Inorg. Chem. **1993**, *32*, 2753–2760

Thermodynamic, Kinetic, and Structural Study of the Ligational Properties of the Macrobicyclic Aza-Ligand 4,7,10,17,23-Pentamethyl-1,4,7,10,13,17,23-heptaazabicyclo[11.7.5]pentacosane (L1) and of Its Macrocyclic Precursor 1,4,7,13-Tetramethyl-1,4,7,10,13,16-hexaazacyclooctadecane (L2). Crystal Structure of [Zn(L1)(H_2O)](BPh_4)$_2$

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Received November 11, 1992

The ligational properties of the macrobicyclic ligand 4,7,10,17,23-pentamethyl-1,4,7,10,13,17,23-heptaazabicyclo-[11.7.5]pentacosane (L1) and of its monocyclic precursor 1,4,7,13-tetramethyl–1,4,7,10,13,16–hexaazacyclooctadecane (L2) toward transition metal and alkali metal cations are considered. The equilibrium constants of the species formed by L1 with Cu^{2+}, Zn^{2+}, and Cd^{2+} and by L2 with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} have been determined by means of potentiometric measurements in 0.15 mol dm^{-3} NaClO$_4$ at 298.1 K. The enthalpy changes for the reaction of L2 with Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} have been calorimetrically measured. The unmethylated analog of L2, [18]aneN$_6$ (1,4,7,10,13,16-hexaazacyclooctadecane), is also considered for the sake of comparison. The tetramethylated ligand L2 forms complexes of stability lower than that of [18]aneN$_6$; the decrease in stability is due to a great loss in the enthalpic contribution, while the entropic contribution is favorable to the formation of the complexes with L2. The Cu^{2+}, Zn^{2+}, and Cd^{2+} complexes of L1 are even less stable; no *cryptate effect* is observed. The equilibrium and spectral data are in accord for the involvement of only the four nitrogen atoms of the 14-membered tetraazamacrocyclic moiety of L1 in the coordination to these metal ions, as observed in the crystal structure of [Zn(L1)H$_2$O](BPh$_4$)$_2$. Crystals of [Zn(L1)(H$_2$O)](BPh$_4$)$_2$ ($C_{71}H_{93}B_2N_7OZn$) are monoclinic, space group *C*2/*c*, with $a = 38.166(13)$ Å, $b = 13.823(11)$ Å, $c = 24.186(5)$ Å, $\beta = 98.08(2)°$, $Z = 8$, $R = 0.065$, and $R_w = 0.064$. The coordination polyhedron around the Zn^{2+} ion can be described as a distorted trigonal bipyramid, with the methylated nitrogen atoms and the water oxygen in the equatorial plane and the bridgehead nitrogens in apical positions. The kinetics of dissociation of the copper(II) complex of L1 in HClO$_4$ solutions has been studied at different temperatures (317, 324, 332, 343 K) in 0.5–1.0 mol dm^{-3} ($I = 1$ mol dm^{-3}) and in 3.0 mol dm^{-3} acid concentrations. The results showed that the dissociating species is [Cu(H$_3$L1)]$^{5+}$, the rate of dissociation ($k = 1.30 \times 10^{-7}$ s^{-1}, $\Delta H^{*} = 23.9 \pm 0.7$ kcal mol^{-1}, $\Delta S^{*} = -10 \pm 2$ cal K^{-1} mol^{-1} at 298 K) being independent of H$^+$ concentration, within the considered range, and first order in the complex concentration. A reaction mechanism in which the rate-determining step is a conformational change occurring on detachment of a coordinated nitrogen is proposed.

Introduction

Since from their discovery, complexes of metal ions with cryptand ligands have attracted a great deal of interest owing to the exceptional thermodynamic and kinetic stability they possess in consequence of the cation inclusion inside the tridimensional cavity.[2]

In comparison with the great amount of work devoted to the study of thermodynamic and kinetic properties of such complexes with alkali and alkaline-earth metal cations in solution[3] only a few works dealt with transition metal cations,[4,5] especially in aqueous solution.[5]

Few aza-crown molecules with macrobicyclic arrangement of donor atoms (cryptand topology) have been synthesized, as metal-free ligands, in recent years.[6–8] Earlier works on this topic dealt with metal-ion template reactions yielding "sepulchrate com-

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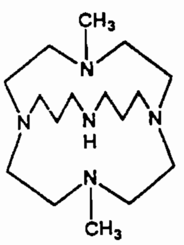
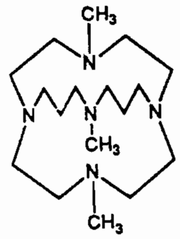
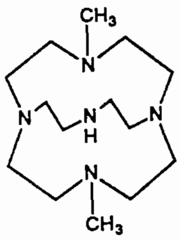
Chart I



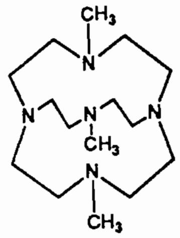
C1



C2

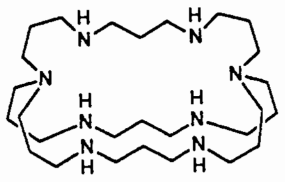


C3

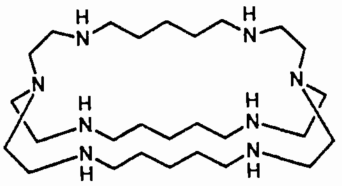


C4

Chart II



I



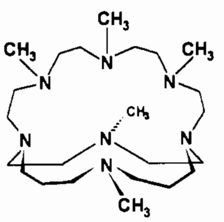
II

plexes".[9] Unfortunately the area of application of such compounds is restricted by the impossibility of obtaining the metal-free ligands, which prevents their implication in complexation equilibria from being investigated.

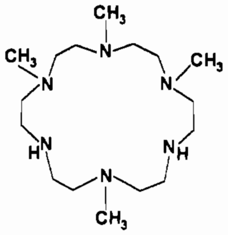
Recently we have synthesized by means of nontemplate reactions a series of cagelike macrobicyclic molecules (C1–C4 in Chart I), containing five nitrogen atoms, and studied their ligational properties toward alkali and transition metal cations.[6,7] These small tridimensional ligands operate a size discrimination toward metal ions allowing, for instance, recognition and selective binding of Li^+ among alkali cations.[7] These molecules are also selective ligands for the complexation of small transition metal ions, but also in this case, the bound metal ion cannot be removed from the complexes.

Larger macrobicyclic ligands containing eight nitrogen atoms (I and II in Chart II) have been also prepared by means of nontemplate synthesis by assembling two tripodal subunits.[8] The dimensions of the molecular cavity defined by these ligands, the number of donor atoms, and their disposition allow for the inclusion of one or more metal ions as well as of anionic species.[8]

Chart III



L1



L2

These results stimulated us to synthesize the new macrobicyclic heptaaza ligand 4,7,10,17,23-pentamethyl-1,4,7,10,13,17,23-heptaazabicyclo[11.7.5]pentacosane (L1)[10] (Chart III), presenting structural features which resemble in part the small azacages C1–C4 and in part the larger macrobicycles I and II, in order to get insight into the role played by the number of the nitrogen donor atoms and the topological features of the macrobicycles (dimensions of the cavity, disposition of donors, nitrogen configuration, and overall ligand conformation) in the coordination properties of ligands with such a molecular architecture.

