

## Oxa–Aza Macrocylic Molecules as Receptors for Metal Cations

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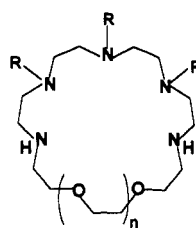
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### Introduction

In the last few years a great deal of interest has been devoted to macrocyclic receptors containing in their framework both oxygen and nitrogen donor atoms.<sup>2</sup> Most of the attention has been focused either on oxa–aza macrocyclic structures able to bind more than one transition metal ion<sup>3</sup> or on cryptands for the coordination of alkaline and alkaline-earth metals.<sup>4</sup> Recently, the interest toward molecular recognition and activation of anionic or neutral substrates has led to a further development in the chemistry of such macrocycles.<sup>5</sup> However, only few studies have been carried out on “compartmental” macrocyclic receptors in which the different donors are located at opposite sides of the molecule,<sup>6</sup> displaying a structure with two binding sites with different hard–soft characteristics.

In a recent paper we reported on the synthesis, basicity, and ligational properties toward Cu(II) of two synthetic macrocyclic receptors, 10,13,16-trimethyl-1,4-dioxa-7,10,13,16,19-pentaazacyclohencicosane (Me<sub>3</sub>[21]aneN<sub>5</sub>O<sub>2</sub>) and 13,16,19-trimethyl-1,4,7-trioxa-10,13,16,19,22-pentaazacyclotetrasosane (Me<sub>3</sub>[24]aneN<sub>5</sub>O<sub>3</sub>).<sup>7</sup>

The Cu<sup>2+</sup> complexes of these polyamines exhibit lower stability than those reported for saturated polyaza macrocycles with more than four amino groups. In order to shed further light on the role played by the nucleophilicity and basicity of the nitrogen donors as well as by steric effects (due to the presence of the methyl groups) in determining the coordination features of such receptors,



R = H, n = 1, [21]aneN<sub>5</sub>O<sub>2</sub>

R = CH<sub>3</sub>, n = 1, Me<sub>3</sub>[21]aneN<sub>5</sub>O<sub>2</sub>

R = CH<sub>3</sub>, n = 2, Me<sub>3</sub>[24]aneN<sub>5</sub>O<sub>3</sub>

we have synthesized the new oxa–aza macrocycle 1,4-dioxa-7,10,13,16,19-pentaazacyclohencicosane ([21]aneN<sub>5</sub>O<sub>2</sub>, n = 1, R = H). With this aim we have analyzed the coordination ability toward Cu(II), Zn(II), Cd(II), and Pb(II) of the three macrocycles cited above.

### Experimental Section

**Synthesis of the Compounds.** The macrocycles Me<sub>3</sub>[21]aneN<sub>5</sub>O<sub>2</sub> and Me<sub>3</sub>[24]aneN<sub>5</sub>O<sub>3</sub> were obtained as reported in ref 7. [21]aneN<sub>5</sub>O<sub>2</sub> was obtained by following a similar procedure.

**1,4-Dioxa-7,10,13,16,19-pentakis(p-tolylsulfonyl)-7,10,13,16,19-pentaazacyclohencicosane (1).** This compound was synthesized from 1,4,7,10,13-pentakis(p-tolylsulfonyl)-1,4,7,10,13-pentaazaterdecane<sup>8</sup> (24.1 g, 0.02 mmol) and triethylene glycol bis(p-toluenesulfonate) (9.2 g, 0.02 mol, Aldrich Chemical Co.) by following the procedure reported in ref 7. The crude product was purified by chromatography on alumina (80–230 mesh, activity I). Yield: 9.0 g (42%). Anal. Calcd for C<sub>49</sub>H<sub>63</sub>N<sub>5</sub>O<sub>12</sub>S<sub>5</sub>: C, 54.82; H, 5.91; N, 6.52. Found: C, 54.7; H, 6.0; N, 6.4.

