Transition Metal Complexes of a Functionalised Triazamacrocycle *

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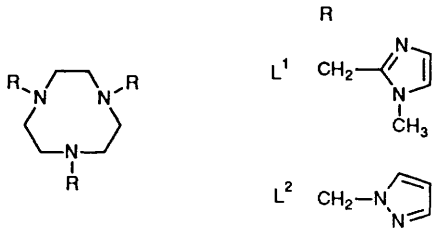
The imidazole- and pyrazole-functionalised macrocyclic ligands 1,4,7-tris(1-methylimidazol-2-ylmethyl)-1,4,7-triazacyclononane, L^1, and 1,4,7-tris(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane, L^2, form stable complexes with some 3d metal cations of formula $[ML]Y_2$ (M = Fe, L = L^1 or L^2, Y = BPh_4; M = Co, L = L^1, Y = ClO_4; L = L^2, Y = BPh_4; M = Ni, L = L^1, Y = BPh_4 or ClO_4; L = L^2, Y = BPh_4; M = Cu, L = L^1, Y = BPh_4; L = L^2, Y = ClO_4; M = Zn, L = L^2, Y = BPh_4). The complexes have been isolated in the solid state and characterised by standard physicochemical methods. The complex $[NiL^2][BPh_4]_2$ affords by slow recrystallisation from an acetonitrile–ethanol solution the new compound $[Ni(CH_3CN)L^3][BPh_4]_2$ where L^3 is the new ligand 1,4-bis(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane formed from L^2 by a N-dealkylation reaction and loss of a pendant arm. Its crystal structure has been determined by X-ray diffraction: space group $P2_1/c$, $a = 18.544(12)$, $b = 12.460(5)$, $c = 23.400(9)$ Å, $\beta = 90.49(4)°$; R 0.069 for 3025 observed reflections. The nickel atom is in a six-co-ordinate environment formed by the five nitrogen atoms provided by the L^3 ligand and by the acetonitrile N atom. All Ni–N distances are in the range 2.00–2.11 Å, those formed by the macrocycle nitrogens spanning the upper half of this interval.

The design and synthesis of polyazamacrocycles bearing flexible pendant arms from the cyclic framework which provide additional co-ordination sites have attracted increasing interest in recent years for the possible relevance of these compounds as model ligands for metal enzymes and metal proteins, as metal-ion selective ligands, and for their more general co-ordination chemistry interest. Functionalised macrocycles have been successfully employed in the synthesis of metal-chelating agents for medical applications owing to the kinetic inertness of the complexes which makes them resistant to decomplexation.[1] A number of such polydentate ligands have now been reported with a variety of pendant arms attached to the nitrogen donor sites of the macrocycle.[2–6] A few examples of C-functionalised macrocycles have also been reported.[7]

We have already reported on the ready synthesis of N-functionalised tri- and tetra-azamacrocycles with the biomimetic donor groups pyrazole and imidazole and the characterisation of their complexes with some alkali[8] and transition-metal ions.[9,10] We report here on the co-ordination properties of the hexadentate ligands 1,4,7-tris(1-methylimidazol-2-ylmethyl)-1,4,7-triazacyclononane (L^1) and 1,4,7-tris(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane (L^2), towards some 3d metal ions with which we have synthesised complexes having the general formula $[ML]Y_2$ (M = Fe; L = L^1 or L^2, Y = BPh_4; M = Co, L = L^1, Y = ClO_4; L = L^2, Y = BPh_4; M = Ni, L = L^1, Y = BPh_4 or ClO_4; L = L^2, Y = BPh_4; M = Cu, L = L^1, Y = BPh_4; L = L^2, Y = ClO_4; M = Zn, L = L^2, Y = BPh_4). The complexes $[CoL^1][ClO_4]_3$ and $[Cu(HL^1)][ClO_4]_3$ (HL^1 denotes the monoprotonated ligand L^1) have also been obtained. Quite unexpectedly the complex $[NiL^2][BPh_4]_2$ affords by slow crystallisation from an acetonitrile–ethanol mixture the new compound $[Ni(CH_3CN)L^3][BPh_4]_2$ [L^3 = 1,4-bis(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane] where the parent ligand L^2 has undergone a N-dealkylation reaction with loss of a pendant arm. Although the compounds were obtained in crystalline form, they generally did not provide good material for X-ray diffraction, except for $[Ni(CH_3CN)L^3][BPh_4]_2$ whose structure was investigated in order to ascertain its nature and co-ordination geometry. A preliminary account of the structure of the complex $[NiL^1][ClO_4]_2$ has already appeared.[10]