In the present paper the coordinating ability of L1 toward transition metal (Cu^{2+}, Zn^{2+}, Cd^{2+}) and alkali metal (Li^+, Na^+, K^+) ions in aqueous solution has been considered from a thermodynamic, kinetic, and structural point of view. We report also the equilibrium constants and the enthalpy changes for the formation of the Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} complexes of the ligand 1,4,7,13-tetramethyl-1,4,7,10,13,16-hexaazacyclooctadecane (L2) (Chart III), which is the synthetical precursor of L1.

Experimental Section

Synthesis of [Na(L1)]ClO$_4$. A 1 mol dm^{-3} NaOH solution was added to a solution of L1·4HClO$_4$ (100 mg, 0.12 mmol) in water (20 cm^3), until the complete precipitation of [Na(L1)]ClO$_4$ as a white solid. The sodium complex was filtered off, washed with cold water, and dried in desiccator. The product was recrystallized from a chloroform/cyclohexane mixture; yield 54 mg (82%). Anal. Calcd for $C_{23}H_{51}N_7ClO_4Na$: C, 50.49; H, 9.39; N, 17.92. Found: C, 50.6; H, 9.4; N, 18.0.

Synthesis of [Zn(L1)(H$_2$O)](BPh$_4$)$_2$. [Na(L1)]ClO$_4$ (30 mg, 0.055 mmol) and $ZnBr_2$ (12 mg, 0.055 mmol) were dissolved in methanol (20 cm^3), and the resulting solution was refluxed for a few minutes and then cooled at room temperature. $NaBPh_4$ (37 mg, 0.11 mmol) and 1-butanol (10 cm^3) were added. Crystals of [Zn(L1)(H$_2$O)](BPh$_4$)$_2$ were obtained by slow evaporation of this solution at room temperature. The crystals were collected and dried in vacuo; yield 46 mg (73%). Anal. Calcd for $C_{71}H_{93}B_2N_7OZn$: C, 74.32; H, 8.16; N, 8.54. Found: C, 74.1; H, 8.2; N, 8.5.

Collection and Reduction of X-ray Intensity Data. Investigation on a colorless, prismatic, single crystal of [Zn(L1)(H$_2$O)](BPh$_4$)$_2$, approximate dimensions 0.8 × 0.8 × 0.6 mm, was carried out with an Enraf-Nonius CAD4 X-ray diffractometer, employing an equatorial geometry. A summary of the crystallographic data is reported in Table I. Unit cell parameters were determined by least-squares refinement of 25 carefully centered reflections. A total of 6438 reflections were collected up to $2\theta = 50°$ by using Mo Kα, graphite-monochromated radiation. During data collection three standard reflections were monitored periodically as a check of the stability of the diffractometer and of the crystal: no loss of intensity was observed. Intensities were corrected for Lorentz and polarization effects; an absorption correction was applied, once the structure was solved, by using the method of Walker and Stuart.[11]

Solution and Refinement of the Structure. The structure was solved by the heavy-atom technique, which showed the position of the zinc atom.

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Table I. Crystallographic data for $[Zn(L1)H_2O)](BPh_4)_2$

chem formula	$C_{71}H_{93}B_2N_7OZn$	D_{calcd}, g cm^{-3}	1.21
fw	1147.56	D_{obsd}, g cm^{-3}	1.2
space group	*C*2/*c*	*T*, °C	25
a, Å	38.166(13)	radiation (λ, Å)	Mo Kα, graph monochrom (0.7107)
b, Å	13.823(11)	μ, cm^{-1}	4.44
c, Å	24.186(5)	transm coeff	0.70–0.77
β, deg	98.08(2)	*F*(000)	4928
V, Å^3	12633(11)	R^a	0.065
Z	8	$R_w{}^b$	0.064

$^a\ R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b\ R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Subsequent Fourier maps showed all the non-hydrogen atoms. Refinement was performed by means of the full-matrix least-squares method by using the 4856 reflections having $I > 4\sigma(I)$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = a/(\sigma^2(F) + 0.0002F^2)$, where a is an adjustable parameter. Anisotropic temperature factors were used for all the non-hydrogen atoms, except the carbon and boron atoms of the tetraphenylborate anions, which were treated isotropically. The hydrogen atoms bound to the carbon atoms were included in calculated positions with an overall temperature factor U of 0.05 Å^2, and their positions were refined accordingly to the linked atoms. The hydrogen atoms of the water molecule were found in a ΔF map calculated in the last refinement cycle and their positional parameters refined, while their thermal factors were kept at 0.05 Å^2. The final agreement coefficient for 495 refined parameters was 0.065 (R_w = 0.064). All calculations were performed on an IBM PS/2 80 computer with the SHELX-76[12] set of programs that use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from ref 13. Table II reports the list of the final atomic coordinates for the non-hydrogen atoms and thermal parameters with estimated standard deviations. The molecular plots were produced by the program ORTEP.[14]

EMF Measurements. All the potentiometric measurements were carried out in 0.15 mol dm^{-3} $NaClO_4$ at 298.1 ± 0.1 K, by using the equipment that has been already described.[15] The reference electrode was an Ag/AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO_2-free NaOH solutions and determining the equivalent point by Gran's method,[16] which allows one to determine the standard potential $E°$, and the ionic product of water (pK_w = 13.73(1) at 298.15 K in 0.15 mol dm^{-3} $NaClO_4$). The concentrations of the metal ion solutions were determined by standard methods. Ligands L1 and L2 were prepared and purified as already described.[10]

The complexation equilibria between L2 and Co^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} have been studied by means of common potentiometric titrations. At least three measurements were performed for each system. The computer program SUPERQUAD[17] was used to calculate stability constants from emf data. The titration curves for each system were treated either as a single set or as separated entities without significant variations in the values of the stability constants.

Due to the long time required for the equilibrium reactions between L2 and Ni^{2+}, and between L1 and Cu^{2+}, Zn^{2+}, and Cd^{2+}, to be reached, a batchwise potentiometric procedure was employed to determine the stability constants of the complexes formed. Fifteen solutions containing different amounts of Ni^{2+}, L2, and OH^- in 0.15 mol dm^{-3} $NaClO_4$ aqueous media were prepared in separate bottles and maintained at 298 K. The value of $-\log[H^+]$ for each solution was measured periodically until a constant value was reached. In the case of L1 preliminary sets of 20 solutions for each metal ion (Cu^{2+}, Zn^{2+}, Cd^{2+}) were prepared, as described for the Ni^{2+} complex of L2, in the pH ranges 4–10 for Cu^{2+} and 5–10 for Zn^{2+} and Cd^{2+}. Further solutions were prepared, once a first estimation of the stability constants was obtained, in order to better define the chemical models and improve or verify the values of the constants. The computer program SUPERQUAD[17] was also used to calculate the equilibrium constants from these batchwise measurements. The protonation constants of L1 and L2 employed in the calculations were previously determined.[10] Under the experimental condition employed no formation of complexes of these ligands with Na^+ of the media was observed.