**1,4-Dioxa-7,10,13,16,19-pentaazacyclohencicosane ([12]aneN<sub>5</sub>O<sub>2</sub>).** This macrocycle was obtained as a colorless oil from 1 (5.3 g, 0.005 mol) as described for Me<sub>3</sub>[21]aneN<sub>5</sub>O<sub>2</sub>.<sup>7</sup> Yield: 0.65 g (43%). Anal. Calcd for C<sub>14</sub>H<sub>33</sub>N<sub>5</sub>O<sub>2</sub>: C, 55.41; H, 10.96; N, 23.08. Found: C, 55.2; H, 10.8; N, 22.9.

**[21]aneN<sub>5</sub>O<sub>2</sub>·4HClO<sub>4</sub>.** The tetraperchlorate salt was obtained in a quantitative yield by adding 70% HClO<sub>4</sub> to an ethanolic solution containing the free amine. The white solid formed was filtered off and recrystallized by a methanol/ethanol mixture. Anal. Calcd for C<sub>14</sub>H<sub>37</sub>N<sub>5</sub>O<sub>18</sub>Cl<sub>4</sub>: C, 23.84; H, 5.28; N, 9.93. Found: C, 23.8; H, 5.3; N, 9.9.

**[Zn(Me<sub>3</sub>[21]aneN<sub>5</sub>O<sub>2</sub>)](BPh<sub>4</sub>)<sub>2</sub>.** A solution of Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (37.3 mg, 0.1 mmol) in methanol (5 cm<sup>3</sup>) was added to a methanolic solution (5 cm<sup>3</sup>) of Me<sub>3</sub>[21]aneN<sub>5</sub>O<sub>2</sub> (30.3 mg, 0.1 mmol). To the resulting solution were added NaBPh<sub>4</sub> (68.4 mg, 0.2 mmol) and butanol (10 cm<sup>3</sup>). Crystals of the complex suitable for X-ray analysis were obtained by slow evaporation at 298 K of this solution. Yield: 68 mg (68%). Anal. Calcd for C<sub>62</sub>H<sub>73</sub>N<sub>5</sub>O<sub>2</sub>B<sub>2</sub>Zn: C, 73.93; H, 7.30; N, 6.95. Found: C, 73.7; H, 7.3; N, 6.8.

**Emf Measurements.** All the potentiometric measurements were carried out at 298.1 ± 0.1 K, in the pH range 2.5–10, by using the equipment that has been already described.<sup>9</sup> The protonation constants were obtained in 0.15 mol dm<sup>-3</sup> NaClO<sub>4</sub> or NET<sub>4</sub>ClO<sub>4</sub>, while complex formation constants were obtained in 0.15 mol dm<sup>-3</sup> NaClO<sub>4</sub>. 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<sub>2</sub>-free NaOH solutions and determining the equivalent point by using Gran's method,<sup>10</sup> which allows one to determine the standard potential, E°, and the ionic product of water (pK<sub>w</sub> = 13.73 ± 0.01 in 0.15 mol dm<sup>-3</sup> NaClO<sub>4</sub>, pK<sub>w</sub> = 13.83 ± 0.01 in 0.15 mol dm<sup>-3</sup> NET<sub>4</sub>ClO<sub>4</sub> at 298 ± 0.1 K). At least three measurements were performed for each system (about 100 data points for each measurement). In the measurements for the determination of the stability constants, the metal to ligand molar ratio was varied from 0.5 to 2 to verify the formation of polynuclear complexes. The computer program SUPERQUAD<sup>11</sup> was used to calculate both protonation and stability constants from emf data.