Experimental

Materials and Reagents.—All reagents were reagent grade. Solvents were dried according to standard procedures just before their use. The ligands L^1 and L^2 were synthesised as described previously.[8–10]

Synthesis of the Complexes.—Complexes were prepared by mixing warm solutions (20–30 cm^3) of the appropriate ligand L^1 or L^2 (1 mmol) and of the metal salt in a 1:1 molar ratio. Solvents were methanol, ethanol, acetone, acetonitrile, or their mixtures. In some cases the desired complexes crystallised in a short time; otherwise the solutions were allowed slowly to evaporate at 20–40 °C. The crystalline products were collected by suction filtration, washed with small amounts of suitable solvents followed by diethyl ether, and finally dried in a vacuum oven. Recrystallisation from suitable solvent mixtures gave analytically pure products. Iron(II) and cobalt(II) complexes were prepared under a purified nitrogen atmosphere. Details on the syntheses and the analytical data are given below.

$[FeL^1][BPh_4]_2$. Warm ethanol solutions of $FeCl_2·6H_2O$ and L^1 were mixed and $NaBPh_4$ in acetone was added. A light yellow solid soon formed which was redissolved in acetone and the solution allowed to evaporate at about 40 °C under

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

a current of nitrogen until a white crystalline product separated (Found: C, 74.8; H, 6.60; N, 10.9. $C_{69}H_{73}B_2FeN_9$ requires C, 74.9; H, 6.65; N, 11.4%).

$[FeL^2][BPh_4]_2$. This was obtained as above as purple crystals (Found: C, 74.7; H, 6.55; N, 11.8. $C_{66}H_{67}B_2FeN_9$ requires C, 74.5; H, 6.35; N, 11.9%).

$[CoL^1][ClO_4]_2$. Hydrated cobalt(II) perchlorate and L^1 in ethanol were mixed and the desired compound obtained as pink crystals (Found: C, 37.3; H, 4.90; N, 18.4. $C_{21}H_{33}Cl_2CoN_9O_8$ requires C, 37.7; H, 4.95; N, 18.8%).

$[CoL^1][ClO_4]_3$. The compound was prepared as the above cobalt(II) derivative, but in the air, in the form of orange crystals (Found: C, 33.2; H, 4.50; N, 16.8. $C_{21}H_{33}Cl_3CoN_9O_{12}$ requires C, 32.8; H, 4.35; N, 16.4%).

$[CoL^2][BPh_4]_2$. The compound $CoCl_2 \cdot 6H_2O$ in warm ethanol was added to L^2 in ethanol. A turquoise product immediately formed which was redissolved in acetone. The addition of an acetone solution of $NaBPh_4$ immediately gave a pink compound which was recrystallised from acetonitrile–acetone (Found: C, 74.4; H, 6.50; N, 12.1. $C_{66}H_{67}B_2CoN_9$ requires C, 74.3; H, 6.35; N, 11.8%).

$[NiL^1][BPh_4]_2$. To a solution of $NiCl_2 \cdot 6H_2O$ and L^1 in warm ethanol was added an acetone solution of $NaBPh_4$. The compound immediately crystallised. Recrystallisation from acetonitrile–ethanol gave the desired mauve compound (Found: C, 74.2; H, 6.50; N, 11.1. $C_{69}H_{73}B_2N_9Ni$ requires C, 74.7; H, 6.65; N, 11.4%).

$[NiL^1][ClO_4]_2$. Hydrated nickel(II) perchlorate and L^1 were mixed in warm ethanol. The precipitate was redissolved in a water–ethanol mixture and the solution allowed to evaporate overnight at about 40 °C. Mauve crystals separated which were suitable for X-ray analysis[10] (Found: C, 37.3; H, 5.00; N, 18.6. $C_{21}H_{33}Cl_2N_9NiO_8$ requires C, 37.7; H, 4.95; N, 18.8%).

$[NiL^2][BPh_4]_2$. This compound was prepared as for $[NiL^1][BPh_4]_2$ in the form of mauve crystals (Found: C, 74.4; H, 6.45; N, 11.6. $C_{66}H_{67}B_2N_9Ni$ requires C, 74.3; H, 6.35; N, 11.8%).

$[Ni(CH_3CN)L^3][BPh_4]_2$. Slow crystallisation of the above L^2 derivative at room temperature over 1 week from an acetonitrile–ethanol solution afforded mauve crystals of the L^3 complex which were found to be suitable for X-ray analysis (Found: C, 74.5; H, 6.50; N, 11.0. $C_{64}H_{66}B_2N_8Ni$ requires C, 74.8; H, 6.45; N, 10.9%).