Microcalorimetry. Reactions of Cu^{2+}, Zn^{2+}, and Cd^{2+} ions with the L2 free amine are fast: thermal equilibrium was reached within 30 min from the reaction starting. The enthalpy changes for these reactions in 0.15 mol dm^{-3} $NaClO_4$ solution were determined by means of a fully automatized equipment having a Model 2277 thermal activity monitor (Termometric AB) microcalorimeter as calorimetric unit. On the contrary Ni^{2+} reacts slowly with L2; therefore, the enthalpy change of the reaction $Ni^{2+} + L2 = [Ni(L2)]^{2+}$ was indirectly determined by cyanolysis of the preformed $[Ni(L2)]^{2+}$ complex. The heat of the reaction $[Ni(L2)]^{2+} + 4CN^- = [Ni(CN)_4]^{2-} + L2$ was measured by means of a LKB Batch Model 10700-2 microcalorimeter, accordingly to a procedure already described, and combined with the value (42.8 ± 0.4 kcal mol^{-1})[18] of the enthalpy change for the reaction $Ni^{2+} + 4CN^- = [Ni(CN)_4]^{2-}$. Corrections for the heats of dilution of all reacting solutions were applied. A similar procedure was used in this work to determine the enthalpy change for the reaction of Ni^{2+} with 1,4,7,10,13,16-hexaazacyclooctadecane ([18]aneN_6).

Spectrophotometric Measurements. The electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer equipped with 1-cm cell thermostated at 298 K.

Kinetic Measurements. Solutions containing known amounts of $[Cu(L1)]^{2+}$ and $[Cu(L1)(OH)]^+$ (total complex concentration 0.025 mol dm^{-3}) in pure water were prepared from a $L1 \cdot 4HClO_4/Cu^{2+}$ stock solution and the calculated volume of standardized NaOH solution and allowed to equilibrate at 298 K. Solutions of the complex in 1 mol dm^{-3} $HClO_4$ were prepared by mixing the previous complex solution with the appropriate quantities of concentrated standardized acid. In the case of 0.5 mol dm^{-3} $HClO_4$ solutions the ionic strength was kept at 1 mol dm^{-3} by addition of concentrated standardized $NaClO_4$ solution. Further measurements were carried out in 3 mol dm^{-3} $HClO_4$ solution. All the acidic solutions were stored in a thermostat. The temperatures for the different experiments were 317, 324, 332, and 343 K. The kinetic of dissociation of the complex was followed by monitoring the 665-nm absorbance. The dissociation of the complex at 298 K is very slow, as shown by preliminary measurements, allowing thus for the handling of the acidic complex solutions at this temperature. Portions of these solutions were taken from the thermostat, rapidly cooled at room temperature, and set in the spectrophotometer, thermostated at 298 K, by using a 1-cm quartz cell.

First-order plots of data were linear for at least 4 half-lives.

NMR Spectroscopy. The 200.0-MHz ^1H NMR and 50.32-MHz ^{13}C spectra were recorded in Varian Gemini and Bruker AC-200 spectrometers in D_2O solutions with dioxane as a reference standard (δ = 67.4 ppm) and in $CDCl_3$ solutions with TMS as a reference standard.

Results and Discussion

Description of the Structure.[19] Table III presents bond distances and angles around the zinc ion calculated by the PARST[20] program.

The crystal structure of $[Zn(L1)(H_2O)](BPh_4)_2$ is made up of $[Zn(L1)(H_2O)]^{2+}$ complexed cations and BPh_4^- anions. The zinc ion shows a five-coordinate stereochemistry (Figure 1) with coordinating sites occupied by four nitrogen atoms of the macrobicyclic ligand and one water oxygen. The coordination polyhedron can be described as a distorted trigonal bipyramid, with the nitrogen atoms N2 and N7 and the water oxygen O1 on the equatorial plane, containing the Zn^{2+} ion, and the bridgehead nitrogens N1 and N3 in apical positions. The Zn–N distances with the apically coordinated nitrogen atoms (Zn–N1 = 2.384(6) Å, Zn–N3 = 2.332(6) Å) are significantly longer than those with the equatorial nitrogens (Zn–N2 = 2.041(6) Å, Zn–N7 = 2.093(6) Å). The Zn–O bond distance (1.903(4) Å) compares well with the Zn–N distances in the equatorial plane. The bond angles around the metal ion are rather irregular (Table

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Table II. Positional Parameters ($\times 10^4$) and Isotropic or Equivalent Temperature Factors ($Å^2 \times 10^3$) with Esd's in Parentheses

atom	*x/a*	*y/b*	*z/c*	*U*	atom	*x/a*	*y/b*	*z/c*	*U*
Zn	1270(1)	1775(1)	1251(1)	48(1)	C39	2871(2)	5258(5)	890(3)	63(2)
O1	1418(1)	2945(3)	1628(2)	49(3)	C40	3215(2)	5024(5)	998(3)	58(2)
N1	977(2)	2558(4)	437(2)	64(5)	C41	3318(2)	4156(4)	1277(2)	46(2)
C1	600(2)	2261(6)	439(3)	82(6)	C42	2950(2)	2154(4)	2204(3)	47(2)
C2	568(2)	1275(7)	728(4)	101(7)	C43	2825(2)	2866(5)	2537(3)	54(2)
N2	767(2)	1304(4)	1291(3)	67(4)	C44	2655(2)	2634(5)	2998(3)	65(2)
C3	796(2)	333(6)	1552(4)	96(7)	C45	2602(2)	1697(5)	3121(3)	70(2)
C4	1041(2)	355(6)	2095(3)	80(6)	C46	2712(2)	978(6)	2812(3)	77(2)
N3	1390(2)	792(4)	2038(3)	60(4)	C47	2886(2)	1195(5)	2348(3)	68(2)
C5	1581(2)	1104(5)	2578(3)	79(6)	C48	3597(2)	2417(4)	1949(3)	47(2)
C6	1400(2)	1849(6)	2913(3)	85(6)	C49	3723(2)	2595(4)	2513(3)	52(2)
N4	1407(2)	2860(5)	2716(2)	64(5)	C50	4078(2)	2700(5)	2723(3)	60(2)
C7	1150(2)	3446(6)	2972(3)	77(6)	C51	4329(2)	2611(5)	2358(3)	65(2)
C8	1056(2)	4380(6)	2664(3)	82(6)	C52	4222(2)	2412(5)	1811(3)	64(2)
N5	803(2)	4256(4)	2157(3)	69(5)	C53	3867(2)	2314(5)	1612(3)	56(2)
C9	792(2)	5144(5)	1815(3)	79(6)	B2	5704(2)	2619(5)	−216(3)	49(2)
C10	1113(2)	5330(5)	1535(3)	77(6)	C54	6125(2)	2675(4)	61(3)	47(2)
N6	1205(2)	4558(4)	1148(3)	69(5)	C55	6392(2)	2674(4)	−280(3)	57(2)
C11	902(2)	4339(6)	716(3)	76(6)	C56	6751(2)	2645(5)	−64(3)	66(2)
C12	973(2)	3614(5)	288(3)	79(6)	C57	6853(2)	2653(5)	495(3)	69(2)
C13	1116(2)	2026(6)	−12(3)	82(6)	C58	6603(2)	2684(5)	850(3)	62(2)
C14	1506(2)	2199(6)	−38(3)	85(7)	C59	6245(2)	2699(4)	629(3)	54(2)
C15	1760(2)	2104(5)	498(3)	78(6)	C60	5638(2)	3359(5)	−752(3)	49(2)
N7	1688(2)	1256(4)	859(3)	61(4)	C61	5782(2)	4288(5)	−716(3)	61(2)
C16	1974(2)	1201(5)	1325(3)	68(5)	C62	5727(2)	4944(5)	−1172(3)	71(2)
C17	1963(2)	309(5)	1690(3)	77(6)	C63	5535(2)	4674(5)	−1653(3)	70(2)
C18	1607(2)	4(5)	1830(3)	76(6)	C64	5383(2)	3783(5)	−1708(3)	74(2)
C19	592(2)	1965(6)	1647(4)	97(7)	C65	5437(2)	3127(5)	−1254(3)	62(2)
C20	1763(2)	3271(6)	2853(3)	95(6)	C66	5453(2)	2892(4)	259(3)	47(2)
C21	1513(2)	4916(6)	910(4)	98(7)	C67	5264(2)	3762(5)	276(3)	51(2)
C23	1691(2)	361(5)	514(3)	88(6)	C68	5060(2)	3968(5)	687(3)	56(2)
B1	3182(2)	2408(5)	1694(3)	46(2)	C69	5033(2)	3316(5)	1110(3)	55(2)
C30	3093(2)	1623(4)	1184(2)	44(2)	C70	5207(2)	2449(5)	1108(3)	54(2)
C31	2839(2)	1741(5)	726(2)	48(2)	C71	5409(2)	2248(5)	691(3)	52(2)
C32	2755(2)	1045(5)	309(3)	60(2)	C72	5607(2)	1506(4)	−443(3)	46(2)
C33	2930(2)	179(5)	351(3)	66(2)	C73	5849(2)	906(5)	−669(3)	55(2)
C34	3185(2)	7(5)	800(3)	73(2)	C74	5745(2)	20(5)	−912(3)	62(2)
C35	3267(2)	715(5)	1208(3)	61(2)	C75	5411(2)	−312(5)	−934(3)	71(2)
C36	3070(2)	3500(4)	1434(2)	45(2)	C76	5168(2)	215(5)	−708(3)	77(2)
C37	2718(2)	3798(5)	1325(3)	54(2)	C77	5266(2)	1133(5)	−468(3)	64(2)
C38	2617(2)	4675(5)	1050(3)	63(2)					