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**Table 1.** Crystallographic Data for  $[\text{Zn}(\text{Me}_3[21]\text{aneN}_5\text{O}_2)](\text{BPh}_4)_2$ 

formula	$\text{C}_{65}\text{H}_{77}\text{B}_2\text{N}_5\text{O}_2\text{Zn}$
mol wt	1047.36
cryst dimens, mm	$0.6 \times 0.4 \times 0.2$
<i>a</i> , Å	17.44(1)
<i>b</i> , Å	17.688(9)
<i>c</i> , Å	18.145(9)
$\beta$ , deg	90.86(5)
<i>V</i> , Å <sup>3</sup>	5597(5)
<i>Z</i>	4
space gp	<i>Cc</i>
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.24
radiation	Mo K $\alpha$ , graphite monochromated
$\lambda$ , Å	0.7107
temp, °C	25
$\mu$ , cm <sup>-1</sup>	4.95
<i>R</i> <sup>a</sup>	0.086
<i>R</i> <sub>w</sub> <sup>b</sup>	0.089

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

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. Finally all the measurements for both protonation and complexation were merged together and the equilibrium constants for protonated and complexed species were simultaneously refined to give the final values. All the ligands used in the potentiometric titrations ( $\text{Me}_3[21]\text{aneN}_5\text{O}_2\cdot\text{HClO}_4$ ,  $\text{Me}_3[24]\text{aneN}_5\text{O}_2\cdot 5\text{HNO}_3$ ,  $[21]\text{aneN}_5\text{O}_2\cdot 4\text{HClO}_4$ ) had satisfactory elemental analysis.

**NMR Spectroscopy.** The 50.32-MHz <sup>13</sup>C spectra in D<sub>2</sub>O solutions were recorded at 298 K in a Bruker AC-200 spectrometer. Dioxane was used as a reference standard in the <sup>13</sup>C NMR spectra ( $\delta = 67.74$  ppm).

**Collection and Reduction of X-ray Intensity Data.** Investigation on a selected single crystal of  $[\text{Zn}(\text{Me}_3[21]\text{aneN}_5\text{O}_2)](\text{BPh}_4)_2$  was carried out with an Enraf-Nonius CAD4 X-ray diffractometer. A summary of the crystallographic data is reported in Table 1. Unit cell parameters were determined by least-squares refinement of diffractometer setting angles for 25 carefully centered reflections. Intensities were corrected for Lorentz and polarization effects. The absorption correction was applied, when the structure had been solved, by means of the DIFABS routine.<sup>12</sup> During data collection, two reflections were monitored periodically as a check of the stability of the diffractometer and of the crystal: no loss of intensity was noticed during the collection.

**Solution and Refinement of the Structure.** The structure was solved by the heavy-atom technique, which showed the position of the zinc atom. Subsequent Fourier maps showed all non-hydrogen atoms. Refinement was performed by means of the full-matrix least-squares method. The function minimized was  $\sum w = (|F_o| - |F_c|)^2$ , with  $w = a / [\sigma^2(F) + 0.0005F^2]$ , where *a* is an adjustable parameter. Hydrogen atoms were included in calculated positions with an overall temperature factor *U* of 0.08 Å<sup>2</sup>. Anisotropic thermal parameters were used for all the other atoms except for the carbon and the boron atoms of the two tetraphenylborate ions. Some atoms of the macrocyclic ligand show rather high thermal factors especially if they are compared with those of the atoms belonging to the tetraphenylborate anions (the mean values for the thermal parameters of the carbon atoms belonging to the macrocycle and to the tetraphenylborate ions are 115.1 and 61.4 Å<sup>2</sup>, respectively). This feature, together with the rather unusual values of some bond distances, indicates the macrocyclic likely is affected by disorder. This disorder largely affected the goodness of the intensity data and the results of refinement.

The final  $\Delta F$  map didn't show any peak near those belonging to the atoms of the macrocycle. The maximum electron density ( $1.2 \text{ e } \text{Å}^{-3}$ ) has been localized near the zinc atom; the minimum was  $-0.42 \text{ e } \text{Å}^{-3}$ .

All resolution and refinement calculation were performed on an IBM Model 80 PS/2 computer with the SHELX-76 set of programs,<sup>13</sup> which use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from ref 14. Table 2 reports the list of the final atomic coordinates for the non-hydrogen atoms of the complex cation with estimated standard deviations.