$[NiL^2][ClO_4]_2$. Hydrated nickel(II) perchlorate and L^2 were mixed in a boiling acetone–methanol mixture. The desired compound was obtained as red crystals upon concentration of the solution and addition of diethyl ether (Found: C, 34.2; H, 4.45; N, 19.9. $C_{18}H_{27}Cl_2N_9NiO_8$ requires C, 34.5; H, 4.35; N, 20.1%).

$[Cu(HL^1)][ClO_4]_3$. Hydrated copper(II) perchlorate and L^1 were mixed in methanol. The initially light blue solution became darker and subsequently blue-violet crystals separated. The compound was recrystallised from acetonitrile–butanol solution (Found: C, 32.9; H, 4.45; N, 16.1. $C_{21}H_{34}Cl_3CuN_9O_{12}$ requires C, 32.6; H, 4.40; N, 16.3%).

$[CuL^1][BPh_4]_2$. The previous protonated complex in ethanol was neutralised with the stoichiometric amount of sodium ethoxide. The initially blue solution became green and addition of $NaBPh_4$ in ethanol yielded turquoise crystals. The same compound was also obtained by slow oxidation of an ethanol solution of $[Cu(CH_3CN)_4]BF_4$, L^1, and $NaBPh_4$ with N_2 containing traces of O_2 (Found: C, 75.0; H, 6.70; N, 11.5. $C_{69}H_{73}B_2CuN_9$ requires C, 74.4; H, 6.60; N, 11.3%).

$[CuL^2][ClO_4]_2$. Solutions of hydrated $Cu(ClO_4)_2$ and L^2 in warm ethanol were mixed. Recrystallisation from acetonitrile–butanol gave light blue crystals (Found: C, 34.7; H, 4.85; N, 19.8. $C_{18}H_{27}Cl_2CuN_9O_8$ requires C, 34.2; H, 4.30; N, 19.9%).

$[ZnL^2][BPh_4]_2$. Zinc chloride and L^2 were dissolved in ethanol. Addition of $NaBPh_4$ in acetone gave white crystals of the desired complex (Found: C, 74.0; H, 6.50; N, 11.8. $C_{66}H_{67}B_2N_9Zn$ requires C, 73.9; H, 6.30; N, 11.7%).

Physical Measurements.—Magnetic susceptibility measurements were made on solid samples at room temperature by the Faraday method using a DMS-5 automated magnetometer. Electronic spectra were recorded in the range 300–2000 nm with a Perkin-Elmer Lambda 9 spectrophotometer. The concentrations of the solutions in acetonitrile, ethanol, or water were about 10^{-3} mol dm^{-3}. Solution spectra of iron(II) and cobalt(II) complexes were recorded in a nitrogen atmosphere. Infrared spectra were recorded with a Perkin-Elmer 283 grating spectrophotometer on Nujol mulls and KBr plates, ^1H NMR spectra on a Bruker MSL instrument operating at 200.13 MHz. The ^1H chemical shifts are reported in ppm downfield with respect to the internal standard $SiMe_4$.

Crystal Structure Determination of $[Ni(CH_3CN)L^3][BPh_4]_2$. —*Crystal data.* $C_{64}H_{66}B_2N_8Ni$, $M = 1027.62$, monoclinic, space group $P2_1/c$ (no. 14), $a = 18.544(12)$, $b = 12.460(5)$, $c = 23.400(9)$ Å, $\beta = 90.49(4)°$ [by least-squares refinement of 24 automatically centred reflections ($12 \leqslant \theta \leqslant 17°$), $\lambda = 0.710\,69$ Å], $U = 5407(5)$ Å^3, $Z = 4$, $D_c = 1.262$ g cm^{-3}, $F(000) = 2176$, μ(Mo-Kα) = 4.06 cm^{-1}.

Data collection. A rhomb-shaped crystal (0.25 × 0.40 × 0.40 mm) was mounted on an Enraf-Nonius CAD4 diffractometer. Data were collected at room temperature, in the ω–2θ scan mode with $(1.30 + 0.35\tan\theta)°$ scan width, variable (3–8° min^{-1}) scan speed and graphite-monochromated Mo-Kα radiation. Of the 8490 reflections measured ($\pm h$, k, l; $2.5 \leqslant \theta \leqslant 24°$), 6225 were unique and 3025, having $I > 3\sigma(I)$, were used for the final refinement. The intensities of three standard reflections measured periodically revealed a steady decrease (7% overall) which was corrected for. An empirical absorption correction[11] was applied at isotropic convergence, after the structure had been solved (maximum, minimum corrections 1.25, 0.83). Additional computer programs used in the crystallographic calculations are listed in refs. 12 and 13. Scattering factors for the neutral atoms were taken from ref. 14.