Table III. Bond Distances (Å) and Angles (deg) of the Coordination Sphere

Bond Distances			
Zn–O1	1.903(4)	Zn–N3	2.332(6)
Zn–N1	2.384(6)	Zn–N7	2.093(6)
Zn–N2	2.041(6)		
Bond Angles			
N3–Zn–N7	95.5(2)	N1–Zn–N2	81.2(2)
N2–Zn–N7	133.9(3)	O1–Zn–N7	108.3(2)
N2–Zn–N3	81.6(3)	O1–Zn–N3	95.4(2)
N1–Zn–N7	94.7(2)	O1–Zn–N2	117.8(2)
N1–Zn–N3	162.7(2)	O1–Zn–N1	94.7(2)

III). Particularly the angles N1–Zn–N2 (81.2(2)°), N2–Zn–N3 (81.6(3)°), and N1–Zn–N3 (162.7(2)°), due to the ethylenic bits, differ significantly from their ideal values. As a consequence of this distortion the apically coordinated nitrogens are shifted toward the equatorial N2 atom. This strained geometry is reflected by the angular values around the carbon atoms of ethylenic and propylenic chains, which are considerably larger than their usual values.

It is noteworthy that only a portion of the macrobicyclic ligand is directly involved in the coordination sphere around the metal ion. However the nitrogen atoms N4 and N6 interact via hydrogen bonds with the coordinated water molecule (H1···N4 = 1.58(6), H2···N6 = 1.64(6) Å); the remaining nitrogen atom N5 does not form any relevant intra- or intermolecular contact.

As a consequence of the coordination mode of L1, the Zn^{2+} cation is not completely embedded inside the macrobicyclic cavity (Figure 1b), in contrast with what is usually observed for cryptate complexes, allowing for the coordination of the exogen water molecule.

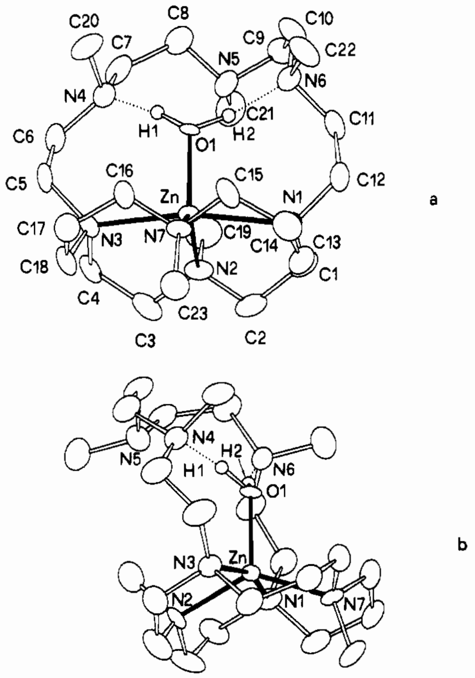


Figure 1. ORTEP drawings of the $[Zn(L1)(H_2O)]^{2+}$ cation.

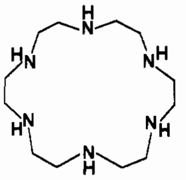
Complexation Equilibria of L2. The thermodynamic parameters obtained for the equilibrium reactions of L2 with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}, in 0.15 mol dm^{-3} $NaClO_4$ solution at 298.1 K, are reported in Table IV. For the sake of comparison,

Table IV. Thermodynamic Parameters for the Formation of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} complexes with L2 and Its Unmethylated Analog $[18]aneN_6$[a]

reacn	log *K*		$-\Delta H°$ (kcal mol^{-1})		$T\Delta S°$ (kcal mol^{-1})	
	L2[b]	$[18]aneN_6$	L2[b]	$[18]aneN_6$	L2[b]	$[18]aneN_6$
$Co^{2+} + L = Co(L)^{2+}$	13.14(1)[c]	18.9[d]				
$Co^{2+} + LH^+ = Co(LH)^{3+}$		11.8[d]				
$Ni^{2+} + L = Ni(L)^{2+}$	16.24(6)	21.1[e]	8.9(5)	21.1(5)[b]	13.2	7.7[b]
$Ni^{2+} + LH^+ = Ni(LH)^{3+}$		13.9[d]				
$Cu^{2+} + L = Cu(L)^{2+}$	20.49(1)	24.40[f]	17.3(2)	23.9[f]	10.6	9.4[f]
$Cu^{2+} + L + H^+ = Cu(LH)^{3+}$	23.49(2)	27.40[f]				
$Cu^{2+} + L + 2H^+ = Cu(LH_2)^{4+}$	26.39(2)	30.88[f]				
$Cu(L)^{2+} + H^+ = Cu(LH)^{3+}$	2.00	3.00[f]				
$Cu(LH)^{3+} + H^+ = Cu(LH_2)^{4+}$	2.90	3.48[f]				
$Cu^{2+} + LH^+ = Cu(LH)^{3+}$	13.74	17.25[f]				
$Cu^{2+} + LH_2^{2+} = Cu(LH_2)^{4+}$	7.53	11.25[f]				
$Zn^{2+} + L = Zn(L)^{2+}$	13.29(1)	18.70[g]	5.3(1)	14.0[g]	12.8	11.5
$Zn^{2+} + LH^+ = Zn(LH)^{3+}$		12.48[g]				
$Cd^{2+} + L = Cd(L)^{2+}$	16.75(3)	18.80[h]	10.6(3)	15.3[h]	12.2	10.3[h]

[a] All values have been determined in 0.15 mol dm^{-3} $NaClO_4$ aqueous solution at 298.15 K, unless otherwise noted. [b] This work. [c] Values in parentheses are standard deviations on the last significant figure. [d] From ref 21; 0.2 mol dm^{-3} at 308.15 K. [e] See ref 22. [f] From ref 23. [g] From ref 24. [h] From ref 24.

the thermodynamic parameters already presented[21–25] for the formation of the analogous complex of the unmethylated ligand $[18]aneN_6$ (1,4,7,10,13,16-hexaazacyclooctadecane) have also been reported in Table IV together with the value of the enthalpy change, determined in this work, for the reaction of Ni^{2+} with $[18]aneN_6$.



