Studies of Pendant-arm Macrocyclic Ligands. Part 4.† Two Penta-aza Macrocycles based on 1-(2'-Dimethylaminoethyl)-1,5,9,13-tetra-azacyclohexadecane and its Complexes with Bivalent Metal Ions‡

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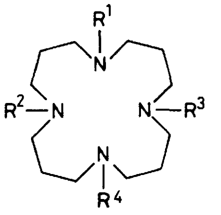
Two new pendant-arm sixteen-membered ring penta-aza macrocycles, 1-(2'-dimethylaminoethyl)-1,5,9,13-tetra-azacyclohexadecane (L^1) and 1-(2'-dimethylaminoethyl)-5,9,13-trimethyl-1,5,9,13-tetra-azacyclohexadecane (L^2) have been prepared, and the complexes of L^1 with Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} investigated. The ions Ni^{2+}, Cu^{2+}, and Co^{2+} form high-spin five-co-ordinate complexes. Carbon-13 n.m.r. spectroscopy shows $[Zn(L^1)][NO_3]_2$ to be a 1 : 1 mixture of two species, one symmetric and the other asymmetric, and $[Cd(L^1)][NO_3]_2$ is analogous but with evidence of a small amount of a third species. Attempts to prepare $[Hg(L^1)]^{2+}$ have led to its immediate reduction to metallic mercury.

We are developing new pendant-arm macrocyclic ligands in which the pendant arm terminates in a functional group which is capable of further co-ordination to a centrally placed metal ion. Previously we reported two such ligands based on a fourteen-membered tetra-aza macrocyclic ring,[1,2] and now report two closely related penta-aza macrocycles (L^1 and L^2) based on a sixteen-membered ring. It was expected that these new macrocycles would be more suitable for co-ordination to larger metal ions such as Hg^{2+}, since previous studies show that a sixteen-membered ring has a cavity which fits the ionic radius of Hg^{2+} closely.[3,4] The analogous fourteen-membered penta-aza macrocycles were found to fold readily to give pseudo-trigonal-bipyramidal complexes with Ni^{2+} and Cu^{2+}, and it was of interest to establish whether the sixteen-membered ring macrocycles behave in the same way. We report here the complexes of L^1 with Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}, together with attempts to make a complex of L^1 with Hg^{2+}.



