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Complexes formed by Zn^{II}, Cd^{II} and Hg^{II} in the presence of the octadentate ligand 1,4,7,10-tetrakis(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane. X-ray structure of the cadmium complex

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Abstract—The potentially octadentate ligand 1,4,7,10-tetrakis(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane (L^1) yields with cadmium(II) compounds of formula $[CdL^1]Y_2$ (Y = BPh_4, ClO_4, PF_6) in which the metal ion is coordinated by the eight nitrogen donor atoms of the ligand. The crystal structure of $[CdL^1](BPh_4)_2$ has been determined by X-ray diffraction. With zinc(II) and mercury(II) L^1 affords the compounds $[ML^2]Y_2$ [L^2 = 1,7-bis(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane. M = Zn; Y = ClO_4, PF_6. M = Hg; Y = PF_6] where the ligand L^2 originates from L^1 by loss of the methylpyrazole groups from two pendant arms of the macrocycle in *trans* positions. The compounds have been characterized by ^1H and ^{13}C NMR data. A variable temperature ^{13}C NMR study on $[CdL^1](PF_6)_2$ suggests that the cation undergoes rearrangements in solution between two geometric isomers. © 1997 Elsevier Science Ltd

Keywords: zinc(II); cadmium(II) and mercury(II) complexes; functionalized tetraazamacrocycle complexes; crystal structure.

In recent years pendant arm tetraazamacrocylic ligands have been widely investigated [1] and their metal complexes have been found to exhibit a considerable variety of structures and a wide range of stability which is largely determined by the nature of the functional groups in the pendant arms as well as by that of the metal ions being coordinated. These metal complexes are interesting both in view of their possible applications and for the study of their properties within the field of coordination chemistry. The macrocyclic ligand 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid (H_4DOTA), in particular, exhibits a very high complexing ability toward lanthanide(III) ions [2] because with its eight donor sites it provides a preformed cavity well suited to encapsulate such metal ions. The lanthanide metal complexes of this ligand are widely exploited for applications in diagnostic [3] and therapeutic medicine [4], the compound Na[Gd(DOTA)(H_2O)] (DOTA = 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetate) being used as a magnetic resonance imaging (MRI) contrast agent in the clinical practice [5]. More generally, by varying the nature of the functional groups and the length of the pendant arms [6] the coordinating properties of such ligands may be finely tuned to fit specific metal ions [7]. The ligands have accordingly been considered as specific sequestring agents for toxic heavy metals. Also, the increase in denticity brought about by the pendant arms of the macrocyclic ligand broadens the range of accessible coordination modes and of possible intramolecular processes for the metal complexes [8].

In recent years we have investigated the coordination chemistry of 1,4,7,10-tetraazacyclododecane functionalized with such residues as imidazole [9] and pyrazole [10], which are relevant for biomimetic purposes. In particular, the ligand 1,4,7,10-tetrakis

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(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane, L^1, has been found to form metal complexes with the metal ions in unusually high coordination numbers [10–12]. In some cases the ligand has been found to undergo transformations upon complexation which modify, but do not impair its coordinating ability [10]. It appeared interesting to investigate the chemical behaviour of the potentially octadentate L^1 ligand with respect to the zinc group metal ions, also to the purpose of investigating its possible selectivity toward the heavier and toxic, cadmium and mercury, metals of the group.

EXPERIMENTAL

All reagents were reagent grade. Solvents, when required by the synthetic procedures, were dried according to standard methods just before their use. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry of the University of Florence. The ^{13}C NMR spectra of the compounds were obtained with a Varian FT 80 spectrometer operating at 20.00 MHz. The ^{13}C spectra of $[CdL^1](PF_6)_2$ at various temperatures and the ^1H spectra of all compounds were obtained with a Bruker AC-200 spectrometer operating at 200 MHz (^1H) and 50.32 MHz (^{13}C). Chemical shifts are reported in ppm downfield with respect to the external standard $SiMe_4$. The ligand 1,4,7,10-tetrakis(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane was prepared according to published procedures [10]. Hydrated zinc(II) and cadmium(II) perchlorates (Aldrich), mercury(II) chloride (Fluka) and thallium(I) hexafluorophosphate (Strem) were used as received.

