Co-ordination of 1,4,7-Tris(pyrazol-3-ylmethyl)-1,4,7-triazacyclononane with Iron(III), Nickel(II) and Zinc(II). Crystal and Molecular Structures of $[ML][ClO_4]_2 \cdot nH_2O$ ($M = Ni$, $n = 0.5$; $M = Zn$, $n = 1$)†

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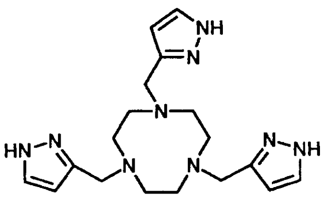
The new potentially hexadentate compound 1,4,7-tris(pyrazol-3-ylmethyl)-1,4,7-triazacyclononane (L) has been synthesised. In protonated form, L·6HCl, it reacted with metal perchlorates to give the complexes $[ML][ClO_4]_2 \cdot nH_2O$ ($M = Ni$, $n = 0.5$; $M = Zn$, $n = 1$) and $[FeL][ClO_4]_3 \cdot H_2O$. The crystal structures of the nickel(II) **1** and zinc(II) **2** complexes have been determined by single-crystal X-ray diffraction: **1**, monoclinic, space group $C2/c$, $a = 18.270(4)$, $b = 14.179(6)$, $c = 21.714(4)$ Å, $\beta = 115.57(2)°$, $Z = 8$; **2** triclinic, space group $P\bar{1}$, $a = 10.322(4)$, $b = 10.563(3)$, $c = 14.460(4)$ Å, $\alpha = 92.61(3)$, $\beta = 108.25(3)$, $\gamma = 116.07(3)°$, $Z = 2$. In both complex cations the metal ion is co-ordinated by the six nitrogen donor atoms of the ligand.

In recent years we have begun to investigate the co-ordination chemistry of tri- and tetra-azamacrocycles functionalised with *N*-bound imidazole and pyrazole. Some information has been obtained on the solid-state structures of a number of both transition[1] and alkali-metal[2] complexes. Owing to their flexibility and donor ability, these ligands can bind metal ions with different steric and electronic requirements and the resulting complexes are, in general, remarkably stable and inert. Nonetheless, some complexes may rapidly undergo loss of one of the ligand pendant arms under very mild conditions, which reduces their stability and inertness.[3] The mechanism of such loss is not completely clear; it occurs through cleavage of the C(bridge)–N(pyrazole) polar bond, which is apparently favoured by the electron-withdrawing pyrazole group and by the electrostatic field due to the metal cation.

In order to prevent such loss of one pendant group by the functionalised macrocycle we have designed a compound in which each methylene bridge from the 1,4,7-triazacyclononane is linked to the C^3 atom of the pyrazole. Here we report on the synthesis of the new potentially hexadentate ligand 1,4,7-tris(pyrazol-3-ylmethyl)-1,4,7-triazacyclononane (L) and on its co-ordination properties towards some 3d metal ions with which we have obtained the complexes $[ML][ClO_4]_2 \cdot nH_2O$ ($M = Ni$, $n = 0.5$; $M = Zn$, $n = 1$) and $[FeL][ClO_4]_3 \cdot H_2O$. The structures of the nickel(II) and zinc(II) complexes have been investigated by single-crystal X-ray analyses in order to ascertain the co-ordination geometries and compare them with those of complexes already reported, formed by other pyrazole-functionalised macrocycles.

Owing to their stability, inertness and water solubility, some metal complexes with such ligands may be of potential interest in several biomedical applications, as metal-sequestering,[4] NMR imaging-contrast[5] and radiotherapeutic agents,[6] apart from their general interest in the field of co-ordination chemistry and that of biomimetic complexes. There has been a rapid growth in polyazamacrocycles functionalised with a wide variety of pendant donor groups,[7] but the co-ordination chemistry of macrocycles bearing pyrazole or imidazole groups has been scarcely exploited.[8]