L^1 $R^1 = CH_2CH_2NMe_2$
R^2—R^4 = H

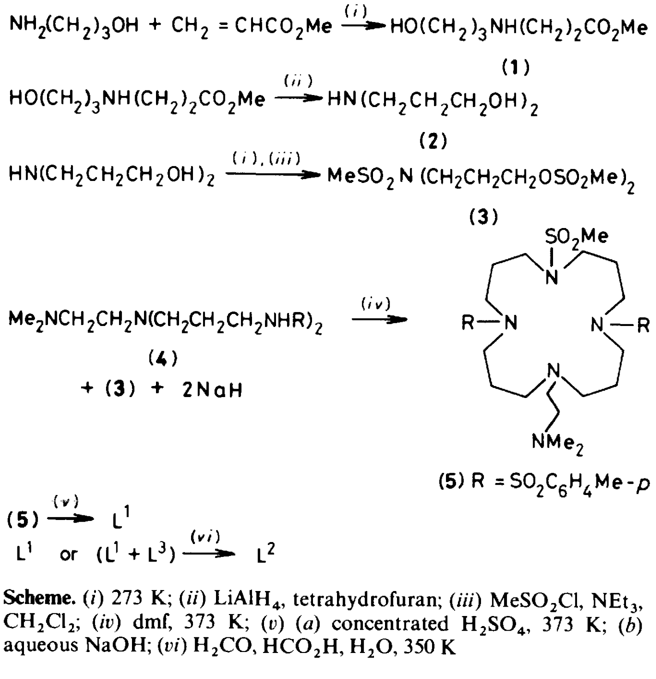
L^2 $R^1 = CH_2CH_2NMe_2$
R^2—R^4 = Me

L^3 $R^1 = CH_2CH_2NMe_2$
R^2 = Me
R^3, R^4 = H

L^4 R^1—R^4 = H

Results and Discussion

Ligand Syntheses.—The preparative routes to L^1 and L^2 are shown in the Scheme. Condensation of 3-aminopropan-1-ol with 1 equivalent of methyl acrylate gives the mono-adduct (**1**). Attempts to purify (**1**) by distillation led to retrocondensation, so it was reduced immediately with lithium aluminium hydride in tetrahydrofuran solutions to give 1,7-dihydroxy-4-aza-heptane (**2**) as an easily purified viscous oil. Treatment of (**2**) with methanesulphonyl chloride using the method of Crossland and Servis,[5] gives the tris(methanesulphonyl) derivative (**3**) as a colourless, low-melting solid. Standard Richman–Atkins conditions[6] were used for the coupling of compounds (**3**) and (**4**) to give the protected macrocycle (**5**). This was isolated as a brown, viscous oil, and immediately hydrolysed with concentrated H_2SO_4. Ligand L^1 was isolated after aqueous work-up as a colourless high-boiling oil. Initial attempts to prepare L^1 led to the isolation of a mixture of products containing the desired macrocycle together with the monomethylated derivative (L^3), which was identified by ^{13}C n.m.r. and mass spectrometry (M^+, $m/z = 313$). This derivative was found to arise as a consequence of incomplete removal of dimethylformamide (dmf) from the crude product (**5**) prior to its hydrolysis with concentrated H_2SO_4. Attempts to separate mixtures of L^1 and L^3 have so far failed. However, treatment of the mixture of L^1 and L^3 with formic acid–formaldehyde[7] gave the fully methylated macrocycle L^2 as a colourless oil. Thus, in order to obtain pure L^1 it is necessary to remove all traces of dmf from the precursor (**5**) prior to hydrolysis.



Scheme. (*i*) 273 K; (*ii*) $LiAlH_4$, tetrahydrofuran; (*iii*) $MeSO_2Cl$, NEt_3, CH_2Cl_2; (*iv*) dmf, 373 K; (*v*) (*a*) concentrated H_2SO_4, 373 K; (*b*) aqueous NaOH; (*vi*) H_2CO, HCO_2H, H_2O, 350 K

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† Part 3 is regarded as N. W. Alcock, H. A. A. Omar, P. Moore, and C. Pierpoint, *J. Chem. Soc., Dalton Trans.*, 1985, 219.

‡ *Non-S.I. units employed:* B.M. ≈ 9.27×10^{-24} A m^2; mmHg ≈ 133 Pa.

Table 1. U.v.–visible spectra [λ/nm (ε/dm^3 mol^{-1} cm^{-1})] and magnetic moments ($\mu_{eff.}$/B.M.)

	$\lambda_{max.}(\varepsilon)$		
Solvent	Nitromethane	Water	$\mu_{eff.}$[a]
$[Ni(L^1)][ClO_4]_2$	380 (136)	380 (121)	3.0
	605 (53)	605 (47)	
	1 300 (15)	1 295 (10)	
$[Cu(L^1)][ClO_4]_2$	670 (283)	675 (249)	2.3
	915 (133)	910 (104)	
$[Cu(HL^1)][ClO_4]_3$	610 (187)		
$[Co(L^1)][ClO_4]_2$	465 (50)	470 (40)	3.8
	515 (49.5)	512 (41)	
	590 (sh)	585 (23.5)	
	670 (sh)	670 (sh)	
	820 (sh)	810 (sh)	
$[Ni(L^4)][ClO_4]_2$	470 (69)	375 (14.5)[b]	0
		610 (6.5)	
		900 (3)	
$[Cu(L^4)][ClO_4]_2$	590 (346)	605 (260)[b]	2.1
$[Co(L^4)][ClO_4]_2$	510 (180)		3.8
	545 (204)		
	940 (63)		
	1 020 (61)		

[a] Determined by the method of D. F. Evans (*J. Chem. Soc.*, 1959, 2003), in [$^2H_3$]nitromethane solution; ±0.1 B.M. [b] Axial co-ordination of H_2O.

Table 2. Resonances (δ/p.p.m.) observed at 368 K *in* the 400-MHz ^1H n.m.r. spectrum of $[Ni(L^1)][ClO_4]_2$ in [$^2H_3$]nitromethane solution (relative areas 1 unless specified otherwise in parentheses)

305.98,[a] 301.71,[a] 270.52, 208.33, 178.92, 146.60, 134.64, 105.41(3),[b] *ca.* 102, 84.04, 76.24, 70.87, 59.73, 54.21, 49.03, 41.98, 34.69, 32.48(3),[b] 30.69, 3.02, 2.70, 1.58, −5.19(2),[c] −8.23,[c] −8.40,[c] −13.51,[c] −13.69,[c] −119.67,[d] −171.90,[d] −214.62[d]

[a] Broad overlapping resonances of total relative area 3 (2 + 1). [b] CH_3N. [c] CCH_2C. [d] NH.