Synthesis of the compounds

$[ZnL^2](ClO_4)_2$. [L^2 = 1,7-bis(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane] $Zn(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1 mmol) dissolved in ethanol (30 cm^3) was slowly added to a warm solution of the ligand L^1 (0.49 g, 1 mmol) in ethanol (20 cm^3). The resulting solution was concentrated to a small volume until a crystalline product was obtained. The complex was recrystallized from methanol. Yield 0.43 g, 72%. Found: C, 32.1; H, 4.75; N, 18.5; Zn, 10.8. Calc. for $C_{16}H_{28}Cl_2N_8O_8Zn$: C, 32.2; H, 4.73; N, 18.8; Zn, 11.0. ^1H NMR in D_2O δ 7.87 [dd, 2H, H^3, $^3J(H^3–H^4)$ = 2.5, $^4J(H^3–H^5)$ = 0.6 Hz], 7.69 [dd, 2H, H^5, $^3J(H^5–H^4)$ = 2.4, $^4J(H^5–H^3)$ = 0.6 Hz], 6.52 [t, 2H, H^4, $^3J(H^4–H^3)$ = $^3J(H^4–H^5)$ = 2.4 Hz], 4.84 (s, 4H, CH_2 bridge), 2.90 (bm, 16H, CH_2 macrocycle). $^{13}C\{^1H\}$ NMR in D_2O δ 141.92 (C^3), 133.69 (C^5), 108.75 (C^4), 68.27 (CH_2 bridge), 49.03 (CH_2 macrocycle), 44.95 (CH_2 macrocycle).

$[CdL^1](ClO_4)_2$. $Cd(ClO_4)_2 \cdot xH_2O$ (0.35 g, *ca* 1 mmol) dissolved in ethanol (30 cm^3) was slowly added to a warm solution of the ligand L^1 (0.49 g, 1 mmol) in ethanol (30 cm^3). The resulting solution was concentrated to a small volume until a crystalline product was obtained. The complex was recrystallized from methanol. Yield 0.57 g, 71%. Found: C, 35.7; H, 4.58; N, 20.7. Calc. for $C_{24}H_{36}CdCl_2N_{12}O_8$: C, 35.8; H, 4.51; N, 20.9. ^1H NMR in D_2O δ 7.89 [dd, 4H, H^3, $^3J(H^3–H^4)$ = 2.5, $^4J(H^5–H^3)$ = 0.5 Hz], 7.07 [dd, 4H, H^5, $^3J(H^5–H^4$ = 2.5, $^4J(H^5–H^3)$ = 0.5 Hz], 6.61 [t, 4H, H^4, $^3J(H^4–H^3)$ = $^3J(H^4–H^5)$ = 2.5 Hz], 4.71 (s, 8H, CH_2 bridge), 3.07 (bm, 16H, CH_2 macrocycle). $^{13}C\{^1H\}$ NMR in D_2O δ 141.42 (C^3), 133.17 (C^5) 107.91 (C^4), 69.81 (CH_2 bridge), 49.16 (CH_2 macrocycle).

$[HgL^2](PF_6)_2$. $TlPF_6$ (0.35 g, 1 mmol) dissolved in ethanol (20 cm^3) was added to a solution of $HgCl_2$ (0.13 g, 0.5 mmol) in ethanol (25 cm^3), the resulting suspension was warmed to *ca* 50°C for 30 min and filtered. The solution was added to L^1 (0.25 g, 0.5 mmol) in ethanol (20 cm^3). Crystals of the complex were precipitated by slowly evaporating the resulting solution. The complex was recrystallized from ethanol. Yield 0.31 g, 75%. Found: C, 23.4; H, 3.45; N, 13.6. Calc. for $C_{16}H_{28}F_{12}HgN_8P_2$: C, 23.4; H, 3.43; N, 13.6. ^1H NMR in CD_3CN δ 7.81 [dd, 2H, H^3, $^3J(H^3–H^4)$ = 2.5, $^4J(H^3–H^5)$ = 0.5 Hz], 7.72 [dd, 2H, H^5, $^3J(H^5–H^4)$ = 2.5, $^4J(H^5–H^3)$ = 0.5 Hz], 6.48 [t, 2H, H^4, $^3J(H^4–H^3)$ = $^3J(H^4–H^5)$ = 2.5 Hz], 4.82 (s, 4H, CH_2 bridge), 2.75 (bm, 16H, CH_2 macrocycle). $^{13}C\{^1H\}$ NMR in CD_3CN δ 143.41 (C^3), 134.96 (C^5), 108.44 (C^4), 68.09 (CH_2 bridge), 48.41 (CH_2 macrocycle), 43.09 (CH_2 macrocycle).

