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Synthesis and co-ordination chemistry of 1,5,9-triazacyclododecane monosubstituted with imidazole and pyrazole

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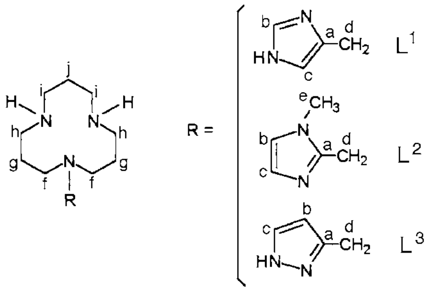
The potentially tetradentate ligands 1-(imidazol-4-ylmethyl)- (L^1), 1-(1-methylimidazol-2-ylmethyl)- (L^2) and 1-(pyrazol-3-ylmethyl)-1,5,9-triazacyclododecane (L^3) have been synthesized; L^1 was isolated as the tetrahydrochloride, $L^1{\cdot}4HCl$. The basicity constants of L^1 and L^3 have been determined by potentiometry at 25 °C in NaCl. The co-ordination chemistry of L^1 and L^3 toward some 3d metal ions has been investigated and the complexes $[ML^3(Cl)]Y$ (M = Mn or Fe, Y = BPh_4; M = Ni, Y = BF_4) and $[ML(ClO_4)]BPh_4$ (M = Co, L = L^3; M = Cu or Zn, L = L^1 or L^3) have been isolated and characterized. The structures of the iron(II) and nickel(II) complexes of L^3 have been determined by single-crystal X-ray analyses. Both contain dimeric $[\{ML^3(Cl)\}_2]^{2+}$ complex cations in which each metal ion is six-co-cordinated by four nitrogen donors of one L^3 ligand and by two bridging Cl^- ions in an approximately octahedral environment.

The co-ordination chemistry of macrocycles with pendant arms bearing donor atoms is receiving great attention.[1] Azamacrocycles with three or four nitrogen donors bearing pendant co-ordinating arms have been found to bind metal ions in a selective way[2] or to form metal complexes which are important for medical applications due to their high stability.[3] Triazamacrocycles (namely 1,4,7-triazacyclononane or 1,5,9-triazacyclododecane) and 1,4,7,10-tetraazacyclododecane with or without a dangling co-ordinating arm yield metal complexes which have relevance as models for metal enzymes. Iron(II),[4] copper(II)[5] and zinc(II)[6] complexes with such ligands exhibit co-ordinating, thermodynamic and catalytic properties similar to those of metal enzymes and accordingly play an important role in improving our understanding of the structure–function relationships in natural systems. The zinc complexes with 1,5,9-triazacyclododecane[7] and 1,4,7,10-tetraazacyclododecane,[6] in particular, have been widely studied being good models for the Zn–OH nucleophilic group in carbonic anhydrase[7] and for hydrolytic zinc(II) enzymes.[8] In these model complexes the zinc-bound OH group, which is easily generated at physiological pH from the zinc-co-ordinated H_2O the pK_a value of which is slightly higher than 7, acts as a nucleophile at the electrophilic centres of the substrates.

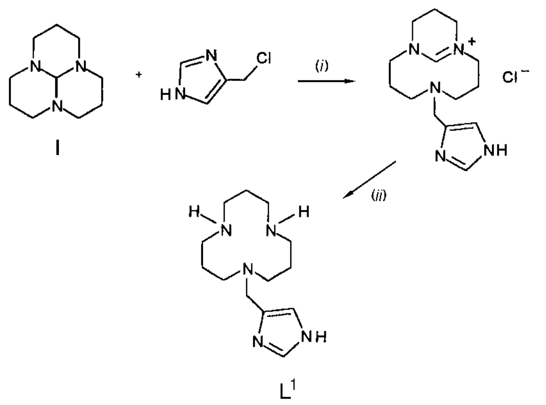
Such points of interest prompted us to undertake the synthesis and the study of the co-ordinating properties of compounds having a residue attached to the triazacyclododecane framework. Essentially three strategies have been followed to synthesize such molecules. One is based on a macrocyclization method such as the Richman–Atkins procedure.[2,9] The second leads to monosubstituted species through the use of cyclic oxapolyamines.[10] The third relies on the introduction in the triazamacrocycle of an *N*-formyl group masked as a tricyclic orthoamide and subsequent reaction of the orthoamide functional group.[11] The above synthetic strategies, however, present features which either limit their use to the introduction of dangling groups having stable synthons, or give the final products in low yield after long synthetic procedures. For these reasons polyazamacrocycles bearing dangling groups which may be of importance for biomimetic purposes, like imidazole, have received scarce attention.[5] We are investigating the chemical behaviour of tri- and tetra-azamacrocycles substituted with pyrazole and imidazole groups[12] and we are interested, in particular, in the efficient synthesis of such molecules. Recently the easy and high-yield synthesis of the orthoamide of triazacyclododecane has been reported.[13] It appeared interesting to investigate the use of that compound as the synthon to monosubstituted triazacyclododecane with pyrazole or imidazole residues.



We report herein the high-yield synthesis of 1-(imidazol-4-ylmethyl)- (L^1), 1-(1-methylimidazol-2-ylmethyl)- (L^2) and 1-(pyrazol-3-ylmethyl)-1,5,9-triazacyclododecane (L^3). Compound L^1 was isolated as the tetrahydrochloride, $L^1{\cdot}4HCl$. The basicities of L^1 and L^3 have been determined and their co-ordinating properties toward some 3d metals investigated. The crystal structures of the iron(II) and nickel(II) derivatives of L^3 have been determined.

Experimental

Commercial solvents were dried from an appropriate drying agent just before use according to standard procedures. The NMR spectra were obtained with a Varian FT80 spectrometer operating at 20 MHz (^{13}C). Positive chemical shifts are to high frequency relative to $SiMe_4$ internal standard. Room-temperature electronic spectra were recorded in the range 250–1500 nm with a Perkin-Elmer Lambda 9 spectrophotometer, infrared spectra with a Perkin-Elmer 283 grating spectrophotometer. Conductivity measurements were carried out with a WTW model CBR/b conductivity bridge. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry of the University of Florence. The compounds 1,5,9-triazatricyclo[7.3.1.0]tridecane[13] **I**, 4-(chloromethyl)imidazole hydrochloride,[14] 2-(chloromethyl)-1-methylimidazole hydrochloride[15] and 3-(chloromethyl)pyrazole hydrochloride[16] were prepared according to published procedures. Hydrated manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) salts were prepared by standard methods.