Structure solution and refinement. The structure was solved by standard heavy-atom techniques. A set of Fourier and Fourier difference maps yielded the positions of all non-hydrogen atoms, showing that the L^2 ligand had undergone transformation to L^3 and one CH_3CN molecule was co-ordinated to the metal. In the full-matrix least-squares refinement the function $\Sigma w(|F_o| - |F_c|)^2$ was minimised, where $w = [\sigma^2(F_o) + 0.002F_o^2]^{-1}$. In the final cycles anisotropic thermal parameters were assigned to the metal and the C atoms, except for those attached to B in the anions. In order to limit the number of parameters the latter C atoms, as well as all N and B atoms, were refined isotropically and phenyl rings were treated as rigid groups with idealised geometry. Hydrogen atoms were introduced in calculated positions with C–H (and one N–H) distances of 0.96 Å and U_H values 20% larger than the U_{eq} (or U) of the corresponding C (or N) atoms. The final cycle (490 parameters, largest shift/error ratio < 0.001 : 1) gave $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.069$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}} = 0.077$. Extreme values of residual electron density in the final Fourier difference map were 0.78 (for a peak lying close to the metal atom position, all the other peaks having heights < 0.3 e Å^{-3}) and −0.60 e Å^{-3}.

Atomic coordinates are listed in Table 1 and selected bond lengths and angles in Table 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 hexadentate ligands L^1 and L^2 were prepared in good yields by one-step reaction of the preformed macrocycle 1,4,7-

Table 1 Atomic coordinates for $[Ni(CH_3CN)L^3][BPh_4]_2$*

Atom	x	y	z
Ni	0.276 34(7)	0.275 9(1)	0.385 61(6)
N(1)	0.290 8(5)	0.380 2(7)	0.455 1(3)
N(2)	0.209 1(5)	0.191 9(7)	0.442 4(4)
N(3)	0.355 3(4)	0.187 5(6)	0.426 9(4)
N(4)	0.208 1(5)	0.475 8(7)	0.400 3(4)
N(5)	0.203 9(5)	0.388 8(8)	0.364 2(4)
N(6)	0.188 5(5)	0.098 8(8)	0.356 1(4)
N(7)	0.241 2(5)	0.158 0(7)	0.331 7(4)
C(1)	0.242 1(6)	0.346(1)	0.502 6(5)
C(2)	0.179 8(6)	0.276 3(9)	0.481 2(5)
C(3)	0.251 3(7)	0.107 9(9)	0.473 2(5)
C(4)	0.323 0(6)	0.086 5(8)	0.443 6(5)
C(5)	0.387 9(7)	0.247 7(8)	0.476 4(5)
C(6)	0.366 0(6)	0.368 2(9)	0.471 6(5)
C(7)	0.273 5(6)	0.485 0(8)	0.434 1(5)
C(8)	0.149 7(7)	0.539(1)	0.394 5(7)
C(9)	0.107 1(8)	0.494(1)	0.351 9(7)
C(10)	0.143 0(7)	0.403(1)	0.334 5(6)
C(11)	0.151 5(6)	0.145(1)	0.405 5(5)
C(12)	0.177 9(8)	0.004 7(9)	0.327 7(7)
C(13)	0.229(1)	0.002(1)	0.285 7(7)
C(14)	0.265 4(7)	0.098(1)	0.288 9(5)
N(8)	0.344 7(5)	0.345 5(7)	0.327 9(4)
C(15)	0.364 8(6)	0.392 7(9)	0.289 4(5)
C(16)	0.381 9(7)	0.457(1)	0.240 2(5)
C(21)	0.370 3(3)	0.746 5(5)	0.321 0(3)
C(22)	0.392 9(3)	0.759 1(5)	0.264 7(3)
C(23)	0.343 6(3)	0.747 8(5)	0.219 8(3)
C(24)	0.271 6(3)	0.724 0(5)	0.231 1(3)
C(25)	0.249 0(3)	0.711 4(5)	0.287 4(3)
C(26)	0.298 3(3)	0.722 6(5)	0.332 4(3)
C(31)	0.458 3(3)	0.898 1(5)	0.373 8(2)
C(32)	0.502 7(3)	0.932 7(5)	0.418 5(2)
C(33)	0.529 8(3)	1.037 1(5)	0.418 6(2)
C(34)	0.512 5(3)	1.107 0(5)	0.374 0(2)
C(35)	0.468 0(3)	1.072 4(5)	0.329 3(2)
C(36)	0.440 9(3)	0.967 9(5)	0.329 2(2)
C(41)	0.501 1(3)	0.686 2(5)	0.359 0(3)
C(42)	0.484 6(3)	0.578 3(5)	0.349 8(3)
C(43)	0.539 5(3)	0.505 0(5)	0.338 6(3)
C(44)	0.610 9(3)	0.539 5(5)	0.336 5(3)
C(45)	0.627 5(3)	0.647 4(5)	0.345 7(3)
C(46)	0.572 6(3)	0.720 7(5)	0.357 0(3)
C(51)	0.400 2(3)	0.739 9(5)	0.437 7(3)
C(52)	0.430 8(3)	0.660 4(5)	0.472 1(3)
C(53)	0.402 6(3)	0.639 6(5)	0.526 1(3)
C(54)	0.343 8(3)	0.698 5(5)	0.545 7(3)
C(55)	0.313 1(3)	0.778 0(5)	0.511 3(3)
C(56)	0.341 3(3)	0.798 7(5)	0.457 3(3)
C(61)	−0.031 7(4)	0.755 1(5)	0.295 2(3)
C(62)	0.002 1(4)	0.846 8(5)	0.274 3(3)
C(63)	0.032 2(4)	0.846 1(5)	0.219 9(3)
C(64)	0.028 5(4)	0.753 6(5)	0.186 4(3)
C(65)	−0.005 3(4)	0.661 8(5)	0.207 3(3)
C(66)	−0.035 4(4)	0.662 5(5)	0.261 8(3)
C(71)	0.001 7(4)	0.801 4(6)	0.407 1(3)
C(72)	0.074 0(4)	0.783 6(6)	0.394 2(3)
C(73)	0.127 7(4)	0.810 3(6)	0.433 9(3)
C(74)	0.109 0(4)	0.854 8(6)	0.486 4(3)
C(75)	0.036 6(4)	0.872 6(6)	0.499 3(3)
C(76)	−0.017 0(4)	0.845 9(6)	0.459 6(3)
C(81)	−0.131 9(4)	0.850 7(5)	0.366 9(3)
C(82)	−0.203 7(4)	0.819 2(5)	0.371 8(3)
C(83)	−0.258 0(4)	0.896 4(5)	0.375 0(3)
C(84)	−0.240 4(4)	1.005 2(5)	0.373 2(3)
C(85)	−0.168 5(4)	1.036 8(5)	0.368 2(3)
C(86)	−0.114 3(4)	0.959 5(5)	0.365 1(3)
C(91)	−0.092 0(3)	0.636 6(6)	0.383 2(2)
C(92)	−0.148 6(3)	0.586 6(6)	0.354 0(2)
C(93)	−0.172 3(3)	0.485 4(6)	0.371 1(2)
C(94)	−0.139 3(3)	0.434 1(6)	0.417 4(2)
C(95)	−0.082 7(3)	0.484 1(6)	0.446 7(2)
C(96)	−0.059 1(3)	0.585 3(6)	0.429 6(2)
B(1)	0.431 4(6)	0.768 4(9)	0.373 0(4)
B(2)	−0.063 4(6)	0.759 6(9)	0.362 8(5)