The complexes $[ZnL^2](PF_6)_2$ and $[CdL^1](PF_6)_2$ were prepared by adding to a solution of the ligand L^1 (0.25 g, 0.5 mmol) in ethanol (20 cm^3) a solution of $Zn(PF_6)_2$ or $Cd(PF_6)_2$ (0.5 mmol) which was prepared as described for the mercury complex. The complexes were recrystallized from ethanol. Yield *ca* 70%. $[ZnL^2](PF_6)_2$, found: C, 27.7; H, 4.19; N, 16.1. Calc. for $C_{16}H_{28}F_{12}N_8P_2Zn$: C, 27.9; H, 4.10; N, 16.3. ^1H NMR in CD_3CN δ 7.03 [dd, 2H, H^3, $^3J(H^3–H^4)$ = 2.5, $^4J(H^3–H^5)$ = 0.5 Hz], 6.88 [dd, 2H, H^5, $^3J(H^5–H^4)$ = 2.5, $^4J(H^5–H^3)$ = 0.5 Hz], 5.70 [t, 2H, H^4, $^3J(H^4–H^3)$ = $^3J(H^4–H^5)$ = 2.5 Hz], 4.12 (s, 4H, CH_2 bridge), 2.03 (bm, 16H, CH_2 macrocycle). $^{13}C\{^1H\}$ NMR in CD_3CN δ 142.10 (C^3), 133.65 (C^5), 108.84 (C^4), 68.11 (CH_2 bridge), 48.91 (CH_2 macrocycle), 44.91 (CH_2 macrocycle). $[CdL^1](PF_6)_2$, found: C, 32.1; H, 4.11; N, 18.7. Calc. for $C_{24}H_{36}CdF_{12}N_{12}P_2$: C, 32.2; H, 4.05; N, 18.8. ^1H NMR in $(CD_3)_2CO$ δ 7.94 [dd, 4H, H^3, $^3J(H^3–H^4)$ = 2.5, $^4J(H^3–H^5)$ = 0.5 Hz], 6.89 [dd, 4H, H^5, $^3J(H^5–H^4)$ = 2.5, $^4J(H^5–H^3)$ = 0.6 Hz], 6.66 [t, 4H, H^4, $^3J(H^4–H^3)$ = $^3J(H^4–H^5)$ = 2.5 Hz], 4.72 (s, 8H, CH_2 bridge), 3.45 (bm, 16H, CH_2 macrocycle). $^{13}C\{^1H\}$ NMR in CD_3CN δ 140.52 (C^3), 133.76 (C^5), 108.36 (C^4), 68.12 (CH_2 bridge), 47.81 (CH_2 macrocycle).

Crystals of the complex $[CdL^1](BPh_4)_2$ suitable for X-ray analysis were obtained by recrystallizing from acetone and ethanol the white solid that precipitates by adding $NaBPh_4$ dissolved in ethanol to a solution of $[CdL^1](PF_6)_2$ in the 2 : 1 stoichiometric ratio in the same solvent. Found: C, 69.4; H, 6.19; N, 13.4. Calc. for $C_{72}H_{76}B_2CdN_{12}$: C, 69.5; H, 6.16; N, 13.5.

X-ray crystallographic study

All measurements were carried out at room temperature on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å). The crystal used for all operations was a prism with dimensions $0.30 \times 0.40 \times 0.60$ mm. Cell constants were obtained from least-squares refinements of the setting angles of 24 reflections with $14 < \vartheta < 16$.

Crystal data for $[CdL^1](BPh_4)_2$.

$C_{72}H_{76}B_2CdN_{12}$, $M = 1243.51$, triclinic, space group $P\bar{1}$, $a = 12.809(4)$, $b = 13.954(6)$, $c = 20.112(7)$ Å, $\alpha = 74.55(3)$, $\beta = 83.62(3)$, $\gamma = 64.74(3)^\circ$, $V = 3133(2)$ Å^3, $Z = 2$, $D_{calc} = 1.318$ g cm^{-3}, μ(Mo-K_α) = 3.97 cm^{-1}, $F(000) = 1300$.