Scheme 1 (*i*) MeCN, proton sponge, *ca.* 50 °C, 12 h; (*ii*) 3 mol dm^{-3} HCl, *ca.* 70 °C, 48 h, obtained as L^1·4HCl

Macrocycle synthesis

The procedure for the synthesis of L^1·4HCl is depicted in Scheme 1.

5-(Imidazol-4-ylmethyl)-1,5-diaza-9-azoniabicyclo[7.3.1]tridec-9(13)-ene chloride II. Solid 4-(chloromethyl)imidazole hydrochloride (3.06 g, 20 mmol) was slowly added to a solution of the tricyclic orthoamide **I** (3.62 g, 20 mmol) and the 'proton sponge'® 1,8-bis(dimethylamino)naphthalene (Aldrich) (4.28 g, 20 mmol) in MeCN (80 cm^3). The resulting solution was warmed (*ca.* 50 °C) overnight; the solid obtained on removing the solvent at reduced pressure was dissolved in water (25 cm^3) and the solution was adjusted to pH 9 by adding a NaOH solution (10%). The suspended solid (proton sponge) was extracted twice with diethyl ether (25 cm^3). Compound **II** was obtained by removing the solvent from the aqueous phase at reduced pressure. Yield 5.6 g, 94% (Found: C, 56.2; H, 8.2; N, 23.4. Calc. for $C_{14}H_{24}ClN_5$: C, 56.4; H, 8.1; N, 23.5%).

1-(Imidazol-4-ylmethyl)-1,5,9-triazacyclododecane tetrahydrochloride, L^1·4HCl. The salt **II** (5.6 g, 19 mmol) was dissolved in 3 mol dm^{-3} HCl (30 cm^3) and the resulting solution warmed (*ca.* 70 °C) for 2 d. The tetrahydrochloride was obtained by removing the solvent at reduced pressure. It may be recrystallized from water–methanol. Yield 6.7 g, 91% (Found: C, 39.1; H, 7.3; N, 17.3. Calc. for $C_{13}H_{29}Cl_4N_5$: C, 39.3; H, 7.35; N, 17.6%).

5-(1-Methylimidazol-2-ylmethyl)-1,5-diaza-9-azoniabicyclo-[7.3.1]tridec-9(13)-ene chloride III. This salt was obtained by the procedure described for the synthesis of **II**, adding solid 2-(chloromethyl)-1-methylimidazole hydrochloride (1.67 g, 10 mmol) to a solution of the orthoamide **I** (1.81 g, 10 mmol) and proton sponge (2.14 g, 10 mmol). Yield 2.8 g, 90% (Found: C, 57.5; H, 8.45; N, 22.4. Calc. for $C_{15}H_{26}ClN_5$: C, 57.8; H, 8.4; N, 22.5%).

1-(1-Methylimidazol-2-ylmethyl)-1,5,9-triazacyclododecane, L^2. The salt **III** (2.8 g, 9 mmol) was dissolved in 5% NaOH (40 cm^3) and refluxed for 20 h. The solution was extracted three times with chloroform (80 cm^3). The organic phase was dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to give L^2 as a yellowish oil. Yield 1.5 g, 62% (Found: C, 63.3; H, 10.3; N, 26.1. Calc. for $C_{14}H_{27}N_5$: C, 63.3; H, 10.2; N, 26.4%).

5-(Pyrazol-3-ylmethyl)-1,5-diaza-9-azoniabicyclo[7.3.1]tridec-9(13)-ene chloride IV. A solution of 3-(chloromethyl)-pyrazole (4.55 g, 39.0 mmol) in MeCN (50 cm^3), prepared as described,[17] was slowly added to 1,5,9-triazatricyclo-[7.3.1.0]tridecane **I** (6.44 g, 35.5 mmol) dissolved in MeCN (100 cm^3). The resulting clear solution was gently warmed (*ca.* 50 °C) overnight and a white precipitate formed. The solvent was reduced to 10–15 cm^3 *in vacuo* and the solid **IV** was filtered off, washed with diethyl ether and dried. Yield 9.25 g, 87% (Found: C, 56.2; H, 8.2; N, 23.5. Calc. for $C_{14}H_{24}ClN_5$: C, 56.5; H, 8.1; N, 23.5%).

1-(Pyrazol-3-ylmethyl)-1,5,9-triazacyclododecane, L^3. The crude compound was obtained from the salt **IV** with a procedure analogous to that described for L^2. Yield 7.0 g, 90%. The yellowish oil may be distilled through the Kugelrhor apparatus (120 °C; 0.05 Torr, *ca.* 6.65 Pa). Yield 60% (Found: C, 62.0; H, 10.1; N, 27.5. Calc. for $C_{13}H_{25}N_5$: C, 62.1; H, 10.0; N, 27.9%).

1-(Pyrazol-3-ylmethyl)-1,5,9-triazacyclododecane tetrahydrochloride, L^3·4HCl. Hydrogen chloride was bubbled through a water solution (5 cm^3) of L^3 (2.51 g, 10 mmol); the solid tetrahydrochloride was obtained by adding ethanol. Yield 3.8 g, 96% (Found: C, 39.1; H, 7.3; N, 17.3. Calc. for $C_{13}H_{29}Cl_4N_5$: C, 39.3; H, 7.35; N, 17.6%).

The ^{13}C NMR data for L^1–L^3 and for the intermediate compounds **II**–**IV** are reported in Table 1.