L

Experimental

All chemicals were reagent grade; solvents, when required by the synthetic procedures, were dried according to standard methods just before their use. Electronic spectra were recorded in the range 300–2500 nm with a Perkin-Elmer Lambda 9 spectrometer. The concentrations of the solutions in water were about 10^{-3} mol dm^{-3}. Infrared spectra were recorded with a Perkin-Elmer 283 grating spectrophotometer as Nujol mulls between KBr plates. Magnetic susceptibility measurements were made on solid samples at room temperature by the Faraday method using a DMS-5 automated magnetometer. The ^1H NMR spectrum of $[ZnL][ClO_4]_2 \cdot H_2O$ in D_2O was recorded on a Bruker MSL instrument operating at 200.13 MHz and the ^{13}C NMR spectra of all compounds with a Varian CFT 80 spectrometer operating at 20.00 MHz, from solutions in $CDCl_3$ or D_2O. Chemical shifts are reported in ppm downfield with respect to the internal standard $SiMe_4$. The intermediate compounds 1,4,7-triazacyclononane[9] and 3-(chloromethyl)-pyrazole hydrochloride[10] were prepared according to published procedures. Hydrated nickel(II) and zinc(II) perchlorates were prepared by standard methods. Anhydrous $FeCl_3$ (Merck) was used as supplied without further purification. 3-(Chloromethyl)pyrazole was obtained by slow addition of the stoichiometric amount of ethyldiisopropylamine (Aldrich) in diethyl ether to a suspension of 3-(chloromethyl)pyrazole hydrochloride in the same solvent. When the reaction was complete the solution was filtered and the solvent removed by rotary evaporation to give a sticky colourless oil which was satisfactorily employed in the synthesis of the ligand. ^{13}C NMR ($CDCl_3$): δ 146.6 (C^3), 104.9 (C^4), 131.2 (C^5) and 37.5 (CH_2 bridge).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

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

CAUTION: 3-(chloromethyl)pyrazole has been found to be an irritant even in very low concentration in the gas phase. The perchlorate salts of metal complexes with organic ligands are potentially explosive. For this reason the drying temperature was kept below 50 °C and small amounts of sample were handled at a time.

Synthesis of the Macrocycle.—The synthesis of macrocycle L was carried out under a moisture-free atmosphere. 3-(Chloromethyl)pyrazole (5.03 g, 43.2 mmol) in MeCN (50 cm^3) and Proton Sponge^R [1,8-bis(dimethylamino)naphthalene] (Aldrich) (9.24 g, 43.2 mmol) in MeCN (75 cm^3) were slowly added, in the stoichiometric ratio, to a stirred solution of 1,4,7-triazacyclononane (1.86 g, 14.4 mmol) in MeCN (100 cm^3). The solution was stirred for 24 h at 35 °C and then for 8 h at 60 °C. The solvent was removed under reduced pressure by rotatory evaporation until a slightly sticky yellow solid was obtained. This was dissolved in an ethanol–chloroform mixture (50 cm^3) and HCl was bubbled through the ice-cooled solution until a crystalline product was obtained. This was filtered and washed with $CHCl_3$ to eliminate the 1,8-bis(dimethylamino)naphthalene hydrochloride. The macrocycle was thus obtained as the hexakis (hydrochloride) (yield: 5.5 g; 65%). ^{13}C NMR (D_2O): δ, 141.7 (C^3), 108.7 (C^4), 133.6 (C^5), 52.4 (CH_2 bridge) and 49.7 (CH_2 of macrocycle) (Found: C, 37.6; H, 6.35; N, 21.6. Calc. for $C_{18}H_{33}Cl_6N_9$: C, 36.8; H, 5.65; N, 21.4%).

Syntheses of the Complexes.—The nickel(II) and zinc(II) complexes were prepared by mixing warm solutions (20–30 cm^3) of L·6HCl (0.33 mmol) in methanol and the appropriate hydrated metal(II) perchlorates in ethanol in 1 : 1 molar ratio. The iron(III) complex was prepared in a water–ethanol mixture (30 cm^3) using $FeCl_3$ and L·6HCl, in 1 : 1 molar ratio, and an excess of $NaClO_4$. The mixtures were concentrated to small volume until crystalline products were obtained. Crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature of ethanol–water solutions of the nickel(II) and zinc(II) complexes. All the products contain water of crystallisation as inferred from the IR data and confirmed by X-ray analysis of the nickel and zinc derivatives. The complexes are soluble in water and warm methanol (Found: C, 33.5; H, 4.40; N, 19.4. Calc. for $C_{18}H_{28}Cl_2N_9NiO_{8.5}$: C, 34.0; H, 4.45; N, 19.8. Found: C, 33.2; H, 4.45; N, 19.3. Calc. for $C_{18}H_{29}Cl_2N_9O_9Zn$: C, 33.2; H, 4.50; N, 19.3. Found: C, 29.6; H, 3.85; Fe, 7.35; N, 17.0. Calc. for $C_{18}H_{29}Cl_3FeN_9O_{13}$: C, 29.1; H, 3.95; N, 17.0; Fe, 7.55%).