**Table 2.** Positional Parameters ( $\times 10^4$ ) with Esd's in Parentheses for the  $[\text{Zn}(\text{Me}_3[21]\text{aneN}_5\text{O}_2)]^{2+}$  Cation

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Zn	-4200	-2965(1)	-4600
N1	-3348(7)	-2440(7)	-4015(7)
C1	-2617(14)	-2733(15)	-4271(14)
C2	-2608(12)	-2758(12)	-5123(11)
N2	-3221(8)	-3266(9)	-5350(8)
C3	-3335(14)	-3109(14)	-6139(13)
C4	-3124(11)	-4072(10)	-5276(12)
C5	-3849(12)	-4450(12)	-5110(12)
N3	-4192(8)	-4150(6)	-4512(8)
C6	-3867(13)	-4405(13)	-3818(13)
C7	-5108(10)	-4351(10)	-4519(11)
C8	-5483(12)	-3822(11)	-3999(12)
N4	-5332(9)	-3059(8)	-4121(9)
C9	-5469(15)	-2553(15)	-3498(14)
C10	-5904(14)	-2775(13)	-4710(14)
C11	-5613(15)	-2128(14)	-5127(16)
N5	-4738(10)	-2279(10)	-5430(9)
C12	-4520(14)	-1583(12)	-5620(12)
C13	-4424(14)	-897(12)	-5120(12)
O1	-4222(8)	-1112(6)	-4380(6)
C14	-4056(11)	-455(10)	-3961(10)
C15	-3810(11)	-763(12)	-3226(11)
O2	-3099(7)	-1123(7)	-3335(8)
C16	-2942(12)	-1754(11)	-2898(12)
C17	-3362(10)	-2432(9)	-3253(9)

## Results and Discussion

**Basicity.** The protonation constants of  $[21]\text{aneN}_5\text{O}_2$  were determined by means of potentiometric titrations in 0.15 mol dm<sup>-3</sup> NaClO<sub>4</sub> or NEt<sub>4</sub>ClO<sub>4</sub> at 298.1 ± 0.1 K. Under such experimental conditions the ligand behaves as a tetraprotic base:  $\log K_1 = 9.57(2)$ ,  $\log K_2 = 8.87(2)$ ,  $\log K_3 = 7.70(2)$ , and  $\log K_4 = 3.41(2)$  in 0.15 mol dm<sup>-3</sup> NaClO<sub>4</sub>.<sup>15</sup> The protonation constants determined in 0.15 mol dm<sup>-3</sup> NEt<sub>4</sub>ClO<sub>4</sub> are equal within the experimental error suggesting the absence of interaction between the ligand and Na<sup>+</sup> ion, at least under the experimental conditions used. The higher basicity exhibited by  $[21]\text{aneN}_5\text{O}_2$  (ca. 0.2–0.3 logarithmic units in each step of protonation) with respect to  $\text{Me}_3[21]\text{aneN}_5\text{O}_2$  and  $\text{Me}_3[24]\text{aneN}_5\text{O}_2$ <sup>7</sup> can be explained taking into account the presence of three tertiary nitrogens in the latter macrocycles. Instead,  $[21]\text{aneN}_5\text{O}_2$  is less basic in each step of protonation than the dimensionally analogous polyazacycloalkane  $[21]\text{aneN}_7$ , in which all the donors are secondary nitrogen atoms.<sup>16</sup> A statistical effect can reasonably explain the slight difference in the first basicity constant (ca. 0.2 logarithmic units) but does not justify completely the more remarkable drop in the successive three protonation steps. Indeed, with respect to polycharged species of  $[21]\text{aneN}_5\text{O}_2$ , in the equally polyprotonated forms of  $[21]\text{aneN}_7$  the protons can be localized farther from each other, achieving a better minimization of the electrostatic repulsion between positive charges.