Synthesis of the complexes [ML^3(Cl)]Y (M = Mn or Fe, Y = BPh$_4$; M = Ni, Y = BF$_4$) and [ML(ClO$_4$)]BPh$_4$ (M = Co, L = L^3; M = Cu or Zn, L = L^1 or L^3)

The nickel(II) complex was prepared by mixing warm solutions (20 cm^3) of L^3·4HCl in methanol and hydrated nickel(II) tetrafluoroborate in ethanol in 1:1 molar ratio. The complex may be recrystallized from a water–ethanol mixture. The copper(II) and zinc(II) complexes with the ligands L^1 or L^3 were prepared by mixing warm solutions (20 cm^3) of the ligand and of copper(II) or zinc(II) perchlorates in ethanol in 1:1 molar ratio and by adding to the resulting solution the stoichiometric amount of $NaBPh_4$ dissolved in acetone. The solutions were concentrated to a small volume until crystalline products were obtained. The L^1 ligand was freed in solution by adding to L^1·4HCl in water the stoichiometric amount of NaOH dissolved in water. The ligand was extracted with chloroform and the solution diluted with ethanol. The cobalt(II) complex was obtained under nitrogen, by the procedure described for the synthesis of the copper(II) and zinc(II) derivatives. The manganese(II) and iron(II) complexes were prepared under nitrogen by adding $NaBPh_4$ to a warm solution obtained by mixing manganese(II) chloride or iron(II) chloride in ethanol and the pro-ligand in the same solvent in a 1:1 molar ratio. The complexes were recrystallized from acetone and ethanol. The tetraphenylborate complexes were recrystallized from acetone and ethanol: $[MnL^3(Cl)]BPh_4$ (Found: C, 67.2; H, 6.9; Cl, 5.3; N, 10.6. Calc. for $C_{37}H_{45}BClMnN_5$: C, 67.2; H, 6.85; Cl, 5.35; N, 10.6); $[FeL^3(Cl)]BPh_4$ (Found: C, 67.0; H, 6.95; N, 10.5. Calc. for $C_{37}H_{45}BClFeN_5$: C, 67.1; H, 6.85; N, 10.6); $[CoL^3(ClO_4)]BPh_4$ (Found: C, 60.9; H, 6.25; Cl, 4.8; Co, 8.0; N, 9.6. Calc. for $C_{37}H_{45}BClCoN_5O_4$: C, 61.0; H, 6.2; Cl, 4.85; Co, 8.1; N, 9.6); $[NiL^3(Cl)]BF_4$·EtOH (Found: C, 37.5; H, 6.6; N, 14.5. Calc. for $C_{15}H_{31}BClF_4N_5NiO$: C, 37.6; H, 6.55; N, 14.6); $[CuL^1(ClO_4)]BPh_4$ (Found: C, 60.4; H, 6.2; Cu, 8.5; N, 9.5. Calc. for $C_{37}H_{45}BClCuN_5O_4$: C, 60.6; H, 6.2; Cu, 8.65; N, 9.55); $[CuL^3(ClO_4)]BPh_4$ (Found: C, 60.5; H, 6.15; N, 9.4. Calc. for $C_{37}H_{45}BClCuN_5O_4$: C, 60.6; H, 6.2; N, 9.55); $[ZnL^1(ClO_4)]BPh_4$ (Found: C, 60.3; H, 6.2; N, 9.4. Calc. for $C_{37}H_{45}BClN_5O_4Zn$: C, 60.4; H, 6.2; N, 9.5). $[ZnL^3(ClO_4)]BPh_4$ (Found: C, 60.3; H, 6.2; N, 9.5. Calc. for $C_{37}H_{45}BClN_5O_4Zn$: C, 60.4; H, 6.2; N, 9.5%).

Significant absorptions in the UV/VIS spectra of the complexes are [λ_{max}/nm (ε/cm^2 mmol^{-1}); concentration of the solutions *ca.* 10^{-3} mol dm^{-3}]: $[FeL^3(Cl)]BPh_4$, diffuse reflectance, 840, 1160; MeCN solution, 850 (10), 1170 (3); $[CoL^3(ClO_4)]BPh_4$, diffuse reflectance, 530, 690, 930, 1400; Me_2SO solution, 400 (254), 495 (sh), 1100 (8), 1410 (7); $[NiL^3(Cl)]BF_4$·

EtOH, diffuse reflectance, 380, 600, 990; MeCN solution, 380 (55), 600 (29), 940 (20); $[\mathrm{CuL^1(ClO_4)}]\mathrm{BPh_4}$, diffuse reflectance, 305, 670, 960; $\mathrm{Me_2SO}$ solution, 305 (1100), 660 (350), 960 (220); $[\mathrm{CuL^3(ClO_4)}]\mathrm{BPh_4}$, diffuse reflectance, 300, 660, 940; $\mathrm{Me_2SO}$ solution, 300 (1150), 650 (230), 930 (225). ^{13}C NMR data for the cations of the zinc complexes in $\mathrm{(CD_3)_2SO}$: $[\mathrm{ZnL^1(ClO_4)}]\mathrm{BPh_4}$, δ 136.4 ($C_b$, C_c), 114.2 (C_c, C_b), 56.2 (C_f, C_h, C_i), 52.0 (C_d), 50.1 (C_f, C_h, C_i), 49.6 (C_f, C_h, C_i), 23.8 (C_j) and 22.9 (C_g); $[\mathrm{ZnL^3(ClO_4)}]\mathrm{BPh_4}$, δ 136.1 ($C_b$, C_c), 105.1 (C_c, C_b), 58.7 (C_f, C_h, C_i), 55.3 (C_d), 51.9 (C_f, C_h, C_i), 51.4 (C_f, C_h, C_i), 24.9 (C_g) and 24.7 (C_j).

Electromotive force measurements

Deionized water was purified with a MilliQ-Reagent system to produce water with a resistivity greater than 15 MΩ cm. Sodium chloride (Merck, *Suprapur*) was used without further purification. Standard 0.100 mol $\mathrm{dm^{-3}}$ HCl and NaOH stock solutions were prepared using concentrated vials (Fluka) and stored under nitrogen; the concentration was checked periodically by acid–base titration against conventional standards using Gran's method.[18] Analysis grade $\mathrm{CuCl_2\cdot 2H_2O}$ and $\mathrm{ZnCl_2}$ (Merck) were used to prepare approximately 0.2 mol $\mathrm{dm^{-3}}$ stock solutions which were standardized using conventional gravimetric methods.

