w = 1/\sigma(F)$.

Table 2 Selected bond lengths (Å), angles (°) and non-bonded distances (Å)

Complex **2a**

Ni–O(1w)	2.042(6)	Ni–N(4)	2.147(5)
Ni–N(1)	2.063(7)	Ni–N(5)	2.180(5)
Ni–N(2)	2.167(6)	Ni–N(61)	2.152(4)
N(1)–Ni–O(1w)	175.6(2)	N(2)–Ni–N(61)	86.69(4)
N(1)–Ni–N(2)	84.87(2)	N(4)–Ni–N(5)	101.86(5)
N(1)–Ni–N(4)	84.04(4)	N(4)–Ni–N(61)	177.55(3)
N(1)–Ni–N(5)	84.85(3)	N(4)–Ni–O(1w)	93.74(2)
N(1)–Ni–N(61)	95.37(2)	N(5)–Ni–O(1w)	98.48(3)
N(2)–Ni–O(1w)	92.26(3)	N(5)–Ni–N(61)	80.44(4)
N(2)–Ni–N(4)	90.89(2)	N(61)–Ni–O(1w)	86.73(4)
N(2)–Ni–N(5)	162.68(5)		

	L	**2a**
N(1) ··· N(3)	6.249(5)	6.410(6)
N(2) ··· N(4)	4.036(6)	3.082(5)
N(2) ··· N(5)	4.336(5)	4.295(7)
N(4) ··· N(5)	3.536(5)	3.354(4)
O(1) ··· O(2)	4.862(7)	4.603(6)
O(1) ··· O(3)	5.365(5)	5.450(6)
O(2) ··· O(3)	3.992(3)	3.602(4)
H(1)O(w) ··· N(3)		3.118(4)
H(1)O(w) ··· O(1)		3.282(5)
H(2)O(w) ··· O(1)		2.988(4)
H(2)O(w) ··· O(3)		2.535(5)
H(2)O(w) ··· N(3)		2.013(5)

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/384.

Results and Discussion

The cryptand readily forms mononuclear complexes with Cu^{II},

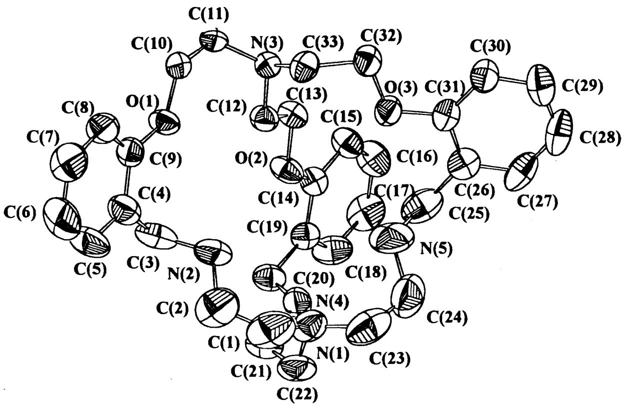

Fig. 1 An ORTEP[22] drawing of L showing the thermal ellipsoids and the atomic numbering scheme. Hydrogen atoms are omitted for clarity

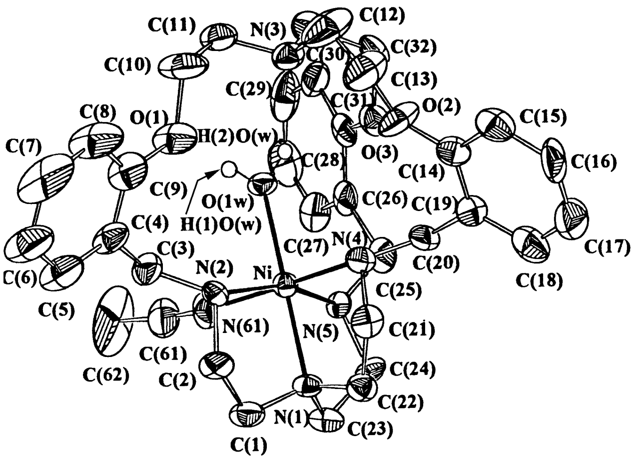

Fig. 2 An ORTEP[22] drawing of complex **2a**. Details as in Fig. 1

1, and Ni^{II}, **2**, as their perchlorate salts. When **1** and **2** are allowed to react with NaN_3 in 1:1 molar ratio, five-co-ordinate cascade complexes $[CuL(N_3)][ClO_4]$ **3** and $[NiL(N_3)][ClO_4]$ **4** are formed respectively with the azide group directly bonded to the metal ion. For **3** and **4**, ν_{asym} shows[20] blue shifts of about 25 cm^{-1} with respect to the free azide group and compares well with the literature data.[21] Complexes **1–4** exhibit a strong and broad peak at 1100 cm^{-1} attributable to ionic perchlorates. The molar conductivity values in MeCN (*ca.* 1×10^{-3} mol dm^{-3}) are consistent with the formulations. The complexes are stable in air and soluble in common organic solvents.