**Description of the Structure.**  $[\text{Zn}(\text{Me}_3[21]\text{aneN}_5\text{O}_2)](\text{BPh}_4)_2$ . The crystal structure consists of  $[\text{Zn}(\text{Me}_3[21]\text{aneN}_5\text{O}_2)]^{2+}$  cations and BPh<sub>4</sub><sup>-</sup> counterions. Figure 1 shows an ORTEP<sup>17</sup> drawing of the complexed cation. Bond distances and angles concerning the coordination sphere around the metal ion are listed in Table 3. The zinc atom is coordinated by all the nitrogen atoms of the macrocycle in a distorted trigonal bipyramidal geometry, with N1, N3, and N5 in the basal plane. The Zn–N distances range from 2.05(1) to 2.22(1) Å, comparing well with those already found in Zn(II) complexes involving polyazacycloalkane ligands.<sup>16,18</sup> The coordination polyhedron is rather distorted, as

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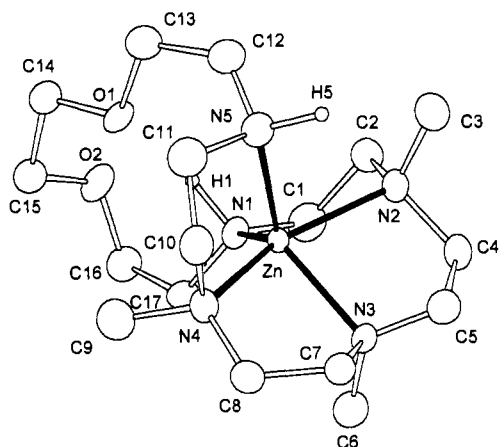


Figure 1. ORTEP drawing of the  $[Zn(Me_3[21]aneN_5O_2)]^{2+}$  cation.

Table 3. Selected Bond Distances (Å) and Angles (deg) for the  $[Zn(Me_3[21]aneN_5O_2)]^{2+}$  Cation

Distances			
Zn-N1	2.05(1)	Zn-N4	2.20(1)
Zn-N2	2.22(1)	Zn-N5	2.11(1)
Zn-N3	2.094(9)		
Angles			
N4-Zn-N5	86.7(6)	N2-Zn-N3	80.2(5)
N3-Zn-N5	129.4(5)	N1-Zn-N5	115.2(5)
N3-Zn-N4	83.1(5)	N1-Zn-N4	117.2(5)
N2-Zn-N5	93.7(5)	N1-Zn-N3	113.4(5)
N2-Zn-N4	158.6(5)	N1-Zn-N2	81.9(5)

demonstrated by the angular values around the  $Zn^{2+}$  ion (see Table 3). The  $N2-Zn-N4$  angle shows the largest deviation from the idealized geometry ( $158.6(5)$  vs  $180^\circ$ ). This value can be explained taking into account the compromise between the stereochemical requirements of the metal ion and the difficulty to accommodate the three donor atoms N2, N3, and N4, linked together by ethylene chains, in such a way N2 and N4 lie on the axial positions of a trigonal bipyramid. Furthermore N1 and N5 form very different angular values with N3 around the zinc atom (the angles  $N3-Zn-N1$  and  $N3-Zn-N5$  are  $113.4(5)$  and  $129.4(5)^\circ$ , respectively). This asymmetrical arrangement of the two unmethylated nitrogens in the equatorial plane could be related to the interactions, *via* hydrogen bonds, between N1 and the two etheral oxygens of the macrocycle O1 and O2 ( $N1\cdots O1 = 2.88(1)$ ,  $N1\cdots O2 = 2.69(2)$  Å).

Recently we have reported the crystal structure of the complex  $[Cu(Me_3[24]aneN_5O_3)]^{2+}$ . Similarly to the present case, the metal ion is coordinated by the five nitrogen atoms, while the oxygens are unbound.<sup>7</sup> Instead, the coordination geometry of the Cu(II) ion differs remarkably from the stereochemical environment of the  $Zn^{2+}$  ion. In fact, Cu(II) prefers a distorted square pyramidal disposition of the five nitrogen atoms.