Potentiometric titrations were carried out using a Crison Micro pH 2002 potentiometer fitted with a Metrohm combined electrode (model 6.0204.000) in conjunction with a Hamilton Microlab M motor-driven syringe under the control of an appropriate program running on an IBM PS/2 model 20 computer.[19] Titration solutions were magnetically stirred and thermostatted at 298.2 ± 0.1 K in a water-jacketed vessel. The ionic strength of the solutions in the cell was adjusted to 0.15 mol $\mathrm{dm^{-3}}$ with NaCl. A stream of nitrogen gas, presaturated with water vapour from a 0.15 mol $\mathrm{dm^{-3}}$ NaCl solution held at the same temperature as the cell, was passed over the solution in order to avoid contamination by atmospheric carbon dioxide. The instrumentation was calibrated by titration of 0.100 mol $\mathrm{dm^{-3}}$ NaOH (about 1 $\mathrm{cm^3}$) from the syringe against 15 mmol $\mathrm{dm^{-3}}$ HCl ($\approx$20 $\mathrm{cm^3}$).

The potentiometric experiments for the determination of the basicity constants were performed by adding the 0.100 mol $\mathrm{dm^{-3}}$ NaOH solution to a solution containing the macrocycle ($\approx$2 mmol $\mathrm{dm^{-3}}$) in the acidic form. In the experiments involving the metal complexes the solution to be titrated contained in addition the appropriate metal ion (metal to macrocycle molar ratio <1). Data were collected in the range pH 2.5–10.5.

Crystallography

Crystal data and refinement parameters for the compounds $[\{\mathrm{FeL^3(Cl)}\}_2][\mathrm{BPh_4}]_2$ **1** and $[\{\mathrm{NiL^3(Cl)}\}_2][\mathrm{BF_4}]_2\cdot 2\mathrm{EtOH}$ **2** are given in Table 4. All operations were performed at 293 K using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated Cu-Kα (λ = 1.5418 Å) (**1**) or Mo-Kα (λ = 0.710 69 Å) (**2**) radiation. The Cu-Kα radiation, which was initially available for data collection on **1**, may be unsuitable for iron-containing compounds, due to significant anomalous dispersion and absorption effects. However, a set of data subsequently collected on **1** using Mo-Kα radiation did not provide any improvement. Unit-cell parameters were obtained from the settings of 24 reflections with $22 < \theta < 25°$ (**1**) and 20 reflections with $13 < \theta < 14°$ (**2**). The ω–2θ scan mode was used. The crystal of **2** was coated with paraffin in order to limit the effects of crystal decay under the X-rays. The intensities of three standard reflections monitored periodically during the data collections revealed overall 10 (**1**) and 5% (**2**) decays, which were corrected for. An empirical absorption correction was applied in each case to the data after structure solution at isotropic convergence.[20] The principal computer programs used in the crystallographic calculations are listed in refs. 20–24. The atomic scattering factors were from refs. 22 (C, H, B, Cl, N and O) and 25 (Fe and Ni), the latter being corrected for anomalous dispersion.[26]

Both structures were solved by direct[21] and heavy-atom methods. The unit cell of complex **1** contains two $[\{\mathrm{FeL^3(Cl)}\}_2][\mathrm{BPh_4}]_2$ units whose symmetry-independent dimeric cations are both centrosymmetric (special positions *d* and *g* of space group no. 2). The content of the unit cell of **2** consists of one $[\{\mathrm{NiL^3(Cl)}\}_2][\mathrm{BF_4}]_2\cdot 2\mathrm{EtOH}$ unit, having a centrosymmetric cation. Three carbon atoms of the aliphatic chains of **1** were found to be affected by high vibrational motion or disorder. Each of these atoms could be refined as being distributed over two positions the occupancy factors of which were initially refined by assigning a unique isotropic thermal parameter to the two fractional sites. Such occupancy factors were not allowed to change in the subsequent cycles, in which the thermal parameters were freed. The bond distances formed by each pair of fractional sites were subject to a soft restraint. In the final refinement cycles performed on *F*, in two blocks for **1** and one block for **2**, all atoms were assigned anisotropic thermal parameters, except for all H atoms and the B atoms of **1**. The hydrogen atoms of both structures were included in calculated positions (except for the hydrogens of the ethanol solvate molecule of **2**, which were not included), at 0.96 Å from the respective C or N atom, with $U_\mathbf{H} = 1.2\ U_{\mathbf{C,N}}{}^{\mathbf{eq}}$, where $U_{\mathbf{C,N}}{}^{\mathbf{eq}}$ is the equivalent isotropic thermal parameter of the carrier atom. The H atoms in the parts of the chains of **1** affected by disorder were assigned the occupancy factors of the carrier fractional atoms. The model for the $\mathrm{BF_4{}^-}$ anion contained in the asymmetric unit of **2**, which was affected by orientational disorder, consisted of two tetrahedral images with common B atom position and a unique B−F value, which was refined allowing for a large standard deviation. The two tetrahedra of fractional F atoms were assigned complementary population parameters. The oxygen atom of the ethanol molecule was identified by comparing peak heights in Δ*F* maps and by the possible hydrogen-bond formation with a macrocycle NH group.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/323.

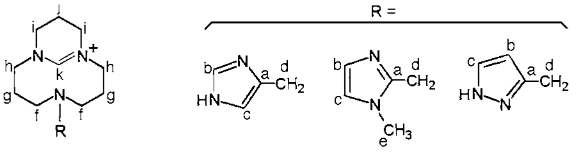
Results and Discussion

Synthesis of macrocycles and protonation constants of L^1 and L^3

The bicyclic amidinium salts **II**–**IV** (Scheme 1 and Table 1) were obtained in high yield by treating the orthoamide **I** with stoichiometric amounts of 4-(chloromethyl)imidazole, 2-(chloromethyl)-1-methylimidazole or 3-(chloromethyl)pyrazole, respectively. The two imidazole halides, which are extremely unstable, were slowly freed in solution by adding the appropriate neat hydrochloride to an MeCN solution of **I** in the presence of proton sponge. The derivatives **II** and **III** from the above reaction contained the quaternary salt of the proton sponge. They were easily purified by dissolving the mixture in alkaline solution and by extracting the proton sponge with diethyl ether. 3-(Chloromethyl)pyrazole, which is a sticky oil sufficiently stable, was separately prepared, dissolved in MeCN and added to **I**. The pure compound **IV** was obtained as a solid from the reaction mixture. The salts **III** and **IV** were normally hydrolysed[13] under alkaline conditions to the monosubstituted triamines L^2 and L^3. The alkaline hydrolysis of compound **II** resulted in the loss of imidazole to yield 1,5,9-triazacyclododecane; in this case the acid hydrolysis was found to be a satisfactory alternative. The hydrolysis conditions were tuned to gain $L^1\cdot 4\mathrm{HCl}$ in highest yield.