* In this and the following crystallographic Table estimated standard deviations on the least significant digit are in parentheses. Atoms Ni to C(16) belong to the cation and C(21) to B(2) to the anions.

Table 2 Selected bond distances (Å) and angles (°) for the compound $[Ni(CH_3CN)L^3][BPh_4]_2$

Ni-N(1)	2.097(8)	Ni-N(5)	2.006(10)
Ni-N(2)	2.109(8)	Ni-N(7)	2.040(9)
Ni-N(3)	2.066(8)	Ni-N(8)	2.052(10)
N(1)-Ni-N(2)	83.7(3)	N(2)-Ni-N(8)	175.2(4)
N(1)-Ni-N(3)	83.2(3)	N(3)-Ni-N(5)	164.0(4)
N(1)-Ni-N(5)	80.8(4)	N(3)-Ni-N(7)	97.3(3)
N(1)-Ni-N(7)	164.5(3)	N(3)-Ni-N(8)	95.4(3)
N(1)-Ni-N(8)	100.0(3)	N(5)-Ni-N(7)	98.1(4)
N(2)-Ni-N(3)	82.0(3)	N(5)-Ni-N(8)	87.4(4)
N(2)-Ni-N(5)	96.1(4)	N(7)-Ni-N(8)	95.4(4)
N(2)-Ni-N(7)	81.0(3)	Ni-N(8)-C(15)	160.9(9)

triazacyclononane[15] with the appropriate imidazole[16] and pyrazole[17] derivatives.