$[18]aneN_6$

All the metal ions here considered form stable ML^{2+} complexes with both ligands. It is worth to note that the methylated ligand L2 forms complexes of stability lower than that of $[18]aneN_6$. This decrease in stability is due to a great loss in the enthalpic contribution (Table IV), particularly in the case of the Ni^{2+} complex. The entropic term compensates in part the lower enthalpy change observed in the formation of $[Ni(L2)]^{2+}$ while it remains only slightly favorable to the Cu^{2+}, Zn^{2+}, and Cd^{2+} complexes (Table IV). In other terms, methylation of the ligand gives rise to a smaller overall interaction with the coordinated metal ions. Especially in the case of Zn^{2+}, the enthalpic contribution to the formation of the complex with L2 is very small ($-\Delta H° = 5.3$ kcal mol^{-1}).

While the principal contribution to the formation of the Zn^{2+} and Cd^{2+} complexes of $[18]aneN_6$ is given by the enthalpic term, the stability of $[Zn(L2)]^{2+}$ and $[Cd(L2)]^{2+}$ has main entropic nature.

As the stoichiometry of the species formed at equilibrium is considered, we can note that Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+}, at least under the experimental conditions employed, do not form complexes with protonated species of L2, while $[M(HL)]^{3+}$ (M = Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}) complexes were found for $[18]aneN_6$.

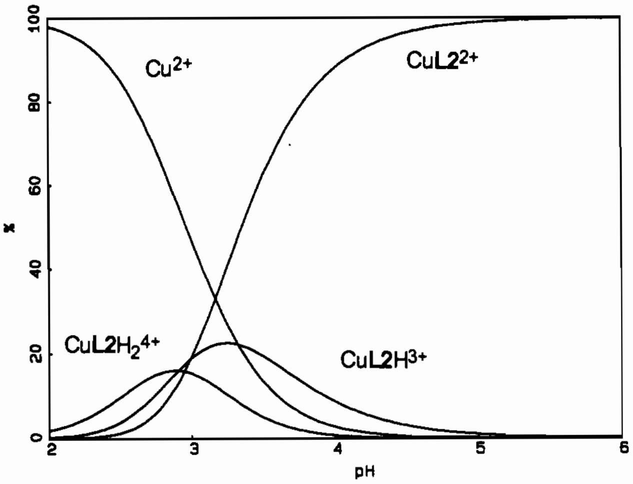


Figure 2. Distribution diagram of the species formed as a function of pH in the system Cu^{2+}/L2 in 0.15 mol dm^{-3} $NaClO_4$ solution at 298.15 K. $[Cu^{2+}] = [L2] = 1 \times 10^{-3}$ mol dm^{-3}.

In the case of Cu^{2+}, beside the species $[Cu(L2)]^{2+}$, also the protonated complexes $[Cu(HL2)]^{3+}$ and $[Cu(H_2L2)]^{4+}$ are formed at equilibrium (Table IV). However $[Cu(L2)]^{2+}$ presents a low tendency to bear protonation (Table IV) and therefore it remains the largely predominating species from acidic to alkaline solution (Figure 2). A similar equilibrium composition was found for the system $Cu^{2+}/[18]aneN_6$ (Table IV).

The complex $[Ni(L2)]^{2+}$ presents, in aqueous solution, a three-band electronic spectrum (λ_{max} 1074 (8.3), 587 (5.4), 368 (10.3) nm (dm^3 mol^{-1} cm^{-1})) typical for an octahedral high-spin nickel(II) chromophore analogous to that reported for $[Ni([18]aneN_6)]^{2+}$ (λ_{max} 835 (19), 530 (11), 345 (11) nm (dm^3 mol^{-1} cm^{-1})).[26] The main difference between the spectral features of both complexes is the shift toward low energies presented by the complex of L2 with respect to that of $[18]aneN_6$, the weaker ligand field interaction, shown by the tetramethylated ligand, coinciding with the lower stability of its Ni^{2+} complex. Of interest is the high value of the molar absorbance for the near-infrared band of $[Ni(L2)]^{2+}$, with respect to those of the other two bands, which has been considered as diagnostic for cis coordination in octahedral nickel(II) complexes[27] and could be indicative of a

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(22) The value log $K = 19.6$ reported in ref 15 for the stability constant of the complex $Ni([18]aneN_6)^{2+}$ in 0.2 mol dm^{-3} at 308.15 K has been corrected at 298.15 K (log $K = 21.1$) once the enthalpy change ($\Delta H = -21.1$ kcal mol^{-1}) for the formation of this complex was determined.

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Table V. Thermodynamic Parameters for the Formation of Cu^{2+}, Zn^{2+}, and Cd^{2+} Complexes of L1 in 0.15 mol dm^{-3} $NaClO_4$ Aqueous Solution at 298.15 K

reacn	log *K*
$Cu^{2+} + L1 = Cu(L1)^{2+}$	16.02(4)[a]
$Cu^{2+} + L1 + H^+ = Cu(HL1)^{3+}$	23.79(3)
$Cu^{2+} + L1 + H_2O = [Cu(L1)(OH)]^+ + H^+$	7.49(4)
$Cu(L1)^{2+} + H^+ = Cu(HL1)^{3+}$	7.77
$Cu(L1)^{2+} + OH^- = [Cu(L1)(OH)]^+$	5.2
$Zn^{2+} + L1 = Zn(L1)^{2+}$	9.36(9)
$Zn^{2+} + L1 + H_2O = [Zn(L1)(OH)]^+ + H^+$	1.2(1)
$Zn(L1)^{2+} + OH^- = [Zn(L1)(OH)]^+$	5.5
$Cd^{2+} + L1 = Cd(L1)^{2+}$	14.22(7)
$Cd^{2+} + L1 + H^+ = Cd(HL1)^{3+}$	20.71(7)
$Cd^{2+} + L1 + H_2O = [Cd(L1)(OH)]^+ + H^+$	6.41(8)
$Cd(L1)^{2+} + H^+ = Cd(HL1)^{3+}$	6.5
$Cd(L1)^{2+} + OH^- = [Cd(L1)(OH)]^+$	5.9

[a] Values in parentheses are standard deviations on the last significant figure.

stronger binding ability of the two secondary amino groups of L2 coordinated in cis positions.