The synthetic route described above appears to be useful to

Table 1 Carbon-13 NMR chemical shifts δ (reference $SiMe_4$) at room temperature for compounds **II**–**IV** and for L^1, L^2 and L^3*



II **III** **IV**

Compound	C_a	C_b, C_c	C_c, C_b	C_d	C_e	C_f, C_h, C_i	C_g	C_h, C_f, C_i	C_i, C_f, C_h	C_j	C_k
II	133.3	136.6	119.8	46.2		56.1	23.2	55.5	43.1	20.0	157.4
III	142.3	124.5	119.7	41.2	35.3	55.8	23.3	54.6	42.9	19.7	157.0
IV	141.5	131.8	105.4	49.7		56.4	22.6	54.9	42.1	19.8	158.7
$L^1\cdot4HCl$		136.3	122.8	47.7		48.7	19.3	42.8	42.0	20.5	
L^2	145.6	127.2	121.5	50.6	32.9	52.9	24.8	49.0	47.1	24.1	
L^3	143.3	138.8	101.9	49.6		55.1	26.6	50.2	47.5	26.6	
$L^3\cdot4HCl$	141.3	132.6	108.0	51.36		48.0	18.8	42.6	41.7	20.5	

* Spectra of L^2 and L^3 were obtained in $CDCl_3$, all the others in D_2O.

Table 2 Stepwise protonation constants (log *K*) of compounds L^1 and L^3 at 298.2 K in 0.15 mol dm^{-3} NaCl*

Reaction	L^1	L^3	L^4	L^5
$H^+ + L \rightleftharpoons HL^+$	10.74(4)	11.87(3)	12.60	≈13
$H^+ + HL^+ \rightleftharpoons H_2L^{2+}$	7.22(2)	6.73(1)	7.57	7.54(2)
$H^+ + H_2L^{2+} \rightleftharpoons H_3L^{3+}$	4.91(2)	1.86(4)	2.4	5.20(2)
$H^+ + H_3L^{3+} \rightleftharpoons H_4L^{4+}$	≈1	≈1	—	≈2

* Values in parentheses are standard deviations on the least significant figure. Data for L^4 and L^5 are from refs. 29 and 5, respectively.

synthesize multigram quantities of cyclic triamines monosubstituted with groups having extremely reactive synthons. Although this approach has been known since the orthoamides of macrocycles containing three or four nitrogen donors were recognized as useful precursors of the monosubstituted macrocycles, it has been employed only occasionally to obtain such compounds.[11,27] This has probably been caused by the difficult synthesis of orthoamides such as **I**, which have been obtained by treating the preformed cyclic amines.[11] In this respect the efficiency of the new synthetic method[13] should be noted.

In the potentiometric studies data were processed using the program HYPERQUAD.[28] The refined values of the stepwise protonation constants for two of the present macrocycles, L^1 and L^3, are given in the first two columns of Table 2. The protonation constants of two related triamines, namely the unsubstituted 1,5,9-triazacyclododecane[29] (L^4) and 2-(imidazol-4-ylmethyl)-1,5,9-triazacyclododecane[5] (L^5) are reported for comparison. It may be noted that the heterocyclic substituent attached to a nitrogen atom of the triazamacrocycle (L^1 and L^3) causes a significant decrease in basicity, with respect to the unsubstituted macrocycle, in the first protonation step. Such decrease in basicity is greater for L^1 than L^3. In the subsequent steps L^1 is more basic than L^3, this feature being particularly evident in the third step, in which the heterocyclic nitrogen is presumably protonated. For both compounds a residual slight basicity has been observed beyond the third step. The fourth protonation constant could be crudely estimated to be of the order of one logarithmic unit.

Metal complexes and formation constants

The complexes have been obtained by mixing solutions with equimolar amounts of the macrocycle L^1 or L^3 and the appropriate hydrated metal salt, and have the formulae $[ML^3(Cl)]Y$ (M = Mn or Fe, Y = BPh_4; M = Ni, Y = BF_4) and $[ML(ClO_4)]BPh_4$ (M = Co, L = L^3; M = Cu or Zn, L = L^1 or L^3). They have all been isolated with tetraphenylborate as counter ion, except for the nickel complex obtained as the tetrafluoroborate. It also crystallizes with one molecule of ethanol, as shown by the crystallographic analysis (see below). The manganese, iron and nickel complexes contain co-ordinated chloride, whereas the other derivatives have a co-ordinated perchlorate ion. The infrared spectra of the complexes, except for that of the nickel derivative, do not exhibit any band which may be assigned as due to O–H stretching, so ruling out the presence of water in the solid compounds. The electronic spectrum of the manganese(II) complex, both in the solid state and in solution, does not present any absorption whereas that of the iron(II) derivative exhibits two very weak transitions, in agreement with what would be expected for high-spin six-co-ordinate derivatives of such ions.[30,31] Moreover, the complexes of these two metals in nitroethane solution have a conductivity typical of 1:2 electrolytes.[32] This suggests that the iron complex retains in solution the six-co-ordinate structure it has been found to possess in the solid state (see below) and allows the same type of geometry to be assigned to the manganese derivative. Also the nickel complex, according to its electronic spectrum, should retain in MeCN solution the six-co-ordinate structure detected in the solid state by the X-ray investigation. The cobalt derivative has a four-band reflectance spectrum typical of a high-spin chromophore with a geometry intermediate between square pyramidal and trigonal bipyramidal. On the other hand, it has a different spectrum in Me_2SO solution, consistent with a high-spin six-co-ordinate chromophore.[30] It is likely that the metal ion in the solid state is bound to four nitrogen donors of the L^3 ligand and one oxygen of the perchlorate anion, whereas the weakly bound anion is probably replaced in solution by two molecules of solvent, to yield a six-co-ordinate complex cation. The electronic spectra of the copper(II) complexes with the ligands L^1 and L^3 exhibit, both in the solid state and in Me_2SO solution, a charge-transfer absorption at *ca.* 300 nm and two bands at *ca.* 650 and 940 nm. Such absorptions are typical of five-co-ordinate chromophores with a N_4X donor set having an intermediate geometry between trigonal bipyramidal and square pyramidal.[33] It is likely that in the solid state the metal ion is co-ordinated by four nitrogen donors of the ligand (L^1 or L^3) and one oxygen atom of the perchlorate anion, whereas in solution the latter is replaced by a solvent molecule. The ^{13}C NMR spectra of the zinc complexes with the ligands L^1 and L^3 exhibit resonances by the same groups of equivalent carbon atoms as those of the free pro-ligands, indicative of symmetric cations. In view of the results obtained by Kimura *et al.*[5] with a related ligand, having the same mode of co-ordination as that of L^3 in the structures of the present iron(II) and nickel(II) complexes, and of the formation constants of the complexes (see below), it is likely that the zinc(II) complexes are five-co-ordinate, with the ClO_4^- ion replaced by a solvent molecule in solution.