**Metal Ion Coordination in Aqueous Solution.** The coordination behavior of  $Me_3[21]aneN_5O_2$ ,  $Me_3[24]aneN_5O_3$ , and  $[21]aneN_5O_2$  has been studied in  $0.15 \text{ mol dm}^{-3} \text{ NaClO}_4$  aqueous solution at  $298.1 \pm 0.1 \text{ K}$ . The stability constants for the equilibrium reactions of these three ligands with  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Pb^{2+}$  are reported in Table 4. All the receptors form  $[ML]^{2+}$  complexes with the metal ions considered: no polynuclear species are present. Monoprotonated complexes have been also observed; only the complexes  $[M(Me_3[21]aneN_5O_2)]^{2+}$  ( $M = Zn, Cd, Pb$ ) do not form protonated species, at least under the experimental conditions used. Finally,  $Cu^{2+}$  gives rise to complexes with both mono- and diprotonated species of such ligands. However, all the  $[ML]^{2+}$  species exhibit a low tendency to bear protonation; the low values found for the protonation

Table 4. Logarithms of the Formation Constants of Metal Complexes of  $Me_3[21]aneN_5O_2$ ,  $Me_3[24]aneN_5O_3$ , and  $[21]aneN_5O_2$  in  $0.15 \text{ mol dm}^{-3} \text{ NaClO}_4$  Aqueous Solution at  $298.15 \text{ K}$

reacn	log K		
	$Me_3[21]aneN_5O_2$	$Me_3[24]aneN_5O_3$	$[21]aneN_5O_2$
$Cu^{2+} + L = CuL^{2+}$	17.66(1) <sup>a,b</sup>	17.30(1) <sup>b</sup>	19.52(1)
$CuL^{2+} + H^+ = CuHL^{3+}$	4.26 <sup>b</sup>	5.20 <sup>b</sup>	4.31(3)
$CuHL^{3+} + H^+ = CuH_2L^{4+}$	2.39 <sup>b</sup>	2.51 <sup>b</sup>	3.35(2)
$Zn^{2+} + L = ZnL^{2+}$	10.71(1)	10.13(2)	12.89(2)
$ZnL^{2+} + H^+ = ZnHL^{3+}$		5.5(1)	5.11(3)
$Cd^{2+} + L = CdL^{2+}$	12.28(1)	11.17(1)	13.73(1)
$CdL^{2+} + H^+ = CdHL^{3+}$		5.56(5)	4.52(4)
$Pb^{2+} + L = PbL^{2+}$	10.58(1)	9.30(1)	11.86(1)
$PbL^{2+} + H^+ = PbHL^{3+}$		6.49(1)	6.35(2)

<sup>a</sup> Values in parentheses are standard deviation on the last significant feature. <sup>b</sup> Values taken from ref 7.

constants of such complexes can be reasonably explained by taking into account the involvement of all the five nitrogen donors in the coordination to the metal ions. This hypothesis agrees with the coordination environments of the metal centers displayed by the crystal structures of  $[Cu(Me_3[24]aneN_5O_3)](ClO_4)_2$  and of  $[Zn(Me_3[21]aneN_5O_2)](BPh_4)_2$ . Furthermore both Cu(II) and Zn(II) form complexes with  $Me_3[21]aneN_5O_2$  and  $Me_3[24]aneN_5O_3$  having very similar stability constants, suggesting an analogous coordination of each metal ion with both receptors. Such data suggest that, in the case of  $Cu^{2+}$  and  $Zn^{2+}$  complexes, the coordination environment of the metal centers is formed by the five nitrogens, while the oxygens are unbound.