The reactions of the ligands L^1 and L^2 with metal(II) salts in equimolar ratios gave a number of crystalline compounds having the general formula $[ML]Y_2$ (M = Fe; L = L^1 or L^2; Y = BPh_4; M = Co, L = L^1, Y = ClO_4; L = L^2, Y = BPh_4; M = Ni, L = L^1, Y = BPh_4 or ClO_4; L = L^2, Y = BPh_4; M = Cu, L = L^1, Y = BPh_4; L = L^2, Y = ClO_4; M = Zn, L = L^2, Y = BPh_4). The compounds $[CoL^1][ClO_4]_3$ and $[Cu(HL^1)][ClO_4]_3$ (HL^1 denotes a monoprotonated derivative of the ligand L^1) were also obtained. Moreover, $[Ni(CH_3CN)L^3][BPh_4]_2$ was obtained with the new ligand 1,4-bis(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane, L^3, formed from L^2 by loss of one pendant arm. This N-dealkylation reaction occurs when an acetonitrile–ethanol solution of the $[NiL^2][BPh_4]_2$ complex is allowed slowly to evaporate nearly to dryness at about 40 °C. The complexes of iron(II) and cobalt(II) were prepared under strictly anaerobic conditions using the standard Schlenk technique. Once formed in the solid state they are reasonably stable but are quickly oxidised in solution. The aerial oxidation of $[CoL^1][ClO_4]_2$ in ethanol solution resulted in the corresponding cobalt(III) derivative. All the complexes are readily soluble in acetone and acetonitrile; moreover, the complexes having perchlorate as counter anion are also soluble in ethanol, methanol and water.

The reaction of hydrated $Cu(ClO_4)_2$ and the ligand L^1, essentially under the same conditions in which L^2 gives the compound $[CuL^2][ClO_4]_2$, afforded the complex $[Cu(HL^1)][ClO_4]_3$. Deprotonation of the complex with the stoichiometric amount of sodium ethoxide, followed by the addition of $NaBPh_4$, gave $[CuL^1][BPh_4]_2$.

The magnetic moments of the cobalt(II) and nickel(II) complexes are normal for the high-spin configurations of these metals and those of the copper(II) compounds are indicative of one unpaired electron. The cobalt(III) and zinc(II) complexes are diamagnetic, as is $[FeL^2][BPh_4]_2$. On the contrary, $[FeL^1][BPh_4]_2$ is high spin (Table 3).

The electronic spectra of the complexes were recorded on solid samples and in acetonitrile solution. Absorption maxima in the visible region are reported in Table 3. The spectra of the

Table 3 Electronic spectral data and effective magnetic moments of the complexes[a]

Complex	μ_{eff} (293 K)	State[a]	λ_{max}/nm(ε/cm^2 mmol^{-1})
$[FeL^1][BPh_4]_2$[b]	5.34	d.r.	370 (sh), 871, 1150
$[FeL^2][BPh_4]_2$	*c*	d.r.	375 (sh), 550, 950
		CH_3CN	380 (sh), 555 (47), 950 (6)
$[CoL^1][ClO_4]_2$	4.35	d.r.	483, 630, 1030
		CH_3CN	481 (62), 650 (sh), 1060 (15)
$[CoL^1][ClO_4]_3$	*c*	d.r.	340, 465, 650 (sh)
		CH_3CN	479 (334), 675 (sh)
$[CoL^2][BPh_4]_2$	4.34	d.r.	480, 630 (sh), 1000
		CH_3CN	488 (55), 650 (sh), 950 (16)
$[NiL^1][BPh_4]_2$	3.34	d.r.	350 (sh), 533, 815, 872
		CH_3CN	345 (28), 535 (20), 810 (21), 875 (20)
$[NiL^1][ClO_4]_2$	3.29	d.r.	340, 530, 820, 872
		CH_3CN	340 (30), 535 (18), 821 (21), 890 (19)
$[NiL^2][BPh_4]_2$	3.31	d.r.	337, 534, 808, 868
		CH_3CN	342 (33), 529 (25), 816 (38), 870 (sh)
$[NiL^2][ClO_4]_2$	3.27	d.r.	365, 510, 805, 870
		CH_3CN	350 (20), 535 (13), 815 (21), 880 (20)
$[Ni(CH_3CN)L^3][BPh_4]_2$	3.33	d.r.	352, 530, 823, 905
		CH_3CN	347 (35), 526 (28), 810 (44), 870 (sh)
$[CuL^1][BPh_4]_2$	1.92	d.r.	785, 1550
		CH_3CN	720 (90), 1450 (24)
$[Cu(HL^1)][ClO_4]_3$	1.91	d.r.	560, 820 (sh)
		CH_3CN	585 (100), 850 (sh)
$[CuL^2][ClO_4]_2$	1.99	d.r.	677, 1480
		CH_3CN	685 (100), 1450 (25)

[a] d.r. = Diffuse reflectance; solutions in CH_3CN are about 10^{-3} mol dm^{-3}. [b] Not sufficiently soluble. [c] Diamagnetic.