The formation constants for the copper(II) and zinc(II) com-

Table 3 Formation constants (log *K*) of representative complexes at 298.2 K in 0.15 mol dm^{-3} NaCl *

Reaction	L^1	L^3	L^4	L^5
$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	15.58(1)	14.89(2)	12.63	17.6(1)
$[CuL]^{2+} + H^+ \rightleftharpoons [Cu(HL)]^{3+}$	2.98(3)	3.19(3)	—	—
$[CuL]^{2+} \rightleftharpoons [CuH_{-1}L]^+ + H^+$	−10.34(2)	−8.64(3)	—	−9.3
$Zn^{2+} + L \rightleftharpoons [ZnL]^{2+}$	10.08(2)	9.25(3)	8.75	11.7(1)
$[ZnL]^{2+} + H^+ \rightleftharpoons [Zn(HL)]^{3+}$	4.96(6)	5.36(6)	—	—
$[ZnL]^{2+} \rightleftharpoons [ZnH_{-1}L]^+ + H^+$	−10.87(4)	−8.97(2)	—	−10.3

* Data for L^4 and L^5 are from refs. 29 and 5, respectively.

Table 4 Crystallographic data for $[\{FeL^3(Cl)\}_2][BPh_4]_2$ **1** and $[\{NiL^3(Cl)\}_2][BF_4]_2\cdot 2EtOH$ **2**[a]

	1	**2**
Formula	$C_{74}H_{90}B_2Cl_2Fe_2N_{10}$	$C_{30}H_{62}B_2Cl_2F_8N_{10}Ni_2O_2$
M	1323.83	956.83
a/Å	13.852(3)	8.898(7)
b/Å	15.031(3)	11.202(10)
c/Å	17.050(3)	12.321(10)
α/°	99.49(1)	65.61(8)
β/°	102.27(1)	88.67(7)
γ/°	90.75(2)	72.23(7)
U/Å^3	3417.3(9)	1058(2)
Z	2	1
D_c/g cm^{-3}	1.286	1.502
F(000)	1400	500
Crystal size/mm	0.20 × 0.40 × 0.50	0.40 × 0.50 × 0.60
μ/mm^{-1}	4.52	1.10
Range of correction factor for absorption[b]	1.20–0.88	1.31–0.71
Scan width[c]/°	1.20	1.50
Collection range/°	$6 \leqslant 2\theta \leqslant 130$	$5 \leqslant 2\theta \leqslant 54$
No. unique data[d]	10 275	3698
No. observed data [$I > 3\sigma(I)$]	7639	2714
No. parameters	834	291
g[e]	0.0010	0.0020
R[f]	0.057	0.066
R'[g]	0.063	0.071
Maximum, minimum electron density/e Å^{-3}	0.5, −0.4	0.6, −0.7

[a] Details in common: triclinic, space group $P\bar{1}$ (no. 2); scan speed 2–8° min^{-1}; data collected $\pm h$, $\pm k$, $+l$. [b] Empirical absorption corrections applied (**1**, Cu-Kα; **2**, Mo-Kα), see text. [c] Value of the *a* parameter in the formula $(a + b \tan\theta)°$ ($b = 0.14$, **1**; 0.35, **2**) for the scan width. [d] Reflections measured: 11 603 (**1**) and 4165 (**2**); internal *R* values 0.04 and 0.05. [e] In the formula $w^{-1} = \sigma^2(F_o) + gF_o^2$. [f] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [g] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

Table 5 Selected bond distances (Å) and angles (°) for $[\{FeL^3(Cl)\}_2][BPh_4]_2$ **1** *