Significant absorptions in the UV/VIS spectra of the complexes are (λ_{max}/nm; ε/cm^2 mmol^{-1}; concentrations of the solutions in water *ca.* 10^{-3} mol dm^{-3}): [FeL][ClO$_4$]$_3$·H$_2$O, diffuse reflectance, 410; solution, 450 (3390); [NiL][ClO$_4$]$_2$·0.5H$_2$O, diffuse reflectance, 360 (sh), 530, 820 and 900; solution, 340 (31), 530 (24), 810 (33) and 880 (sh). ^{1}H NMR (D_2O) of [ZnL][ClO$_4$]$_2$·H$_2$O δ 7.86 (d, 3 H, H^5 of pyrazole, ^3J 2.5), 6.48 (d, 3 H, H^4 of pyrazol, ^3J 2.5); 4.09 (s, 6 H, CH_2 bridge); 3.03, 2.76 [AA′BB′, 12 H, $^2J(H^AH^{A'})$ = 5.58, $^2J(H^BH^{B'})$ = 4.95, $^3J(H^AH^B)$ = $^3J(H^{A'}H^{B'})$ = −13.97, $^3J(H^AH^{B'})$ = $^3J(H^{A'}H^B)$ = 6.72 Hz, CH_2 of macrocycle]. The chemical shifts and coupling constants successfully simulate the experimental ^{1}H NMR spectrum.

Crystal Structure Analysis of [NiL][ClO$_4$]$_2$·0.5H$_2$O.—The crystals of the compound, which were generally thin and slightly bent, did not provide good material for diffraction. An elongated prism with approximate dimensions 0.1 × 0.2 × 0.6 mm was used for all operations, in which an Enraf–Nonius CAD4 diffractometer and Mo-Kα radiation were employed. Unit-cell parameters were obtained from the settings of 24 reflections with 14 < θ < 15°.

Crystal data. $C_{18}H_{28}Cl_2N_9NiO_{8.5}$, M_r = 636.09, monoclinic, space group *C*2/*c*, *a* = 18.270(4), *b* = 14.179(6), *c* = 21.714(4) Å, β = 115.57(2)°, *U* = 5074(3) Å^3, *Z* = 8, D_c = 1.665 g cm^{-3}, *F*(000) = 2632, graphite-monochromated, Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 10.4 cm^{-1}.

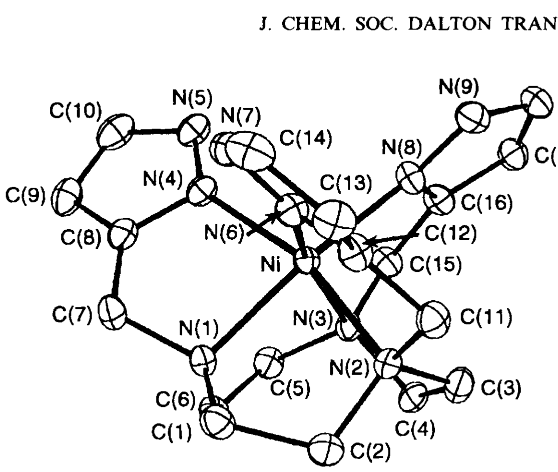

Fig. 1 A view of the cation in the structure of [NiL][ClO$_4$]$_2$·0.5H$_2$O **1**

Intensity data were collected in the range θ 2.5–25° for reflections ±*h* + *k* + *l* using the ω–2θ scan method. Three reflections monitored periodically revealed no decay in intensities. Of the 4776 reflections measured, 3760 were independent and 2534 having $I > 3\sigma_I$ were employed in the final refinement. An empirical absorption correction was applied to all data after structure solution, at isotropic convergence (correction factor range: 0.88–1.17).[11] The principal computer programs used in the crystallographic calculations are listed in refs. 11–15.

The structure was solved by direct and heavy-atom methods. The cation and the anions are in general positions, whereas the water molecule, involved in a net of hydrogen bonds, lies on a two-fold axis. In the final refinement cycles (351 parameters) all non-hydrogen atoms were assigned anisotropic thermal parameters. The symmetry-independent H_2O hydrogen atom was located from a Fourier difference synthesis and its position was refined, whereas all the other H atoms were included in calculated positions, at 0.96 Å from the respective C or N atom; all H atoms were assigned thermal parameters $U_H = 1.2\ U_E$, where U_E is the equivalent isotropic thermal parameter of the respective C or N atom. The weighting scheme was $w^{-1} = \sigma^2(F_o) + 0.0015\ F_o^2$. At convergence, with all shift/error ratios < 0.001 : 1, the *R* and *R*′ values were 0.059 and 0.063, respectively. The extreme values of residual electron density in the final Fourier difference map were 0.4 and −0.4 e Å^{-3}.

The atomic coordinates are given in Table 1, selected bond lengths and angles in Table 2. The structure of the cation is shown in Fig. 1.