Structure determination. Intensity data were collected in the range $2.5 \leqslant \vartheta \leqslant 25^\circ$ by ω–2ϑ scans with $(1.00 + 0.35\text{tg}\vartheta)^\circ$ scan width and 1.5–5° min^{-1} scan speed. The intensities of three standard reflections monitored periodically during data collection did not reveal any decrease or significant fluctuations in intensities. Of the 10,873 reflections measured 10,517 were unique and 9514, having $I > 3\sigma(I)$, were used for structure solution and refinement. The structure was solved by heavy atom [13] methods. An empirical absorption correction was applied at isotropic convergence (correction factors range 1.12–0.92) [14]. In the final model anisotropic temperature factors were assigned to the Cd, N and C atoms. Hydrogen atoms were introduced in calculated positions with C—H = 0.96 Å and $U_H = 1.2U_C^{eq}$, where U_C^{eq} is the equivalent isotropic temperature factor of the carrier atom. The refinement was performed on F in two blocks. Data were weighted according to the formula $w = [\sigma^2(F) + gF^2]^{-1}$, with $g = 0.0015$. In the final cycle shift/error ratios were $\leqslant 0.01$. With 774 parameters the refinement converged at $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.036$ and $R_w = [\Sigma(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2} = 0.041$. The extreme values of the residual electron density in the final ΔF synthesis were 0.74 and -0.56 eÅ^{-3}. Scattering factors were from Refs. [13] (C, H, N and B) and [15] (Cd) the latter being corrected for anomalous dispersion [16]. Values of selected bond distances and angles are given in Table 1.

Supplementary material including non-hydrogen and hydrogen atomic coordinates, thermal parameters for the non-hydrogen atoms, and complete tables of bond distances and angles has been deposited at the Cambridge Crystallographic Data Centre. A listing of observed and calculated structure factors is available upon request from the authors.

RESULTS AND DISCUSSION

The L^1 ligand yields in the presence of cadmium(II) compounds of formula $[CdL^1]Y_2$ (Y = BPh_4, ClO_4, PF_6). Their solubility depends on the nature of the counterion, the perchlorate being soluble in polar solvents, like water and methanol, whereas the hexafluorophosphate and the tetraphenylborate are soluble in less polar solvents, like acetone and acetonitrile. The ^1H and $^{13}C\{^1H\}$ NMR spectra of the complexes, recorded in different solvents, are unaffected by the nature of the counterion and are only slightly affected by that of the solvent. The ^1H spectra exhibit one resonance for each group of equivalent hydrogens in the pendant arms and a complex multiplet for the hydrogens of the macrocycle, the relative intensities of the signals being in accordance with those expected for the intact L^1 ligand [11b]. The $^{13}C\{^1H\}$ spectra exhibit all the signals due to the various groups of equivalent carbon atoms as given by the free ligand. This again suggests that the intact L^1 ligand is coordinating. Moreover, the signal at low field due to the pyrazole C^3 shows coupling to $^{111/113}Cd$, which confirms that the pendant arms are chelating. The ^2J(C, Cd) value, of 9.3 Hz, is in the range found for cadmium complexes with similar ligands [6]. In view of these results as well as of those previously obtained with related ligands [6] and for complexes formed by L^1 with other metal cations [11], the cadmium(II) ion may be considered to be eight coordinated in solution with a similar geometry to that detected for the solid state structure (*vide infra*). The presence of one signal for the carbons of the ligand suggests a dynamic behaviour of the complex cation in solution. Accordingly a variable temperature $^{13}C\{^1H\}$ study was conducted on $[CdL^1](PF_6)_2$ in $(CD_3)_2CO$ solution and the stack of the spectra is shown in Fig. 1. On lowering the temperature the signal due to the macrocycle carbon atoms broadens and eventually it splits, in the slow exchange limit, into two separate resonances of equal intensity; the shifts of such signals (48.04 and 47.07 ppm from external TMS) are close to that of the original signal at room temperature (47.81 ppm) and symmetrically distributed with respect to it. On the other hand, the signals at lower fields due to the pyrazole and to the bridging methylene carbons do not coalesce and their shifts remain basically unchanged. Such temperature dependence points to the equivalence of the four pendant donor groups at all temperatures investigated but to the inequivalence of the macrocyclic ring carbons, which are differentiated into two groups of four at the lower temperatures. In view of the results of detailed investigations on related systems [6,8a,c,d], it may be assumed that the features of the high-temperature spectra are due to the occurence of two types of fast motion affecting, rather independently from each other, the pendant arms and the chains of the macrocycle. The features of the low-temperature spectra may be attributed to magnetic inequivalence arising from slowing down, on the NMR time scale, of the latter type of motion. From the coalescence behaviour of the resonances of the macrocycle carbon atoms the mean site lifetime (τ) for the complex in either diastereoisomeric form is calculated to be 9.2 ms at 259 K, corresponding to a rate constant of 109 s^{-1}