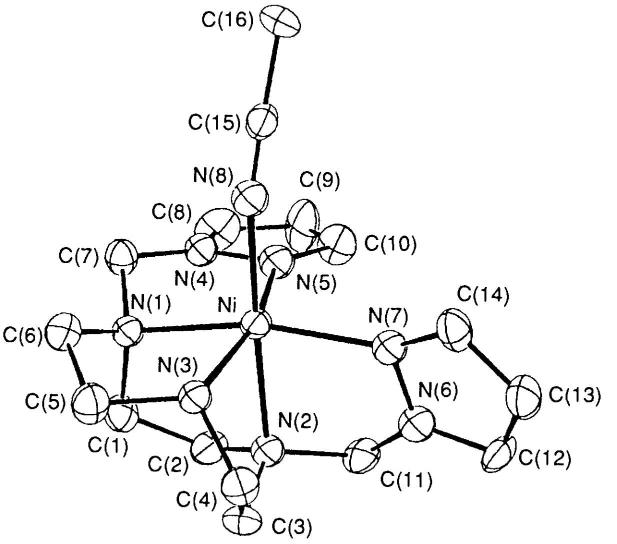

Fig. 1 View of the $[Ni(CH_3CN)L^3]^{2+}$ cation, with 20% probability ellipsoids, showing the labelling of the atoms

complexes of general formula $[ML]Y_2$ (L = L^1 or L^2) and of $[CoL^1][ClO_4]_3$ both in the solid state and in solution are all indicative of a six-co-ordinate environment of the metal atom.[18] This type of co-ordination has actually been established for $[NiL^1][ClO_4]_2$.[10] In particular, in the range 340–900 nm the nickel(II) complexes exhibit the expected three bands which are typical of six-co-ordinated nickel(II). The marked double component of the low-energy band may be due to the splitting of the spin-allowed $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition in trigonally distorted octahedral symmetry.[19] From these spectra *Dq* values in the range 1218–1235 cm^{-1} are computed, which are indicative of a strong ligand field. In view of this it may not be surprising that in addition to the high-spin $[FeL^1][BPh_4]_2$ derivative the diamagnetic compound $[FeL^2][BPh_4]_2$ has also been obtained, both complexes being six-co-ordinated on the basis of their electronic spectra.[20] The attainment of the two spin states suggests that complexes formed by the present ligands are at the verge of the spin transition for six-co-ordinate iron(II). The six-co-ordinate iron(II) complex $[FeL^4{}_2]Br_2{\cdot}3H_2O$ (L^4 = 1,4,7-triazacyclononane) is low spin,[21] whereas both high- and low-spin iron(II) complexes with pyrazolylborate ligands have been reported.[22] The difference between the λ_{max} values in the electronic spectra of $[CuL^1]^{2+}$ and $[Cu(HL^1)]^{3+}$ in CH_3CN solution (Table 3) is close to that (90 nm) previously reported for the $[CuL^5]^-$ and $[Cu(HL^5)]$ complexes in water (L^5 = 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate).[23] This suggests that protonation, conceivably of a pendant arm in each case, may have similar effects on the two types of complexes in spite of some differences in the nature of the ligands and in other properties.

The ^1H NMR data for the diamagnetic $[ZnL^2][BPh_4]_2$ complex in $(CD_3)_2CO$ present features that are in line with a high co-ordination number of the cation in a highly symmetric environment. The hydrogen atoms of the ethylene chains of the macrocycle yield a complicated multiplet having a AA′BB′ pattern, which is split into two mirror-related groups of signals [δ_A 3.24, δ_B 2.58; $^2J(H^AH^{A'}) = {}^2J(H^BH^{B'})$ −6.3, $^3J(H^AH^B) = {}^3J(H^{A'}H^{B'})$ 14.8, $^3J(H^AH^{B'}) = {}^3J(H^{A'}H^B)$ 7.2 Hz]. These signals correspond to two groups of magnetically non-equivalent protons, six being in equatorial positions and six in axial positions with respect to the plane of the co-ordinated macrocyclic ring.[8a] The protons of the methylene arms yield a single resonance (δ 5.13) and those of the pyrazole groups give rise to three resonances (δ 8.12, d, ^3J 2.3, $H^{3,5}$; δ 7.89, d, ^3J 2.3, $H^{3,5}$; δ 6.71, t, ^3J 2.2 Hz, H^4).