Crystal Structure Analysis of [ZnL][ClO$_4$]$_2$·H$_2$O.—The crystal used had the shape of a rod (0.1 × 0.2 × 0.8 mm) with ill defined faces. The unit-cell parameters were obtained from 24 reflections with 13 < θ < 19°.

Crystal data. $C_{18}H_{29}Cl_2N_9O_9Zn$, M_r = 651.76, triclinic, space group $P\bar{1}$, *a* = 10.322(4), *b* = 10.563(3), *c* = 14.460(4) Å, α = 92.61(3), β = 108.25(3), γ = 116.07(3)°, *U* = 1313.7(9) Å^3, *Z* = 2, D_c = 1.647 g cm^{-3}, *F*(000) = 672, graphite-monochromated, Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 12.2 cm^{-1}.

Intensity data were measured for the reflections ±*h* ±*k* +*l* in the range θ 2.5–27° with the ω–2θ scan mode. No systematic decay in intensities was observed. Of the 5493 reflections measured, 4788 were unique and 3505 with $I > 3\sigma_I$ were used in the final refinement. A correction for absorption was applied as for the nickel compound (correction factor range: 0.78–1.24).

The structure was solved by heavy-atom and direct methods. It was soon evident that two ethylenic strands of the macrocycle were affected by large librational motion or (more likely) by disorder. Various models were tested to account for this; the one

Table 1 Fractional coordinates of the non-hydrogen atoms of $[NiL][ClO_4]_2\cdot0.5H_2O$*

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	−0.218 30(5)	0.461 67(6)	−0.329 73(4)	C(11)	−0.266 3(5)	0.318 0(5)	−0.436 2(4)
N(1)	−0.291 4(4)	0.427 4(4)	−0.280 8(3)	C(12)	−0.199 8(5)	0.276 7(5)	−0.374 8(4)
N(2)	−0.308 3(3)	0.391 3(4)	−0.413 1(3)	C(13)	−0.165 6(5)	0.186 2(6)	−0.362 4(4)
N(3)	−0.296 3(4)	0.578 3(4)	−0.367 0(3)	C(14)	−0.106 3(5)	0.191 6(6)	−0.298 5(5)
N(4)	−0.147 9(4)	0.514 4(4)	−0.232 8(3)	C(15)	−0.248 4(5)	0.656 8(5)	−0.376 2(4)
N(5)	−0.094 1(4)	0.583 4(5)	−0.203 8(3)	C(16)	−0.191 9(5)	0.615 1(5)	−0.403 2(4)
N(6)	−0.163 9(4)	0.332 9(4)	−0.320 9(3)	C(17)	−0.161 3(5)	0.650 1(7)	−0.446 8(4)
N(7)	−0.105 2(4)	0.279 3(5)	−0.273 2(3)	C(18)	−0.114 0(5)	0.579 8(7)	−0.453 2(4)
N(8)	−0.162 9(4)	0.529 2(4)	−0.381 4(3)	Cl(1)	−0.001 8(1)	0.300 0(1)	−0.075 6(1)
N(9)	−0.116 2(4)	0.507 4(5)	−0.413 2(3)	Cl(2)	−0.095 3(1)	0.101 2(2)	0.133 0(1)
C(1)	−0.332 3(5)	0.337 9(6)	−0.313 6(4)	O(1)	−0.002 0(4)	0.343 8(4)	−0.135 2(3)
C(2)	−0.367 9(5)	0.347 8(6)	−0.391 8(4)	O(2)	−0.080 8(5)	0.302 4(5)	−0.080 0(5)
C(3)	−0.345 7(5)	0.465 1(6)	−0.464 6(4)	O(3)	0.052 5(6)	0.348 3(6)	−0.019 6(4)
C(4)	−0.366 0(4)	0.552 4(5)	−0.433 0(4)	O(4)	0.021 3(5)	0.204 4(5)	−0.072 3(5)
C(5)	−0.324 1(5)	0.597 1(5)	−0.313 5(4)	O(5)	−0.172 5(5)	0.092 5(9)	0.081 3(4)
C(6)	−0.350 0(5)	0.505 4(6)	−0.292 0(4)	O(6)	−0.101 8(5)	0.161 2(6)	0.182 6(4)
C(7)	−0.237 0(5)	0.414 0(6)	−0.207 4(4)	O(7)	−0.044 3(5)	0.141 7(8)	0.108 9(5)
C(8)	−0.175 2(5)	0.489 6(6)	−0.186 7(4)	O(8)	−0.062 3(7)	0.014 8(6)	0.162 3(6)
C(9)	−0.137 6(6)	0.545 1(6)	−0.127 3(4)	O(9)	0	0.308 3(6)	0.25
C(10)	−0.085 7(6)	0.602 4(7)	−0.140 5(5)				

* The O(9) atom, belonging to the water molecule, lies on a two-fold axis.