Table 1. Selected bond distances (Å) and angles (°) for $[CdL^1](BPh_4)_2$

Cd—N(1)	2.513(3)	Cd—N(5)	2.349(3)
Cd—N(2)	2.499(4)	Cd—N(7)	2.578(4)
Cd—N(3)	2.475(2)	Cd—N(9)	2.408(4)
Cd—N(4)	2.527(3)	Cd—N(11)	2.475(5)
N(1)—Cd—N(2)	72.2(1)	N(3)—Cd—N(5)	161.6(1)
N(1)—Cd—N(3)	112.1(1)	N(3)—Cd—N(7)	91.5(1)
N(1)—Cd—N(4)	70.7(1)	N(3)—Cd—N(9)	68.9(1)
N(1)—Cd—N(5)	67.7(1)	N(3)—Cd—N(11)	123.7(1)
N(1)—Cd—N(7)	122.8(1)	N(4)—Cd—N(5)	122.5(1)
N(1)—Cd—N(9)	161.0(1)	N(4)—Cd—N(7)	162.6(1)
N(1)—Cd—N(11)	89.0(1)	N(4)—Cd—N(9)	92.5(1)
N(2)—Cd—N(3)	73.2(1)	N(4)—Cd—N(11)	67.0(1)
N(2)—Cd—N(4)	113.0(1)	N(5)—Cd—N(7)	74.7(1)
N(2)—Cd—N(5)	89.9(1)	N(5)—Cd—N(9)	117.7(1)
N(2)—Cd—N(7)	66.0(1)	N(5)—Cd—N(11)	74.4(2)
N(2)—Cd—N(9)	124.2(1)	N(7)—Cd—N(9)	75.5(1)
N(2)—Cd—N(11)	159.2(1)	N(7)—Cd—N(11)	120.6(2)
N(3)—Cd—N(4)	72.2(1)	N(9)—Cd—N(11)	76.0(1)

and to a free energy of activation of 53 kJ mol^{-1} for the interconversion process at that temperature.

The structure of $[CdL^1](BPh_4)_2$ (**1**) as revealed by the X-ray analysis, consists of $[CdL^1]^{2+}$ complex cations and tetraphenylborate anions. The cadmium(II) ion in the complex cation is eight-coordinated by the four N atoms (N_m) of the macrocycle and the four nitrogens (N_{pz}) of the dangling pyrazole groups (Fig. 2) arranged at the corners of a polyhedron which, according to recent proposals [8b,g], may be considered as an 'inverted square antiprism', with the basal faces rotated by approximately 23° with respect to each other about the pseudo-fourfold axis. The coordination geometry is similar to that previously found for a manganese(II) [12] (**2**) and a sodium [11] (**3**) complex formed by the same ligand, although there are differences in the bond lengths formed by the metal atoms in these complexes, which are worth noting. In spite of a 0.14 Å increase in the ionic radius going from Mn^{II} to Cd^{II} [17], the Cd–N_m distances (2.47–2.53 Å range, see Table 1) are comparable with the Mn–N_m ones (2.48–2.52 Å). The metal–N_{pz} distances, on the other hand, increase by 0.11 Å, in the mean, from **2** to **1**. Similar trends are exhibited by the non-bonded distances between the donor nitrogen atoms, which measure the dimensions of the coordination polyhedron: there are no substantial increases in the $N_m \cdots N_m$ and the $N_m \cdots N_{pz}$ distances from **2** to **1**, whereas the $N_{pz} \cdots N_{pz}$ distances, which involve the relatively unconstrained pyrazole groups, increase by 0.15 Å, in the mean. In the $[NaL^1]^+$ cation of **3** all the metal–nitrogen distances [Na–N_m = 2.702(4) Å, Na–N_{pz} = 2.582(5) Å] are much longer than in the previous two complexes; in particular, they are longer than expected on the basis of the differences between the ionic radii of cadmium and sodium [17]. Also all the $N \cdots N$ non bonded distances are considerably longer in **3** than in the other two compounds. This should introduce strains in the chelate rings formed by the L^1 ligand in **3**. Possibly in order to release some strains the planes of the pyrazole groups in that compound are oriented in such a way that the Na^+ ion is considerably displaced [by 1.19(1) Å] from them. On the other hand, the deviations of the transition metal ions in the other two compounds from the pyrazole planes are smaller [0.18–0.68 Å in **1** and 0.12–0.29 Å in **2**] and appear to be compatible with proper coordination of the dangling groups through their donor atoms. Finally, the trends of the distances (Å) of the metal atoms in these three compounds from the best planes through the two sets of 'basal' N_m (a) and N_{pz} (b) atoms [(a): 1.389(1) **1**, 1.413(2) **2**, 1.627(3) **3**; (b): 1.239(1) **1**, 1.163(2) **2**, 1.029(3) **3**] diverge and disagree with the trend of the ionic radii. The decreasing value of set (b) may be traced to the relatively easy opening of the face of the coordination polyhedron defined by the N_{pz} atoms and to the consequent shift of the metal ion toward that face, but most of the other structural features discussed above suggest that a different amount of covalent contribution to the bonding is involved in the three compounds, which presumably decreases from **1** to **3**.