Fe(1)–Cl(1)	2.474(1)	Fe(2)–Cl(2)	2.472(2)
Fe(1)–Cl(1′)	2.645(1)	Fe(2)–Cl(2″)	2.586(1)
Fe(1)–N(1)	2.236(3)	Fe(2)–N(6)	2.266(4)
Fe(1)–N(2)	2.134(5)	Fe(2)–N(7)	2.165(4)
Fe(1)–N(3)	2.170(4)	Fe(2)–N(8)	2.177(4)
Fe(1)–N(4)	2.154(4)	Fe(2)–N(9)	2.156(4)
Fe(1) · · · Fe(1′)	3.823(1)	Fe(2) · · · Fe(2″)	3.735(1)
Cl(1) · · · Cl(1′)	3.410(2)	Cl(2) · · · Cl(2″)	3.412(2)
Cl(1)–Fe(1)–Cl(1′)	83.4(1)	Cl(2)–Fe(2)–Cl(2″)	84.8(1)
Cl(1)–Fe(1)–N(1)	165.7(1)	Cl(2)–Fe(2)–N(6)	163.2(1)
Cl(1)–Fe(1)–N(2)	97.4(1)	Cl(2)–Fe(2)–N(7)	101.5(1)
Cl(1)–Fe(1)–N(3)	87.9(1)	Cl(2)–Fe(2)–N(8)	90.8(1)
Cl(1)–Fe(1)–N(4)	91.8(1)	Cl(2)–Fe(2)–N(9)	88.4(1)
Cl(1′)–Fe(1)–N(1)	90.6(1)	Cl(2″)–Fe(2)–N(6)	90.4(1)
Cl(1′)–Fe(1)–N(2)	85.6(1)	Cl(2″)–Fe(2)–N(7)	85.2(1)
Cl(1′)–Fe(1)–N(3)	171.1(1)	Cl(2″)–Fe(2)–N(8)	172.2(1)
Cl(1′)–Fe(1)–N(4)	88.1(1)	Cl(2″)–Fe(2)–N(9)	92.9(1)
N(1)–Fe(1)–N(2)	95.1(2)	N(6)–Fe(2)–N(7)	94.1(2)
N(1)–Fe(1)–N(3)	98.2(1)	N(6)–Fe(2)–N(8)	95.6(1)
N(1)–Fe(1)–N(4)	75.0(1)	N(6)–Fe(2)–N(9)	75.7(1)
N(2)–Fe(1)–N(3)	93.6(2)	N(7)–Fe(2)–N(8)	89.5(1)
N(2)–Fe(1)–N(4)	168.2(2)	N(7)–Fe(2)–N(9)	169.7(1)
N(3)–Fe(1)–N(4)	94.1(1)	N(8)–Fe(2)–N(9)	93.3(1)
Fe(1)–Cl(1)–Fe(1′)	96.5(1)	Fe(2)–Cl(2)–Fe(2″)	95.2(1)

* Values for the two independent cations in the structure are listed in separate columns. Primed atoms are related to the corresponding unprimed ones through inversion centres.

plexes, calculated using the program HYPERQUAD,[28] are given in Table 3, where values for the related triamines L^4 and L^5 are also reported for comparison. The formation constants of the complexes $[CuL]^{2+}$ and $[ZnL]^{2+}$ ($L = L^1$ or L^3) are higher than those previously reported[29] for the unsubstituted macrocyclic triamine L^4. As the latter can act at most as tridentate, these data confirm that the present ligands co-ordinate the metal ions through four nitrogen atoms. The L^1 complexes are slighly more stable than the corresponding L^3 ones, consistent with the higher donor ability of imidazole with respect to pyrazole. The formation constants of the metal complexes for the C-substituted L^5 ligand are significantly higher[5] than those measured for L^1 and L^3. This might be attributed to a more favourable arrangement attained by this ligand, which forms only six-membered chelate rings at variance with the present ones. Protonation constants for the complexes formed by the L^1 and L^3 ligands are also reported in Table 3; they were not available for the other compounds. Such protonation constants, much lower than the first basicity constants of the pro-ligands, support the assumption that the ligands co-ordinate with all their donor atoms. Deprotonation constants have also been determined for the copper(II) and zinc(II) complexes with the ligands L^1 and L^3 and their values are reported in Table 3. These values are not significantly affected by the nature of the metal ion, whereas they decrease by two logarithmic units on substituting the pyrazole dangling group with imidazole. As observed for analogous systems,[34] such constants may be related either to deprotonation of the dangling heterocyclic ring or to ionization of the water molecule bound to the metal ion as an ancillary ligand. The decrease observed on going from L^3 to L^1 appears to be too large to be rationalized in terms of a change of properties of a co-ordinated water molecule. It is better understood in terms of different species undergoing deprotonation, such as the heterocyclic groups of the two ligands. Kimura *et al.*[5] reached the same conclusions for the zinc(II) and copper(II) complexes of L^5 by comparing the NMR spectrum of the zinc(II) derivative with that of the deprotonated species.

Crystal structures

The structure of compound **1** contains dimeric $[\{FeL^3(Cl)\}_2]^{2+}$ cations and tetraphenylborate anions. There are two symmetry-independent cations in the unit cell, which, however, are substantially isostructural, both being centrosymmetric (Fig. 1 and Table 5). Each iron atom is in a pseudo-octahedral environment, formed by four N donors of the L^3 ligand and by the two bridging Cl atoms. The macrocyclic ring occupies one face of the octahedron, whilst the pendant arm co-ordinates almost *trans* to one of the two unsubstituted nitrogen atoms of the macrocycle. Significant differences between the two cations are in the Fe · · · Fe′ separations (Table 5) and the Fe–Cl bond

Table 6 Selected bond distances (Å) and angles (°) for $[\{NiL^3(Cl)\}_2][BF_4]_2 \cdot 2EtOH$ **2***

Ni–Cl	2.494(2)	Ni–N(3)	2.086(5)
Ni–Cl′	2.485(2)	Ni–N(4)	2.058(5)
Ni–N(1)	2.174(5)	Ni $\cdots$ Ni′	3.730(3)
Ni–N(2)	2.070(5)	Cl $\cdots$ Cl′	3.299(4)
Cl–Ni–Cl′	83.0(1)	Cl′–Ni–N(4)	89.0(2)
Cl–Ni–N(1)	90.9(1)	N(1)–Ni–N(2)	93.5(2)
Cl–Ni–N(2)	87.2(2)	N(1)–Ni–N(3)	98.7(2)
Cl–Ni–N(3)	170.3(1)	N(1)–Ni–N(4)	79.1(2)
Cl–Ni–N(4)	90.0(1)	N(2)–Ni–N(3)	92.0(2)
Cl′–Ni–N(1)	166.6(2)	N(2)–Ni–N(4)	172.0(2)
Cl′–Ni–N(2)	98.1(2)	N(3)–Ni–N(4)	92.0(2)
Cl′–Ni–N(3)	87.6(2)	Ni–Cl–Ni′	97.0(1)

* Primed atoms are related to the corresponding unprimed ones through an inversion centre.