Table 2 Selected intramolecular bond lengths (Å) and angles (°) for $[NiL][ClO_4]_2\cdot0.5H_2O$

Ni–N(1)	2.091(6)	Ni–N(4)	2.075(6)
Ni–N(2)	2.099(6)	Ni–N(6)	2.048(6)
Ni–N(3)	2.103(6)	Ni–N(8)	2.045(6)
N(1)–Ni–N(2)	83.9(2)	N(6)–Ni–N(8)	97.7(2)
N(1)–Ni–N(3)	84.4(2)	N(1)–Ni–N(4)	79.7(3)
N(2)–Ni–N(3)	83.9(2)	N(2)–Ni–N(6)	79.9(2)
N(4)–Ni–N(6)	99.4(2)	N(3)–Ni–N(8)	80.4(2)
N(4)–Ni–N(8)	98.7(3)		

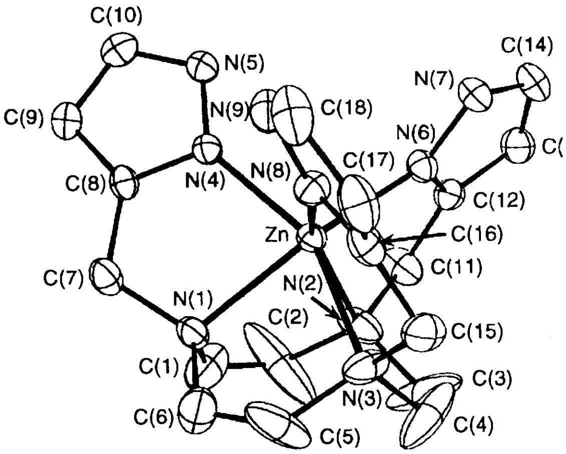

Fig. 2 A view of the cation in the structure of $[ZnL][ClO_4]_2\cdot H_2O$ **2**

finally adopted had only one image for each chain (all carbon occupancy factors 1.0), but the four C–N and, separately, the two C–C distances in the two ethylene chains were tied to unique values. All non-hydrogen atoms, including those of the disordered chains, were refined anisotropically. The H atoms were in calculated positions (those of the water molecule were not introduced) with C–H = N–H 0.96 Å and $U_H = 1.2\ U_{C,N}$. A small damping factor was applied, which did not affect the estimated standard deviations (e.s.d.s) appreciably. With 354 parameters refined and the $w^{-1} = \sigma^2(F_o) + 0.0025\ F_o^2$ weighting scheme, convergence was attained at $R = 0.069$ and $R' = 0.079$ when all shift/error ratios were $< 0.02:1$. Final Fourier-difference map features < 0.8 and > -0.5 e Å^{-3}.

The atomic coordinates are given in Table 3, selected bond lengths and angles in Table 4. The structure of the cation is shown in Fig. 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The potentially hexadentate compound 1,4,7-tris(pyrazol-3-ylmethyl)-1,4,7-triazacyclononane (L) was prepared in good yield by the one-step reaction of the macrocycle 1,4,7-triazacyclononane with 3-(chloromethyl)pyrazole and 1,8-bis(dimethylamino)naphthalene (Proton Sponge^R). The choice of the base for the alkylation reaction is critical for the success of the reaction. A readily protonated base, which however is a poor nucleophile,[16] is required in order to avoid the formation of quaternary ammonium compounds of pyrazole. Neither triethylamine nor ethyldiisopropylamine were found to be suitable bases because by reaction with 3-(chloromethyl)pyrazole they gave, respectively, 3-(triethylmethylammonio)pyrazolyl chloride and 3-(ethyldiisopropylmethylammonio)pyrazolyl chloride in quantitative yield. On the other hand, inorganic bases such as NaOH or Na_2CO_3 transform 3-(chloromethyl)pyrazole into the corresponding alcohol. The macrocycle could be separated from the by-products and the Proton Sponge^R hydrochloride as the hexakis(hydrochloride) which was obtained in fairly pure form and successfully employed in the synthesis of the complexes. The reaction of L·6HCl with $M(ClO_4)_2\cdot6H_2O$ (M = Ni or Zn) in an ethanol–methanol mixture gives complexes of formula $[ML][ClO_4]_2\cdot nH_2O$ (M = Ni, $n = 0.5$; M = Zn, $n = 1$). The reaction of $FeCl_3$ and L·6HCl with an excess of $NaClO_4$ in a water–ethanol mixture gives the $[FeL][ClO_4]_3\cdot H_2O$ complex. The solid-state structures of the nickel and zinc complexes have been established by X-ray diffraction methods.