The bonding within the cadmium(II) complex cation (**4**) formed by the ligand DOTAM, based on the same tetraazamacrocycle as L^1, however with dangling acetamide groups, has been studied in detail [18]. The metal atom in **4** is coordinated by four N and four O atoms. The Cd–N distances in **4** are shorter by 0.06 Å, in the mean, than the Cd–N_m distances in **1**, whereas the Cd–O distances formed by the dangling groups in **4** are longer by 0.04 Å, in the mean, than the Cd–N_{pz} distances in **1**. The existence of two *trans* Cd—O bonds in **4** longer than the other pair of Cd—O bonds has been noted and its possible causes investigated [18]. The Cd—N_{pz} bonds in **1** exhibit a similar trend (Table

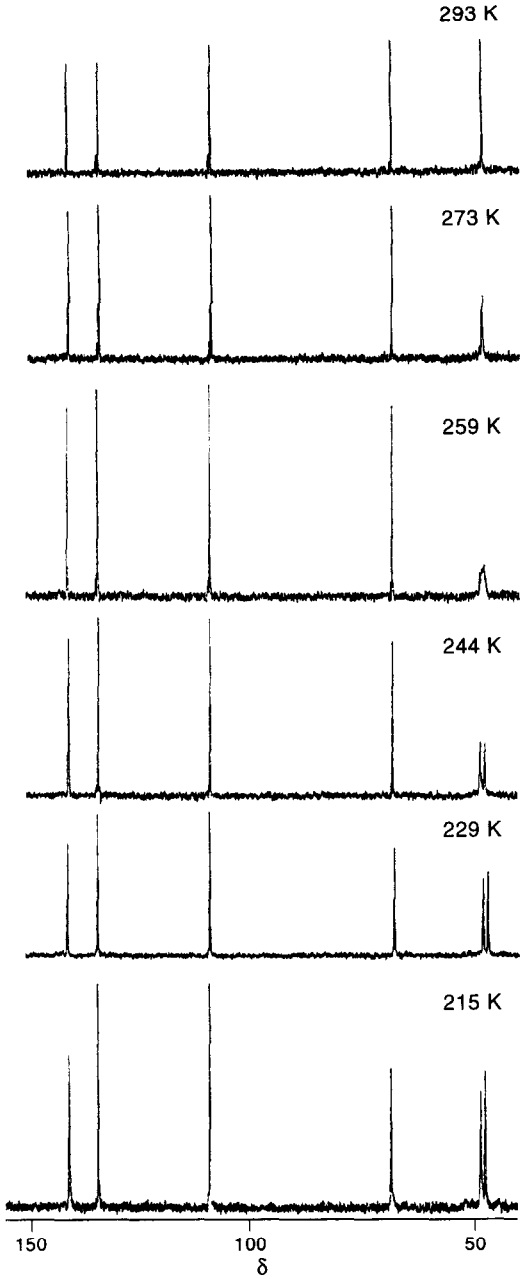

Fig. 1. A selection of $^{13}C\{^1H\}$ 50.32 MHz NMR spectra of $[CdL^1](PF_6)_2$ in $(CD_3)_2CO$ at different temperatures.