As far as the  $Cd^{2+}$  and  $Pb^{2+}$  complexes are concerned, it is worthy to note that no formation of hydroxo species has been observed. It could be explained by taking into account that for these larger metal cations also the oxygen atoms contribute to the coordination. It has been reported<sup>16</sup> that, in the case of cyclic pentaamines, both  $Zn^{2+}$  and  $Cd^{2+}$  complexes show similar stability. In the present case the higher stability exhibited by the  $Cd^{2+}$  complexes accords with the binding of an oxygen atom, giving rise to the formation of a rather usual hexacoordination.

The most significant feature displayed by Table 4 is the larger stability, for all the metal ions considered, showed by the  $[ML]^{2+}$  complexes of  $[21]aneN_5O_2$  among the three oxa-aza macrocycles (the stability constants are *ca.* 1–2 logarithmic units higher). It is well-known that methyls have electron  $\sigma$ -donating properties. On the other hand, nitrogen methylation prevents the formation of H-bonds between water and amino groups, which contribute, *via* the  $H_2O\cdots HN$  interaction, to the  $\sigma$ -donating ability of nitrogen atoms.<sup>19</sup> Most likely this effect represents the main contribution to the higher stability exhibited by the complexes of  $[21]aneN_5O_2$  with respect to its methylated counterparts; however, the different desolvation experienced by secondary and tertiary amino groups upon complexation, as well as stereochemical distortions due to steric effects of *N*-methyl substituents, can also contribute in determining the observed trend.

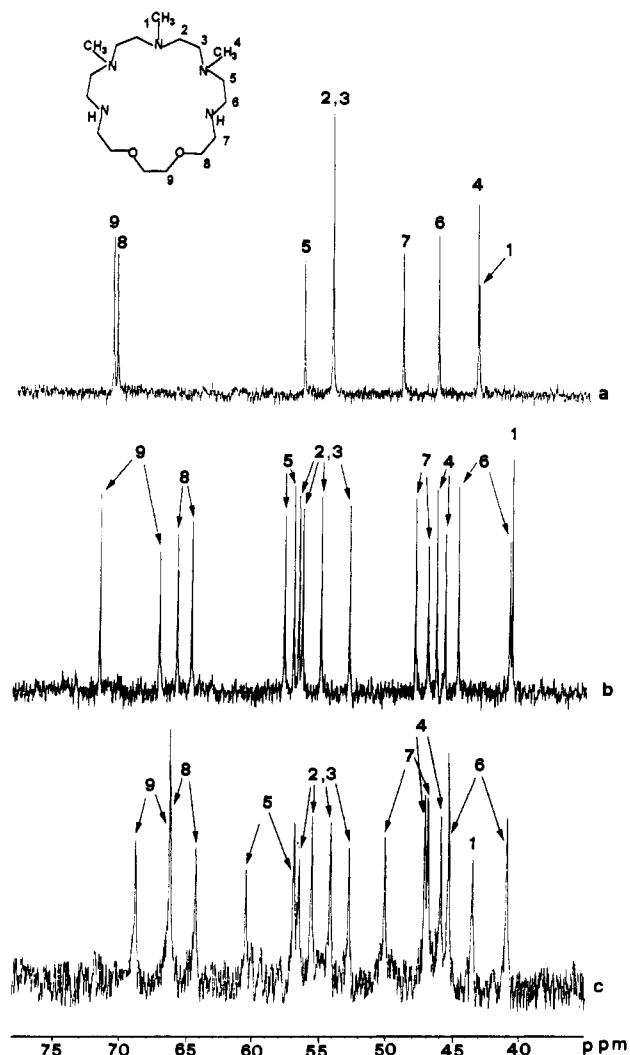
However, for all the metal ions herein considered, 1,4,7,10,13-cyclopentadecane ( $[15]aneN_5$ ) shows higher stability constants than the three oxa-aza receptors, the difference being in the range of 7–9 logarithmic units for each metal ion considered.<sup>20,21</sup> For  $[15]aneN_5$  the involvement of all the nitrogen donors in the coordination to such metal ions has been proved.<sup>21</sup> As a consequence, the remarkable drop in stability exhibited by the mixed-donor pentaaza macrocycles can be attributed mainly to the formation of large chelate rings containing the uncoordinated oxygen atoms.