The magnetic moments at room temperature of the nickel(II) (3.28 μ_B) and of the iron(III) complex (2.34 μ_B) are in the normal ranges for the high-spin and, respectively, low-spin configurations of these ions; the zinc(II) complex is diamagnetic. The electronic spectra of $[NiL][ClO_4]_2\cdot0.5H_2O$ and $[FeL][ClO_4]_3\cdot H_2O$ were recorded on solid samples and in water solution. In the range 300–1300 nm the nickel complex exhibits the expected three absorptions typical for six-co-ordination.[17] In particular, there is a marked splitting of the low-energy band which may arise from that of the spin-allowed $^3A_{2g} \longrightarrow {}^3T_{2g}$

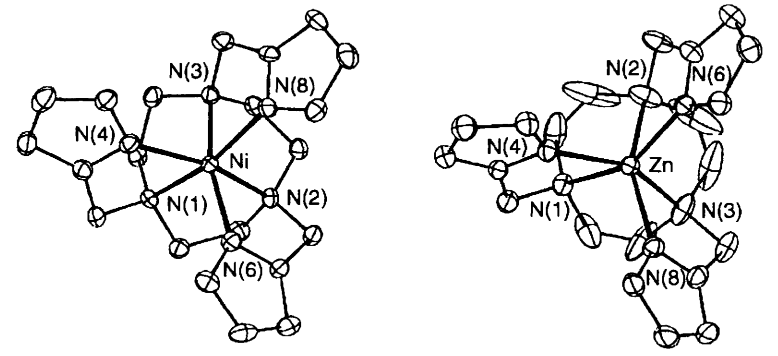

Fig. 3 Views of the two cations along the respective pseudo-three-fold axes, showing the different amounts of deviation from trigonal-prismatic co-ordination

Table 3 Fractional coordinates of the non-hydrogen atoms of $[ZnL][ClO_4]_2 \cdot H_2O$

Atom	*x*	*y*	*z*
Zn	0.258 43(8)	0.175 39(7)	0.282 80(5)
N(1)	0.287 9(7)	0.259 0(6)	0.149 3(4)
N(2)	0.519 9(7)	0.299 3(8)	0.334 7(5)
N(3)	0.309 8(8)	0.018 2(7)	0.218 2(6)
N(4)	0.162 7(6)	0.317 6(5)	0.272 5(4)
N(5)	0.117 0(7)	0.379 7(6)	0.330 3(4)
N(6)	0.331 4(6)	0.193 9(5)	0.436 9(4)
N(7)	0.269 1(7)	0.136 2(6)	0.502 2(4)
N(8)	0.046 3(6)	−0.018 3(5)	0.234 3(4)
N(9)	−0.106 0(6)	−0.059 6(6)	0.212 3(4)
C(1)	0.446 4(9)	0.383 6(10)	0.184 3(9)
C(2)	0.548 7(13)	0.399 1(14)	0.265 9(7)
C(3)	0.565 9(13)	0.186 0(14)	0.326 4(9)
C(4)	0.475 8(9)	0.063 8(10)	0.272 7(11)
C(5)	0.274 7(17)	0.027 8(10)	0.114 1(8)
C(6)	0.265 5(15)	0.136 2(13)	0.080 6(7)
C(7)	0.169 3(9)	0.305 6(8)	0.107 5(5)
C(8)	0.137 4(7)	0.364 0(6)	0.188 5(5)
C(9)	0.076 0(8)	0.456 5(8)	0.191 4(5)
C(10)	0.064 0(9)	0.462 1(8)	0.282 2(6)
C(11)	0.579 5(9)	0.375 3(10)	0.439 8(6)
C(12)	0.480 0(8)	0.287 9(8)	0.492 1(5)
C(13)	0.509 3(9)	0.283 6(9)	0.590 9(6)
C(14)	0.372 0(10)	0.187 2(9)	0.594 9(6)
C(15)	0.207 9(10)	−0.125 4(8)	0.232 9(7)
C(16)	0.053 3(9)	−0.137 7(7)	0.213 7(5)
C(17)	−0.095 2(10)	−0.256 7(8)	0.177 8(6)
C(18)	−0.190 5(10)	−0.201 4(9)	0.178 7(7)
Cl(1)	0.365 0(2)	0.704 9(2)	0.039 6(2)
Cl(2)	0.027 6(2)	−0.233 1(2)	0.474 3(2)
O(1)	0.213 4(8)	0.679 3(9)	0.019 7(7)
O(2)	0.426 5(9)	0.714 0(10)	0.144 9(5)
O(3)	0.457 3(9)	0.839 8(7)	0.022 6(6)
O(4)	0.378 6(12)	0.597 6(8)	−0.008 0(7)
O(5)	−0.017 7(7)	−0.137 5(7)	0.422 8(5)
O(6)	0.094 9(9)	−0.166 8(9)	0.579 5(5)
O(7)	−0.107 1(10)	−0.362 7(8)	0.459 5(8)
O(8)	0.142 6(9)	−0.241 0(8)	0.444 7(6)
O(9)	0.747 3(9)	0.110 7(9)	0.160 0(6)