1), although less well defined. This might be due to different steric requirements of the donor atoms involved in the two cations as well as to packing effects, which are expected to differ for the two structures, also due to the different size of the functionalizing groups.

The L^1 ligand yields in the presence of zinc(II) and mercury(II) complexes which may be formulated, according to the elemental analysis and NMR data, as $[ML^2]Y_2$ [L^2 = 1,7-bis(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane. M = Zn; Y = ClO_4, PF_6. M = Hg; Y = PF_6]. Repeated preparations under the same reaction conditions invariably gave products whose analyses were consistent with the above formulae. It appears that in the course of these preparations the L^1 ligand is transformed to L^2 due to loss of two methylpyrazole groups in *trans* positions. The ^1H NMR spectra of the zinc(II) and mercury(II) compounds (see Experimental) exhibit one resonance for each group of equivalent hydrogens of the pendant arms and a broad multiplet for the hydrogens of the macrocycle. The intensities of signals due to the pyrazole hydrogens and to those of the methylene bridging group in the pendant arms are in the 1:2 ratio and the intensity ratios between the above signals and the broad resonance of the macrocyclic hydrogens are in accordance with the assumption that the L^2 ligand consists of the macrocycle and only two dangling groups. The $^{13}C\{^1H\}$ spectra of these zinc(II) and mercury(II) compounds present one resonance for each group of equivalent carbon atoms of the pendant arms and two resonances for the macrocyclic carbons. Comparison between the intensity ratios for the signals in these $^{13}C\{^1H\}$ spectra and in those of the cadmium derivatives confirms that the intensities due to the dangling groups in L^2 are lower than expected for the fully functionalized macrocycle, in keeping with the assumption that two of the dangling groups of L^1 are lost in the course of the syntheses of these zinc(II) and mercury(II) complexes. The presence of two signals due to the carbons of the macrocycle suggests that the two pyrazole groups still present in L^2 are in *trans* positions, because four resonances would be expected if the dangling groups were in *cis* positions. The coordination geometry of the metal cations in these complexes is probably that of a distorted octahedron formed by the four macrocycle N atoms and by the donors of the two dangling pyrazole groups, as previously found when ligands with geometry strictly related to that of L^2 were employed [9].

In an attempt to understand if the partial disruption of the L^1 ligand was specific for the reactions with the zinc(II) and mercury(II) cations or could also take place in presence of cadmium(II) the cadmium complex $[CdL^1](ClO_4)_2$ was dissolved in ethanol and refluxed for a long time (approximately 2 days). The white solid which separated on slowly concentrating the solution was collected and the $^{13}C\{^1H\}$ spectrum of the sample dissolved in CD_3CN was found to exhibit, in addition to the signals of the $[CdL^1]^{2+}$ cation, a group of six weaker resonances (δ 142.11, 133.52, 109.12, 69.17, 49.04, 43.38). The four of these at lower field are typical of the pyrazole carbons and the bridging CH_2 group, whereas the shifts of the remaining two signals are close to those of the macrocycle carbons in the zinc(II) and mercury(II) compounds (see Experimental). This suggests that a $[CdL^2]^{2+}$ cation, containing the transformed ligand, is formed on prolonged refluxing the L^1 derivative in ethanol. Comparison of the intensities of the signals due to the $[CdL^1]^{2+}$ and $[CdL^2]^{2+}$ cations shows that in the conditions specified above *ca.* 30% of the original species is transformed. While this reveals that the cleavage of the ligand is not specific for the