(19) Golub, G.; Cohen, H.; Meyerstein, D. *J. Chem. Soc., Chem. Commun.* **1992**, 397.

(20)  $\log K_{CuL} = 28.3$ ,  $\log K_{ZnL} = 19.1$ ,  $\log K_{CdL} = 19.2$ , and  $\log K_{PbL} = 17.3$  ( $L = [15]aneN_5$ ).

(21) Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1978**, 104. (b) Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1978**, 1081.

(18) Bencini, A.; Bianchi, A.; Paoletti, P.; Paoli, P. *Coord. Chem. Rev.* **1992**, *120*, 51.



**Figure 2.**  $^{13}\text{C}$  NMR spectra of  $\text{Me}_3[21]\text{aneN}_5\text{O}_2$  (a),  $[\text{Zn}(\text{Me}_3[21]\text{aneN}_5\text{O}_2)]^{2+}$  (b), and  $[\text{Cd}(\text{Me}_3[21]\text{aneN}_5\text{O}_2)]^{2+}$  (c) in  $\text{D}_2\text{O}$ .

Although such ligands show a rather weak interaction with the cations herein examined, with respect to other pentaazacycloal-

kans,<sup>14,16</sup> they behave as versatile receptors for transition metal ions; i.e., as a consequence of their flexible framework, they are able to adapt themselves to the stereochemical requirements of metal cations.

In order to get further information on the coordination behavior of such molecules the  $\text{Cd}(\text{II})$  and  $\text{Zn}(\text{II})$  complexes have been examined by using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The  $^{13}\text{C}$  spectra of the ligand  $\text{Me}_3[21]\text{aneN}_5\text{O}_2$  and of  $[\text{Zn}(\text{Me}_3[21]\text{aneN}_5\text{O}_2)]^{2+}$  and  $[\text{Cd}(\text{Me}_3[21]\text{aneN}_5\text{O}_2)]^{2+}$  in  $\text{D}_2\text{O}$  have been reported in Figure 2. All the resonances have been assigned by using  $^1\text{H}$ - $^1\text{H}$  homonuclear,  $^1\text{H}$ - $^{13}\text{C}$  heteronuclear correlation and DEPT experiments. The main feature outlined by these spectra is the increased number of signals exhibited by the spectra of  $\text{Zn}(\text{II})$  and  $\text{Cd}(\text{II})$  complexes (Figure 2b,c, respectively) with respect to the receptor spectrum. In other words, while the amine  $\text{Me}_3[21]\text{aneN}_5\text{O}_2$  shows a  $\text{C}_2$  symmetry (Figure 2a), averaged on the NMR time scale, its complexes experience a clear loss in symmetry, due to a stiffening of the molecule as a consequence of the coordination of these metal ions. Furthermore, the same behavior is exhibited by  $\text{Zn}(\text{II})$  and  $\text{Cd}(\text{II})$  complexes with  $\text{Me}_3[24]\text{aneN}_5\text{O}_3$  and  $[21]\text{aneN}_5\text{O}_2$ . The absence of symmetry elements, also evidenced in the solid state by the crystal structure of the  $[\text{Cu}(\text{Me}_3[24]\text{aneN}_5\text{O}_3)]^{2+}$ <sup>7</sup> and  $[\text{Zn}(\text{Me}_3[21]\text{aneN}_5\text{O}_2)]^{2+}$  cations, leads to chirality of such metal complexes. Thus, a fascinating perspective is the use of these kinds of complexes as receptors for chiral anionic substrates, such as carboxylate or amino-acid anions.

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**Supplementary Material Available:** Tables of anisotropic and isotropic thermal parameters, positional parameters for the anion and the hydrogen atoms, and complete bond lengths and angles (10 pages). Ordering information is given on any current masthead page.