Table 4 Selected intramolecular bond lengths (Å) and angles (°) for $[ZnL][ClO_4]_2 \cdot H_2O$

Zn–N(1)	2.211(5)	Zn–N(4)	2.119(5)
Zn–N(2)	2.258(6)	Zn–N(6)	2.085(5)
Zn–N(3)	2.203(6)	Zn–N(8)	2.108(5)
N(1)–Zn–N(2)	79.0(2)	N(6)–Zn–N(8)	101.0(2)
N(1)–Zn–N(3)	80.4(2)	N(1)–Zn–N(4)	77.0(2)
N(2)–Zn–N(3)	78.4(3)	N(2)–Zn–N(6)	76.5(2)
N(4)–Zn–N(6)	98.1(2)	N(3)–Zn–N(8)	76.2(2)
N(4)–Zn–N(8)	96.8(2)		

transition in trigonally distorted octahedral symmetry.[18] The electronic spectra of the iron(III) complex are essentially featureless in the range 800–1300 nm. The d–d bands expected for a low-spin d^5 ion in a six-coordinate environment[19] are obscured by the strong ligand-to-metal charge-transfer bands at 410 nm for the solid compound and at 450 nm (ε = 3390 cm^2 $mmol^{-1}$) for aqueous solution which, on the other hand, are responsible for the orange colour of the iron(III) complex and its water solution.

In both complex cations (Figs. 1 and 2) the metal ion is six-co-ordinate, bound by the three nitrogen atoms of the macrocycle and by three pyrazole nitrogen atoms with a co-ordination geometry intermediate between trigonal prismatic and octahedral in the nickel derivative (**1**) but closer to trigonal prismatic in the zinc one (**2**). This is due to different amounts of rotation of the basal faces of the prism with respect to each other about the pseudo-three-fold axis of the prism (Fig. 3). Twist angles of 45(1) **1** and 30(1)° **2** from the trigonal-prism geometry are estimated taking the mean of the three N_m–C_m–C_p–N_p torsion angles involving chelate N atoms in each complex (N_m = macrocycle nitrogen, N_p = co-ordinating pyrazole nitrogen, C_m and C_p = centroids of the triangles formed by the N_m and N_p respectively, atoms of a ligand). The metal–ligand distances (Tables 2 and 4) are shorter, on average, in the nickel derivative than in the zinc one, the overall difference (0.09 Å) being larger than that between the radii of the metal cations (*ca.* 0.05 Å[20]). In particular, the mean Ni–N_m and Ni–N_p values are 2.098(6) and 2.056(16) Å, respectively, whereas the Zn–N_m distances span the range 2.20–2.26 Å and the mean Zn–N_p is 2.104(17)Å. Such differences between the two compounds do not arise from a uniform expansion of the ligand cage on going from **1** to **2** but essentially result from (*i*) a shift of the metal cation inside the cage, away from the macrocycle plane, and (*ii*) from a moderate expansion of the less-strained side of the cage, the one defined by the pyrazole groups. The $N_m \cdots N_m$ distances, spanning the ranges 2.80–2.81 (**1**) and 2.82–2.85 Å (**2**), and the $N_m \cdots N_p$ intrachelate distances [2.66–2.68 (**1**) and 2.66–2.70 Å (**2**)], are comparable for the two compounds, whereas the $N_p \cdots N_p$ ones increase from 3.08–3.14 (**1**) to 3.16–3.23 Å (**2**). The metal cation lies 1.33 Å from the plane through the N_m atoms in **1** but 1.50 Å in **2** (all e.s.d.s < 0.01 Å for distances from least-squares planes); the distances from the planes through the N_p atoms, on the other hand, are comparable for the two compounds [0.99 (**1**) and 1.01 Å (**2**)]. From the latter values the separation between the basal faces of the co-ordination prism is estimated to increase by *ca* 0.2 Å on going from **1** to **2**. Combined with the constancy of the