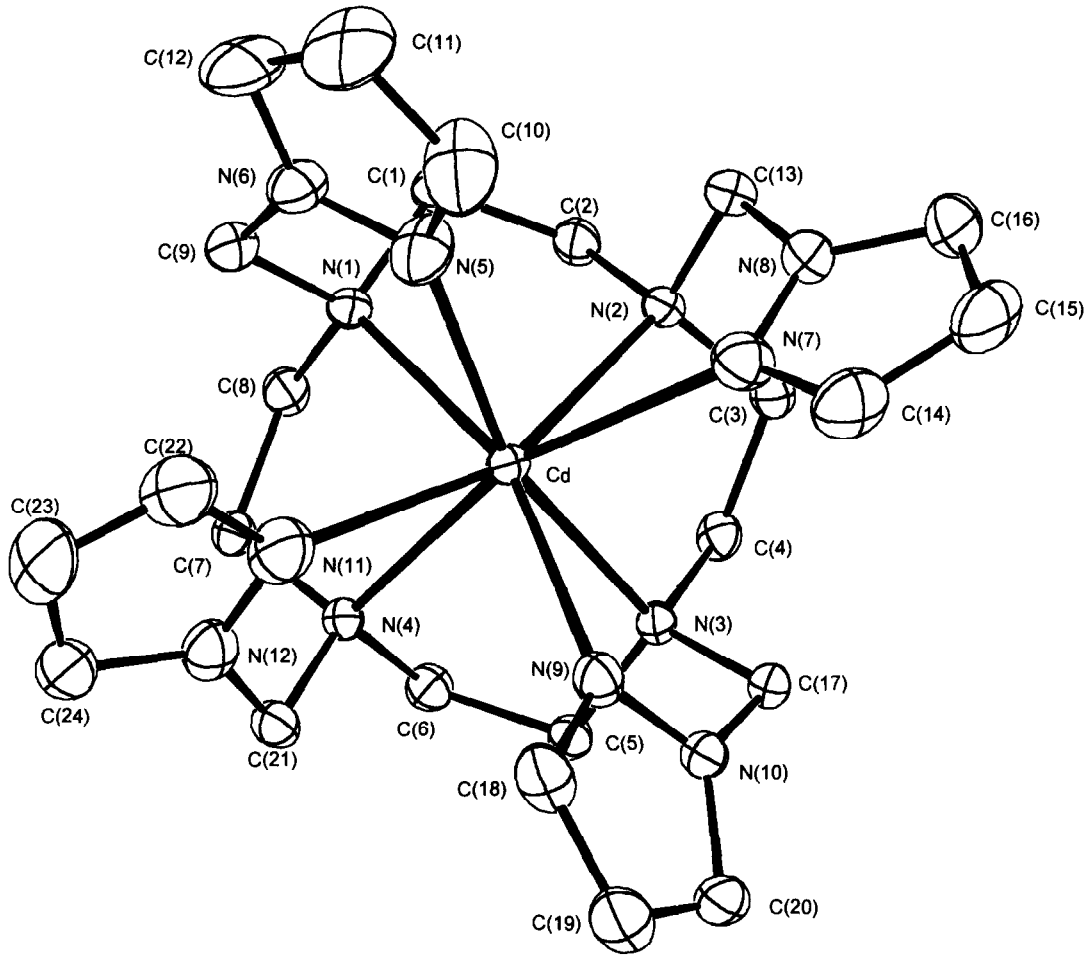

Fig. 2. A view of the $[CdL^1]^{2+}$ cation in the structure of $[CdL^1](BPh_4)_2$ (**1**), with 20% probability ellipsoids.

zinc(II) and mercury(II) derivatives, it also provides evidence for scarce reactivity of the L^1 ligand when it is firmly coordinated to the metal. The detachment of two dangling groups, which occurs immediately in mild conditions in the presence of zinc(II) and mercury(II) ions, might be related to the preference generally exhibited by these ions for coordination numbers not higher than six (although exceptions obviously exist [10]). Presumably, uncoordinated or weakly coordinated arms of the functionalized macrocycle are more easily detached than the firmly coordinated ones.

A slightly different type of transformation of the L^1 ligand was previously observed for the reaction with transition metal ions such as Ni^{II} and Zn^{II} [10], for which eight-coordination is uncommon, in anhydrous conditions (different from the present ones). In presence of the BPh_4^- counterion cleavage of the C—N bond in the pendant arm formed by the pyrazole nitrogen, rather than by the macrocycle N atom as in the present cases, occurred and the pyrazole was substituted by an ethoxo group. The latter was considered to be formed in the dissociation of BPh_4^- in ethanol. On the other hand, no ligand transformation was observed if the I^-, ClO_4^-, or PF_6^- counterions were employed. Overall, these results show that the C—N bonds in the pendant arms of this ligand form rather easy points of attack in suitable conditions. The cleavage which occurs in the cases presently reported (non anhydrous conditions) presumably corresponds to the inverse process with respect to that of the functionalization reaction of the macrocycle [10].

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