The electronic spectrum of aqueous solutions of $[Cu(L2)]^{2+}$ is characterized by a main band at 642 nm (ϵ 90 dm^3 mol^{-1} cm^{-1}) with an additional weaker absorption at 946 nm (ϵ 19 dm^3 mol^{-1} cm^{-1}) and could be ascribed to a tetragonally-elongated octahedral coordination environment of the copper(II) chromophore.[28] In the case of the analogous complex of the unmethylated ligand [18]aneN_6 a single-band spectrum (λ_{max} 658 nm, ϵ 85 dm^3 mol^{-1} cm^{-1}) was observed, accounting a more regular octahedral coordination.[23]

Complexation Equilibria of L1. The equilibrium constants for the reaction of L1 with Cu^{2+}, Zn^{2+}, and Cd^{2+} are reported in Table V.

As far as the stability of the $[M(L1)]^{2+}$ (M = Cu^{2+}, Zn^{2+}, Cd^{2+}) complexes is concerned, some important features can be outlined. First of all it is to be noted that the stability of these species is markedly lower than that presented by the analogous complexes with the precursor ligand L2. Namely, the higher stability generally observed for the complexes of bicyclic ligands with respect to that of their monocyclic counterparts (*cryptate effect*) is not observed for L1 and L2. This could be ascribed to a low number of donor atoms involved by L1 in the formation of the $[M(L1)]^{2+}$ species in solution, accordingly with the ligational behavior of L1 observed in the crystal structure of $[Zn(L1)H_2O](BPh_4)_2$.

Further evidence supporting the persistence of this behavior of L1 in solution can be considered.

The stabilities of all the L1 complexes studied here are by far lower than the complexes of azamacrocyclic ligands containing five and six nitrogen atoms.[29] In fact the complexes $[Cu(L1)]^{2+}$ and $[Zn(L1)]^{2+}$ present a stability intermediate between those reported for triaza- and tetraazamacrocyclic ligands, while the stability of $[Cd(L1)]^{2+}$ is equal, within the experimental errors, to that of $[Cd([12]aneN_4)]^{2+}$, the most stable among the Cd^{2+} complexes with tetraazamacrocyclic ligands.[29]

The stability of the $[Cu(L1)]^{2+}$ species is similar to that of the mononuclear copper(II) complex with the macrobicyclic ligand II (log *K* = 15.39)[8] we have referred to in the Introduction. This ligand, which forms both mono- and dicopper(II) complexes, is constituted by two tripodal subunits located quite apart each other, and thus, even the first coordinated metal ion implicates a tetraaza binding environment.

Furthermore, as observed before, L1 forms very stable hydroxo complexes with Cu^{2+}, Zn^{2+}, and Cd^{2+}. The equilibrium constants for the addition of OH^- to the $[M(L1)]^{2+}$ (M = Cu^{2+}, Zn^{2+}, Cd^{2+}) complexes are significantly high suggesting again a low number of nitrogen atoms involved in the coordination. That is, although L1 contains enough nitrogen atoms to fulfill the first coordination sphere of the metal ions, only few of them are involved in the coordination and hydroxylation can easily occur at the binding sites occupied by water molecules. The values of these constants well compare with those reported for the Zn^{2+} and Cd^{2+} complexes of the tetraazamacrocyclic ligand 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane,[30] for which a relatively distorted coordination geometry was supposed to provide poor overlap for the four in-plane Cd–N bonds, leading to very strong axial coordination of exogen ligands.[31]

The $[Cu(L1)OH]^+$ complex presents in aqueous solution an electronic spectrum characterized by a main absorption band at 644 nm (ϵ 330 dm^3 mol^{-1} cm^{-1}) with a weaker shoulder at higher energies, which could be ascribed to a trigonal-bipyramidal coordination environment of the copper(II) chromophore.[28] This band experiences a slight red shift, by lowering the solution pH, as the involved species change: $[Cu(L1)OH]^+ \rightarrow [Cu(L1)]^{2+} \rightarrow [Cu(HL1)]^{3+}$. $[Cu(L1)]^{2+}$ and $[Cu(HL1)]^{3+}$ present quite similar spectra (λ_{max} 658 nm, ϵ 340 dm^3 mol^{-1} cm^{-1}) still characterized by the presence of a weak shoulder at smaller wavelengths. Further protonation of the complex can occur, without significant changes of the spectral features, up to the formation of the kinetically unstable species $[Cu(H_3L1)]^{5+}$, in which at most four nitrogen atoms are coordinated to Cu^{2+}. This strongly suggests that also in the complexes $[Cu(L1)]^{2+}$ and $[Cu(L1)(OH)]^+$ in solution only four out of the seven nitrogen donors of L1 are bound to the metal ion and an additional water molecule or one OH^- anion completes the trigonal-bipyramidal coordination environment. These spectroscopic data agree with the general thermodynamic observation of the low overall interaction of L1 with the studied metal ions and the crystallographic evidence that Zn^{2+} is coordinated by the four nitrogens of the 14-membered tetraazamacrocyclic moiety of L1. Most likely this N_4 set of nitrogen donor atoms is the preferred lodging within L1 for Cu^{2+}, Zn^{2+}, and Cd^{2+}, which appear in very similar coordination environments.

Owing to the constrain imposed by the bulky 11-term bridge on the tetraazamacrocyclic moiety, the four donors are not coplanarly convergent as generally observed in 14-membered azamacrocycles complexes but they occupy four positions of a trigonal-bipyramidal coordination environment in which an equatorial site is available for the binding of a further ligand. As observed for the coordinated H_2O molecule in the $[Zn(L1)(H_2O)]^{2+}$ structure, the exogen molecule or anion can be stabilized by hydrogen bonds formation with amino groups, or ammonium groups in protonated complexes, of the 11-term bridge.

In order to get further insight into the coordination features of L1, we have analyzed the behavior of L1 toward alkali metal ions (Li^+, Na^+, K^+) by means of potentiometry and ^1H and ^{13}C NMR spectroscopy. Although the Na^+ complex of L1 has been isolated from aqueous solution (see Experimental Section), the formation of this species in aqueous media does not take place at least in the pH range useful for potentiometric measurements. This means that the equilibrium constant of $[Na(L1)]^+$ is very small and, therefore, the formation of this species occurs only at very high pH values where L1 is present in its unprotonated form. The complex $[Na(L1)]^+$ could also not be detected by NMR measurements confirming that, even in very alkaline aqueous solutions, it is formed in very small amounts. Thus, the isolation of the $[Na(L1)]^+$ species in the solid state is favored by the low solubility of its perchlorate salts and not by extensive complex formation.

In the case of Li^+ and K^+ no evidence for the formation of complexed species with L1 in aqueous solution was obtained.