$N_m \cdots N_p$ intrachelate distances for the two compounds, this produces the different amounts of rotation of the basal faces of the co-ordination polyhedra for **1** and **2**, mentioned above and apparent from Fig. 3. The overall dimensions of the co-ordination polyhedron in **1** are closer to those found for a nickel complex **3** formed by a related triazacyclononane ligand functionalised with imidazole groups[1a] than to those detected for the present zinc complex **2** formed by the same L ligand as in **1**. Two six-coo3743dinate nickel(II) complexes have previously been obtained with two ligands formed by tetraazacyclododecane functionalised with *N*-bonded pyrazole groups.[3a] The two ligands differ in the number of attached pyrazoles, which are four (nickel compound **4**) or three (**5**), due to cleavage of one of the pendant arms present in **4**. The cleavage, however, does not affect the co-ordination sphere as in both complexes the six-coordinate metal cation is bound to all of the four N_m and only to two N_p donors. The $Ni-N_m$ distances in the two compounds span the range 2.13–2.21 Å, mean 2.17 Å, significantly higher than that found for **1**, probably due to the different macrocycles involved, whereas the 2.058(4) Å mean of the $Ni-N_p$ distances in **4** and **5** almost matches that in **1**. On the other hand, a seven-coordinate zinc(II) complex **6** formed with the same, partially cleaved, ligand as in compound **5** exhibits a wide range of (long) bond lengths, with mean values 2.35 and 2.24 Å for the four $Zn-N_m$ and the three $Zn-N_p$ distances, respectively.[3a]

With such a wide range of metal–ligand distances and the different co-ordination numbers in **2** and **6** the zinc(II) cation appears to be more facultative than the Ni^{II} in these compounds. A unique feature of the present zinc(II) derivative **2** is that its metal ion lies in the plane of each pyrazole ring, within 0.09 Å. On the contrary, the nickel cation deviates considerably (0.21–0.45 Å) from the planes through the pyrazole groups in **1**. Similar or even larger deviations were found for the other nickel(II) complexes referred to above: 0.17–0.41 for **3**, 0.56 and 0.97 for **4**, 0.42 and 0.48 Å for **5**. The range of deviations (0.06–0.36 Å) for the zinc(II) derivative **6** is slightly smaller than those of the nickel(II) compounds, however larger than in **2**. In conclusion, the metal ion in **2** appears to be better bound to the pendant-arm donor set than to the macrocycle donors. This may reveal a tendency toward a lower co-ordination number than six, at least under the present conditions, and may also be at the origin of the disordered arrangement of the macrocycle chains.

A distinctive feature of the compounds reported here is due to the presence of water molecules in the structure. Besides being hydrogen bonded to the ClO_4^- anions, these are also linked to the N–H bonds of pyrazole groups. The latter type of interaction is not possible in compounds **3**–**6**. The water O(9) atom in **1** forms with one of its H atoms a 2.76(1) Å hydrogen bond to the perchlorate O(6) atom and a 2.79(1) Å bond to N(5) (in the $-x, 1-y, -z$ symmetry-equivalent position) through the H atom of N(5). Being placed on a two-fold axis, atom O(9) also forms a pair of hydrogen bonds symmetry related to the former, giving an overall pseudo-tetrahedral arrangement. In **2** this atom lies 2.81(1) Å from N(9) $(1+x, y, z)$ and is possibly involved through its own H atoms (not located) in additional interactions, both of length 3.05(1) Å, with the O(3) perchlorate oxygen in the positions $1-x, 1-y, -z$ and $x, y-1, z$.

The X-ray analyses on the metal complexes reported here have shown that in each case the ligand provides a rather close environment about the metal atom, which may prevent the access of anionic nucleophiles to the metal centre and contribute to the noticeable inertness of the complexes. Indeed experiments on metal displacement carried out for *ca.* 10^{-3} mol dm^{-3} solutions of $[NiL][ClO_4]_2 \cdot H_2O$ in water with varying amounts of CN^- have shown that the electronic spectrum of $[NiL]^{2+}$ is unchanged for hours in presence of the stoichiometric amount of CN^- required for the formation of $[Ni(CN)_4]^{2-}$, and a substantial decrease in the ε_M of the band at 810 nm is only observed after 24 h with a five-fold excess of CN^-. Also the rapid complexation reaction which occurs between the hexaprotonated macrocycle and the iron(III), nickel(II) and zinc(II) cations is indicative of the remarkable stability of the complexes. The ^1H NMR spectrum of $[ZnL]^{2+}$ in D_2O displays a complicated multiplet due to the CH_2 protons of the macrocyclic ring. It is split symmetrically into two groups of signals (δ_A 2.95–3.12; δ_B 2.68–2.84). This pattern, which can be analysed in terms of an AA′BB′ spin system,[21] is indicative of two groups of magnetically inequivalent protons due to different orientations of the C–H bonds with respect to the co-ordination plane of the macrocyclic ring.

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