The structure of the compound $[Ni(CH_3CN)L^3][BPh_4]_2$ **1** consists of $[Ni(CH_3CN)L^3]^{2+}$ cations and BPh_4^- anions. The arrangement of the L^3 ligand in the cation (Fig. 1) is similar to that attained by the ligand L^1 in the nickel(II) complex $[NiL^1][ClO_4]_2$ **2**[10] or by L^2 in the lithium derivative $[LiL^2]BPh_4{\cdot}0.5Me_2CO$ **3**,[8a] except for the absence of one pendant arm in L^3 compared to the other two ligands. The metal atom in **1** is six-co-ordinated by the five N donor atoms of the L^3 ligand and by the acetonitrile N atom. The presence of a monodentate ligand in addition to the pentadentate L^3 reduces the symmetry of the metal environment with respect to that provided by L^1 or L^2, respectively in compounds **2** or **3**; however, it allows the constraints due to a chelate ring to be released, with an overall increase in flexibility. As a consequence, the co-ordination geometry, which in **2** and **3** could be viewed as intermediate between trigonal prismatic and octahedral, is now probably better described as being distorted octahedral. In particular, the angle N(2)–Ni–N(8), formed by the CH_3CN nitrogen and the macrocycle donor lying *trans* to it, attains a value [175.2(4)°] closer to the idealised 180° than can be apparently reached by the donor atoms of the hexadentate L^1 or L^2 ligands. The distances to the metal formed by the two substituted N atoms of the macrocycle (Table 2) are only slightly shorter (by 0.02 Å, in the mean) than those formed by the three macrocycle N atoms of L^1 in **2**, but the unsubstituted N(3) atom in the present compound forms a distance to the metal which is definitely shorter (by 0.05 Å) than the mean of the Ni–N distances formed by the macrocycle nitrogens bearing dangling groups in compounds **1** and **2**. The N(5) pyrazole nitrogen lying approximately *trans* to N(3) also forms a shorter (by 0.03–0.06 Å) Ni–N bond than any other pyrazole nitrogen in these two structures. The CH_3CN solvent molecule is strongly co-ordinated, the Ni–N(8) distance 2.05(1) Å being shorter than those of 2.10(3) and 2.15(3)[24] or 2.13(1) Å[25] found for two six-co-ordinate nickel(II) complexes formed by tetraazamacrocycles and CH_3CN as coligand. The CH_3CN ligand in **1** is slightly bent with respect to the Ni–N direction [Ni–N(8)–C(15) 160.9(9)°].

Protonation experiments were carried out on *ca.* 10^{-2} mol dm^{-3} solutions of $[NiL^2][ClO_4]_2$ in methanol, acetone, or acetone–water solutions, with $HClO_4$ either 0.1 or 0.5 mol dm^{-3}. >40:1 molar ratio of 0.1 mol dm^{-3} $HClO_4$ did not produce changes in the electronic spectrum of the complex over a period of 2 d. In order to obtain complete decomposition of the complex a very large excess of 0.5 mol dm^{-3} $HClO_4$ and at least 3 d were required. Moreover, the addition of a slight excess of CN^- to a water solution of $[NiL^1][ClO_4]_2$ failed to alter appreciably its electronic spectrum. Both these results indicate that the L^1 and L^2 ligands co-ordinate quite strongly to nickel(II). Also the X-ray structural analyses on the complexes **2**[10] and **3**[8a] have revealed that in both cases the metal atom is tightly bound by the nitrogens of the macrocycle and of the dangling groups, which provide a rather close environment. This prevents access of additional groups to the metal centre, contributing to the substitutional inertness of the complexes.

Such picture may be only apparently in contrast to the detachment of one pendant arm of the ligand L^2 in complex **1**, which occurs under very mild conditions, or to the protonation of L^1 in $[Cu(HL^1)][ClO_4]_3$, which occurs in the absence of external acidic reactants. The mechanisms for detachment of pendant arms or their fractions in functionalised macrocyclic ligands of this sort, as presently or previously found,[9] are not clear and may be varied. However, the cleavage of a polar N–C bond should be generally eased by the proximity of an electron-withdrawing pyrazole group and of the polarising metal cation. In the case of $[Cu(HL^1)][ClO_4]_3$ the protonation may be allowed by a less-tight binding of some donor atoms of the ligand to Cu^{II} than to other metal ions, due to the specific stereochemical requirements of the d^9 copper(II) ion; the higher basicity of imidazole with respect to pyrazole[26] may be at the origin of the different behaviour of the L^1 *vs.* L^2 copper(II) derivatives. Unfortunately, we have been unable so far to obtain suitable crystals for structural investigations on the present copper compounds.

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