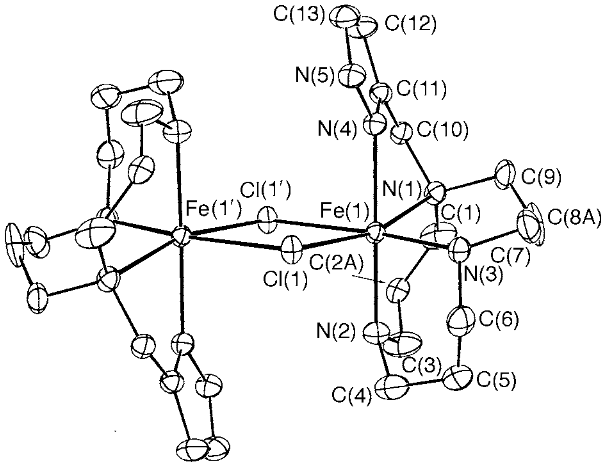


Fig. 1 A view of one of the two independent cations in the structure of $[\{FeL^3(Cl)\}_2][BPh_4]_2$ **1**, with 20% probability ellipsoids. Primed atoms are related to unprimed ones by an inversion centre. The second cation is substantially isostructural to the one shown, except for small differences in the conformations of the six-membered rings. Only one position for each disordered carbon atom is shown for clarity

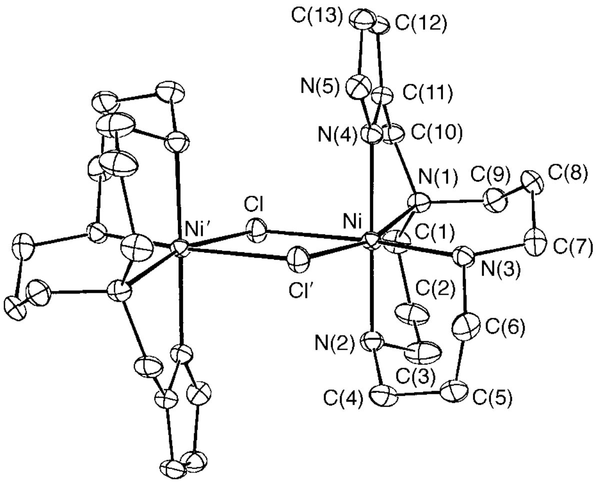


Fig. 2 A view of the cation in the structure of $[\{NiL^3(Cl)\}_2][BF_4]_2 \cdot 2EtOH$ **2**, with 20% probability ellipsoids. Primed atoms are related to unprimed ones by an inversion centre

distances. The bonds formed by a metal atom with the two chlorine atoms in each cation are of different lengths, such differences being unequal for the two cations. The Cl $\cdots$ Cl′ separation, however, is almost identical in the two cations.

The structure of compound **2** consists of dimeric $[\{NiL^3(Cl)\}_2]^{2+}$ cations, tetrafluoroborate anions and solvate ethanol molecules. There is one symmetry-independent cation in the unit cell, which is centrosymmetric and possesses a substantially similar geometry to that of the two independent cations in the structure of **1** (Fig. 2 and Table 6). All metal–nitrogen distances are shorter, by 0.08 Å in the mean, than in the iron complex and also the Ni–Cl distances are shorter, by 0.05 Å in the mean, than the Fe–Cl ones. Nevertheless, the mean values of the angles to the metal formed by the nitrogen atoms of the macrocycle in the two compounds are almost identical: 94.3 (**1**) and 94.7° (**2**). This is due to the flexibility of the six-membered chelate rings formed by the macrocycle, which allows the N $\cdots$ N separations to decrease from the 3.21 Å (mean) in **1** to that of 3.10 Å in **2**.

The chelate rings formed by the macrocycle in the two compounds exhibit various conformations, approaching the chair, boat, skewed and less regular arrangements, with only partial agreement between the two cations of **1**, as well as between these and the cation of **2**. Moreover, the conformations are also dependent on the positions referred to for the fractional carbon atoms in the disordered rings of **1**. The related compound 1-(2-pyridylmethyl)-1,5,9-triazacyclododecane (L^6), based on the same macrocycle as the present ligands and differing from these in the nature of the dangling group, chelates the metal atom in the compound $[NiL^6(O_2NO)]NO_3$[2] **3** with a grossly similar arrangement to that attained by L^3 in the present compounds, forming Ni–N distances slightly shorter (by a 0.04 Å overall amount) than those in **2**. The N $\cdots$ N separations are correspondingly shorter (3.00 Å, mean value in **3**), even though the angles subtended to the metal by the macrocycle donors in **3** are spread over a wider range (87–104°) than in the present compounds. This is again a result of the flexibility of the six-membered chelate rings. In contrast with the variety of arrangements detected for such rings in the compounds **1** and **2**, all of the chelate rings in **3** adopt the chair conformation. It should be noted that the five-membered chelate ring formed by the pendant arm in each of the compounds **1**–**3**, definitely more rigid than the six-membered rings, subtends an angle to the metal which increases with decreasing metal–nitrogen separations: 75.3(5) (**1**), 79.1(2) (**2**) and 83.4(1)° (**3**). The substitution of pyrazole by a pyridine group on going from **1** or **2** to **3** should not affect this trend significantly.

Finally, the Ni $\cdots$ Ni′ separation in complex **2** matches the shorter of the two Fe $\cdots$ Fe′ separations in **1** (Tables 5 and 6), but the Cl $\cdots$ Cl′ distance in **2** is shorter than those in **1**. At variance with the differences existing between the Fe–Cl distances within each dimer and between the independent dimers of **1**, as noted above, the two Ni–Cl distances in **2** are comparable. This might be due to packing effects and to the softness of the rather long metal–halide bonds. Packing forces, in particular, should be responsible for the difference between the two independent cations of **1**, which have different environments (whereas all cations in **2** have the same type of environment). Stereochemical effects due to the d electrons could also play different roles for the derivatives of the two metals, because the orbital occupancy of the high-spin d^6 configuration of Fe^{II} in a (pseudo)octahedral environment appears to be unbalanced, especially when compared to that of the d^8 configuration of Ni^{II}.

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