In the solid state L has an *endo-endo* conformation with a distance of 6.249(5) Å between the bridgehead nitrogens through which a pseudo-three-fold symmetry axis passes (Fig. 1). The bond distances and angles in the molecule are normal within statistical errors. Both ^{1}H and ^{13}C NMR data also indicate a three-fold symmetry in the molecule in chloroform solution.

The structure of complex **2a** consists of the cation $[NiL(H_2O)(MeCN)]^{2+}$ (Fig. 2) and two perchlorate anions. In addition, two molecules of MeCN and one of H_2O are present in the crystal lattice. The Ni^{II} recognizes the N_4-end of the cavity. The water molecule occupies the empty space inside the cavity making hydrogen bonds with the bridgehead N and ether O atoms of the cryptand while its O atom binds the metal ion (Table 2) forming a cascade complex. Similar cascade complexes are known for sodium[23] and copper(II).[17] The two bridgehead N atoms in **2a** are in an *endo-endo* conformation with a separation of 6.410(6) Å which compares well with that found in L. The Ni^{II} achieves six-co-ordination by binding a MeCN molecule from outside the cavity. The Ni–N[24] and Ni–O (H_2O)[25] bond distances are within normal ranges. The nonbonding distances between the secondary amino N atoms are only slightly shorter than those in L (Table 2). Hence, there is a high degree of preorganization of the cryptand prior to metal binding.

Table 3 Ligand-field bands, magnetic and EPR spectral data for the cryptates

Cryptate	λ(d–d)[a]/nm	μ_{eff}/μ_B[b]	$g_{\parallel}$	$g_{\perp}$	$10^4 A_{\parallel}/cm^{-1}$
1	990 (sh)	1.89	2.07 (g_{av})[c]		
	810 (335)		2.12[d]	2.07	63
	680 (260)		2.18[e]	2.06	95
	415 (430)				
2	940 (20)	2.98			
	565 (15)				
	360 (55)				
2a	960 (25)				
	870 (20)				
	560 (30)				
3	805 (175)	2.04	2.09 (g_{av})[c]		
	670 (250)		2.03[d]	2.13	65
			2.01[e]	2.26	64
4	950 (15)	3.07			
	570 (15)				

[a] Electronic spectra of **1–4** at 298 K in MeOH or in MeCN; molar absorption coefficients ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) are in parentheses. [b] At 298 K. [c] Solid sample at 298 K. [d] In MeCN at 298 K. [e] In MeCN glass at 77 K.

For complex **1** in MeOH the ligand-field band positions and their intensities (Table 3) are similar to those obtained for a copper(II) cryptate where the co-ordination geometry is[26] distorted trigonal pyramidal. The corresponding bands of **3** are consistent with a trigonal-bipyramidal geometry.[27,28]

The nickel cryptate **2** in MeOH shows three weak ligand-field bands. The geometry around the Ni^{II} is probably distorted trigonal pyramidal (when H_2O and the MeCN are not bonded as in **2a**). While pseudo-tetrahedral NiN_4 complexes are rare,[29] no nickel(II) complex with a distorted trigonal-pyramidal geometry is known. The bands shift gradually when exposed to moist air and correspond[30] to that obtained for a typical octahedral nickel(II) complex (Table 3). In case of **4** the electronic spectral data compare well[31] with those for high-spin trigonal-bipyramidal nickel(II) complexes.

The effective magnetic moments (μ_{eff}/μ_B) for the copper(II) cryptates after diamagnetic corrections range between 1.89 and 2.04 at 301 K consistent with[32] discrete, mononuclear formulations for these complexes. For the nickel(II) cryptates **2** and **4**, μ_{eff} is 2.98 and 3.07 μ_B respectively consistent with four-[33] and five[31]-co-ordination. Both **1** and **3** display broad EPR signals (Table 3) in the solid state at 298 K which become sharper at 77 K without revealing any fine structure. Complex **1** in MeCN (*ca.* 1×10^{-3} mol dm^{-3}) at 298 K exhibits an axial spectrum. In acetonitrile glass (77 K) the signal is still axial although with significant changes in the $g_{\parallel}$ and $A_{\parallel}$ values. This type of behaviour has been observed previously[26] and is attributable to a change in the ligand superstructure or solvent co-ordination at low temperature. In case of **3** the EPR parameters in MeCN at 298 and 77 K are consistent[27] with a distorted trigonal-bipyramidal geometry.

Conclusion

The cryptand L recognizes Cu^{II} and Ni^{II} at the N_4 end of the cavity forming four-co-ordinate mononuclear cryptates with the other end vacant. The nickel(II) cryptate accepts a water molecule inside the cavity which binds, the H atoms of which are bonded to two of the ether O and bridgehead N atoms. The strong tendency of Ni^{II} to six-co-ordination is manifested in the crystal structure of the nickel(II) cryptate where the metal ion binds to a MeCN group from outside the cavity to complete its co-ordination.

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