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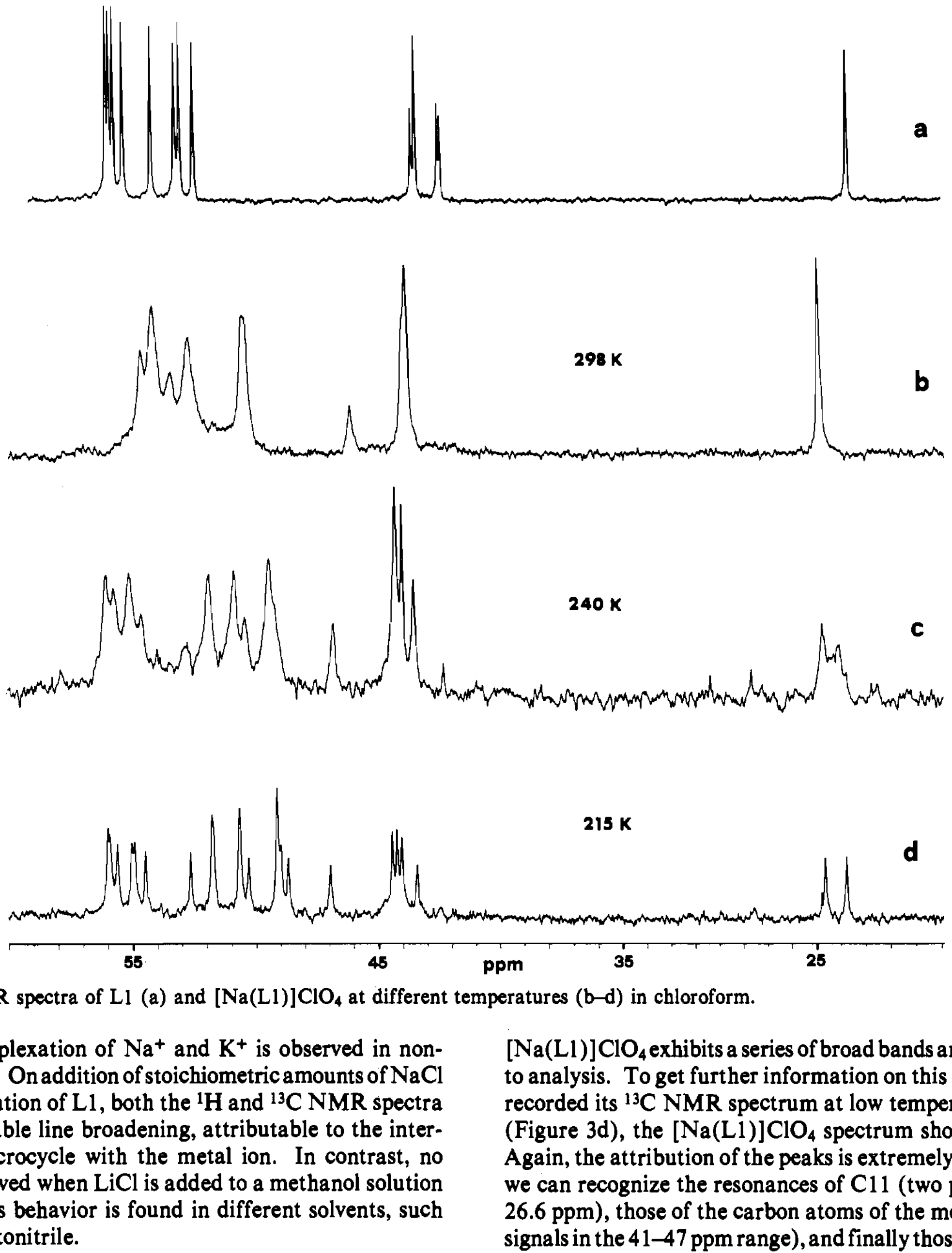
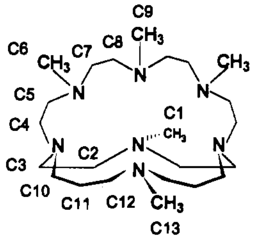


Figure 3. ^{13}C NMR spectra of L1 (a) and $[Na(L1)]ClO_4$ at different temperatures (b–d) in chloroform.

Enhanced complexation of Na^+ and K^+ is observed in nonaqueous solutions. On addition of stoichiometric amounts of NaCl to a methanol solution of L1, both the ^1H and ^{13}C NMR spectra undergo a noticeable line broadening, attributable to the interaction of the macrocycle with the metal ion. In contrast, no changes are observed when LiCl is added to a methanol solution of L1. Analogous behavior is found in different solvents, such as ethanol or acetonitrile.

Figure 3 reports the ^{13}C NMR spectra of L1 (Figure 3a) and $[Na(L1)]ClO_4$ at different temperatures (Figure 3b–d) in chloroform. The ^{13}C NMR spectrum of L1 does not permit an accurate analysis.[10] However, the spectrum shows one signal at 25.8 ppm, corresponding to the carbon atom placed in the middle of the propylenic chain (C11) and two groups of peaks. The first group (42–44 ppm) can be attributed, on the base of DEPT experiments, to the five methyl carbons, and the other one (52–57 ppm) to all the remaining carbon atoms of the propylenic chain (C10 and C12) and those of the different ethylenic chains. The number of signals agrees with a C_v symmetry of the molecule, mediated on the NMR time scale. The ^{13}C NMR spectrum of $[Na(L1)]ClO_4$ exhibits a series of broad bands and is not amenable to analysis. To get further information on this complex, we have recorded its ^{13}C NMR spectrum at low temperature. At 215 K (Figure 3d), the $[Na(L1)]ClO_4$ spectrum shows sharp signals. Again, the attribution of the peaks is extremely complicated, but we can recognize the resonances of C11 (two peaks at 25.7 and 26.6 ppm), those of the carbon atoms of the methyl groups (five signals in the 41–47 ppm range), and finally those of the remaining sixteen carbon atoms (48–57 ppm). With respect to the L1 spectrum, the most noticeable feature is the increase of the number of signals, particularly evident for the carbons of the methyl groups and C11. This increase can be due to the presence of two conformers, slowly interchanging on the NMR time scale at this temperature or, more likely, to the loss of the C_v symmetry, exhibited by the L1 molecule. This loss of symmetry, attributable to the coordination of the sodium ion, has been already found for the encapsulation of metal ions into the cavity of azacage ligands.[7] A similar behavior is presented by the K^+ complex of L1.



L1

It can be concluded that, in contrast with the smaller macrobicyclic ligands we have previously investigated,[7] which are selective toward Li^+ ion among alkali metal ions, L1 does not form Li^+ complexes. Nevertheless, L1 can complex Na^+ and K^+ ions. This selectivity between Li^+ and Na^+ or K^+ ions can be explained taking into account the larger cavity's dimension of L1, in which Na^+ and K^+ can fit better than Li^+.

Acid-Catalyzed Dissociation of the Cu^{2+} Complex of L1. The reaction of Cu^{2+} with alkaline solution of L1, containing the amine in its unprotonated form, has been followed by monitoring the evolution with time of the electronic spectrum of the complex in the range 500–800 nm. Equilibration of these reaction mixtures is rather fast since no spectral changes were observed after about

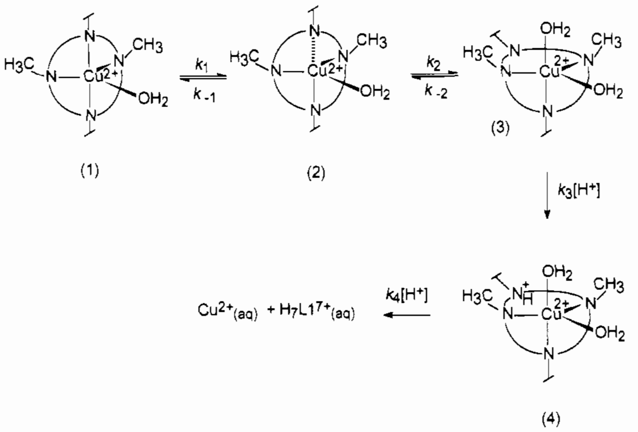


Figure 4. Proposed mechanism for the acid-catalyzed dissociation of $[Cu(L1)]^{2+}$.

half an hour from the mixing of the two reactants. Furthermore, the time required for equilibration is not significantly affected by the relative percentages of $[Cu(L1)]^{2+}$ and $[Cu(L1)OH]^+$ formed in the reaction. Addition of large amounts of strong acids to the alkaline solution of the complex produces a quick change of the spectrum, followed by a very slow absorbance decrease. Potentiometric titrations showed that a consumption of three H^+ ions for one $[Cu(L1)]^{2+}$ ion is required for the attainment of the slowly dissociating species, which thus accounts for a $[Cu(H_3L1)]^{5+}$ stoichiometry.

The kinetics of dissociation of this species in $HClO_4$ solutions has been studied at different temperatures (317, 324, 332, 343 K) in 0.5–1.0 mol dm^{-3} ($I = 1$ mol dm^{-3}) and in 3.0 mol dm^{-3} acid concentrations. The results showed that the rate of dissociation of $[Cu(H_3L1)]^{5+}$ ($k = (1.04 \pm 0.02) \times 10^{-5}$, $(9.56 \pm 0.03) \times 10^{-6}$, and $(1.05 \pm 0.01) \times 10^{-5}$ in 0.5, 1, and 3 mol dm^{-3} $HClO_4$ at 332 K) is independent of H^+ concentration, within the considered range, and first order in the complex concentration.

The observed first-order rate constants for the acid dissociation of the copper(II) complex in 1 mol dm^{-3} $HClO_4$ solution at 317, 324, 332, and 343 K are $(1.53 \pm 0.02) \times 10^{-6}$, $(4.15 \pm 0.02) \times 10^{-6}$, $(9.56 \pm 0.03) \times 10^{-6}$, and $(3.08 \pm 0.01) \times 10^{-5}$, respectively. The rate constants are well fitted by the Arrhenius equation $k = 1.21 \times 10^{11} e^{-12330/T}$ ($\ln k = 25.52 - 12330/T$), which allows one to determine the activation parameters ($\Delta H^* = 23.9 \pm 0.7$ kcal mol^{-1}, $\Delta S^* = -10 \pm 2$ cal K^{-1} mol^{-1}) and the rate constants ($k = 1.30 \times 10^{-7}$ s^{-1}) at 298 K.

The acid dissociation of the copper(II) complex of L1 is very slow if compared with most of polyazacycloalkane complexes,[3] and its slowness is due to a large ΔH^* contribution.

A generally accepted mechanism[32] for the dissociation of polyamine complexes in acidic solutions has been adapted[33] to explain the acid-dependent or -independent pathways involved in the dissociation of polyazamacrocyclic complexes. A modified version can be also used to explain the observed acid-independent dissociation of $[Cu(H_3L1)]^{5+}$. The proposed mechanism involves the four-step pathway reported in Figure 4, in which k_2 is the rate-determining step. Protonation of a fully coordinated nitrogen atom is a highly unfavorable process, and therefore, species 2 and 3, accounting for the breaking of a copper–nitrogen bond, have been introduced. Detachment of a coordinated nitrogen, which allows the donor atom to move away from the metal center and a water molecule to coordinate to the vacant site (step 2 → 3), requires a rearrangement of the tetraazamacrocyclic moiety of L1 to occur against the great hindrance from the methyl groups and the bulky 11-term bridge and the molecular stiffening due to the electrostatic repulsion between many positive charges gathered in $[Cu(H_3L1)]^{5+}$. A similar rate-determining conformational change has previously been suggested to account for some apparently acid-independent dissociation reactions of cryptate complexes.[5] This mechanism accounts for the largely positive ΔH^* contribution to the activation process indicating the rate-determining step 2 → 3 occurs across an energy barrier which is higher than those observed for most of polyazamacrocyclic complexes.[3] However the dissociation of polyazamacrocyclic complexes is mostly acid-dependent and the rate-determining process is the protonation of a partly bound nitrogen atom.

Of interest is also the negative entropic contribution to the activation process which is consistent with the association of a water molecule. Anyway, we cannot exclude the occurrence that the detachment of a nitrogen atom in $[Cu(H_3L1)]^{5+}$ gives rise to the formation of an octahedral species by association of two water molecules.

It is to be note that the breaking of a bond between Cu^{2+} and a bridgehead nitrogen, which we have reported in the schematic representation of the proposed reaction mechanism of Figure 4, is suggested by the values of the Zn–N bond distances (Table III), shown by the molecular structure of the $[Zn(L1)H_2O]^{2+}$ complexed cation, which account, at least in the solid state, for a significantly weaker interaction of the metal ion with the apically coordinated bridgehead nitrogens.

Conclusions. As evidenced by the crystal structure of $[Zn(L1)H_2O](BPh_4)_2$, the macrobicyclic ligand L1 gives rise to a rather weak overall interaction with the metal ions considered here. This binding feature is also revealed by the thermodynamic data for the complexation of Cu^{2+}, Zn^{2+}, and Cd^{2+} in solution. Furthermore, the L1 complexes present a reduced stability with respect to the analogous species formed by the ligand L2, which can be considered the macromonocyclic counterpart of L1. Namely, the higher stability of the macrobicyclic complexes, generally observed when comparing with the stability of the parent macromonocyclic ones (*cryptate effect*), does not result for the L1–L2 couple. Most likely this is due to the involvement in the coordination of only the four nitrogen atoms belonging to the tetraazamacrocyclic moiety of L1. Actually L1 does not behave as a cryptand ligand toward the metal ions Cu^{2+}, Zn^{2+}, and Cd^{2+}. As shown by the presented crystal structure, the metal ion is not completely embedded inside the macrobicyclic cavity of L1 but emerges from the ligand by at least one coordination site. This arrangement allows for the coordination of further ligands, as observed in the crystal structure of $[Zn(L1)H_2O](BPh_4)_2$, where a water molecule occupies this coordination site, or in solution where very stable hydroxylated complexes are formed. A considerable portion of L1 is not directly involved in the coordination to the metal ion, even if two of the nitrogen atoms it contains implement the coordination of the exogen molecule by hydrogen bonds. In this light L1 complexes with transition metal ions are promising metal receptors for substrate molecules or anions.

In contrast with the low thermodynamic stability of L1 complexes, the copper complex presents high inertness toward acid dissociation, in accord with the general behavior of cryptates.[3]

Acknowledgments. Financial support by the Progetto Finalizzato di Chimica Fine e Secondaria of the Italian Research Council (CNR), by the Italian Ministero dell'Universitá e della Ricerca Scientifica e Tecnologica (quota of 40%), and by the Spanish Comisión de Ciencia y Tecnologia (Proyecto BP90-0567) is gratefully acknowledged. We are also indebted to Mr. M. Fontanelli, Dr. P. Mariani, and Dr. S. Seniori Costantini for technical assistance.

Supplementary Material Available: Tables of anisotropic and isotropic thermal parameters, positional parameters for the hydrogen atoms, and complete bond lengths and angles (7 pages). Ordering information is given on any current masthead page.

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