Table 3. Carbon-13 n.m.r. data [δ/p.p.m. (relative populations in parentheses)] for $[Zn(L^1)][NO_3]_2$ and $[Cd(L^1)][NO_3]_2$

$[Zn(L^1)][NO_3]_2$[a]

22.0(1), 24.0(2),[b] 24.4(1), 25.5(2),[b] 25.6(1), 28.9(1), 47.3(1), 48.3(2),[b] 48.5(3),[b] 50.5(1), 50.7(1), 50.9(1), 52.4(1), 52.6(1), 52.9(1), 53.0(2),[b] 53.1(2),[b] 53.3(2),[b] 53.4(1), 54.8(1), 55.3(1), 56.3(1), 57.2(1), 57.4(1)

$[Cd(L^1)][NO_3]_2$[c]

25.1(1),[d] 25.4(1), 25.7, 25.9(1), 28.3, 28.7(1), 47.0, 49.7, 51.4(1), 52.1(1), 52.6, 52.9, 53.8(1), 54.1, 54.4, 54.6(1), 55.0(1), 55.7(1), 55.8(1), 56.8(1), 57.1, 59.3(1), 59.7(1), 59.8(2)

[a] In CD_3OD at 298 K. [b] Seven of the nine resonances assigned to isomers (b), (h); the others relate to isomers (c), (e) (Figure). [c] In D_2O at 298 K. Some additional peaks for minor isomers evident at δ 21.1, 22.5, 25.5, 25.7, 27.1, 54.4, 55.4, 57.5, and 57.7 p.p.m. [d] Figures in parentheses relate to the resonances assigned to isomers (c), (e), others to (b), (h) (Figure).

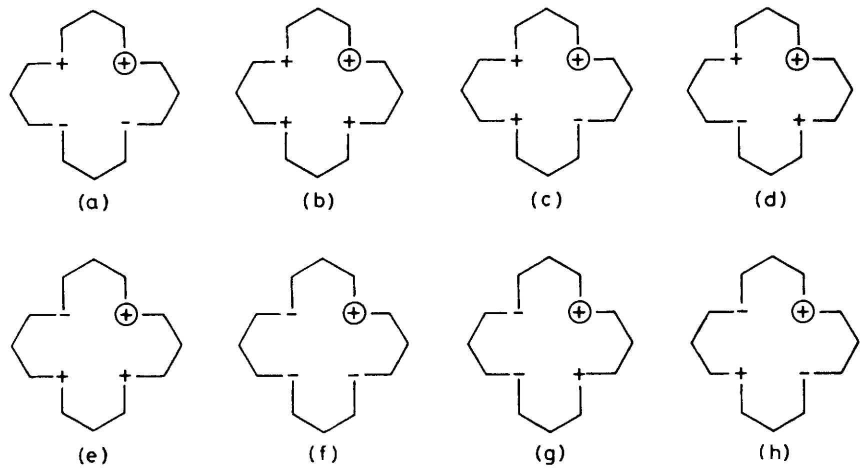

Figure. The eight possible sets of configurations at N for metal complexes of L^1. The pendant-arm position is circled, and + and − represent the relative positions of the pendant arm, or the NH protons, with respect to the macrocyclic plane

Synthesis and Characterisation of Metal Complexes of L^1.—Treatment of a methanolic solution of $[Ni(dmso)_6][ClO_4]_2$ (dmso = dimethyl sulphoxide) with an equimolar methanol solution of L^1 gave an immediate blue precipitate of $[Ni(L^1)][ClO_4]_2$. The complex is paramagnetic ($\mu_{eff.}$ 2.97 B.M.) and five-co-ordinate as shown by its visible spectrum (Table 1). The visible spectrum shows no significant change in co-ordinating and non-co-ordinating solvents, and is very similar to that found previously for the high-spin five-co-ordinate trigonal-bipyramidal nickel(II) complex of 11-(2′-dimethylaminoethyl)-1,4,7,11-tetra-azacyclotetradecane.[1] At 368 K, the paramagnetic ^1H n.m.r. spectrum of $[Ni(L^1)][ClO_4]_2$ in [$^2H_3$]nitromethane extends from *ca.* +306 to −215 p.p.m. The three NH protons appear upfield of tetramethylsilane at δ −119.7, −171.9, and −214.6 p.p.m., and the CCH_2C protons are at δ 2.70 and −5.19 (relative area 2), and −8.23, −8.40, −13.51, and −13.69 p.p.m. (relative area 1). The two CH_3N groups (relative area 3) appear at δ 32.48 and 105.41 p.p.m., and the remaining 20 resonances of relative area 1 are as shown in Table 2. The spectrum is entirely consistent with a single, unsymmetrical trigonal-bipyramidal structure in which the macrocycle is folded. Based on our earlier studies,[2] the configurations at N shown for the enantiomeric pair of structures (c), (e) (Figure) are the most likely. Attempts to protonate the pendant arm to give $[Ni(HL^1)][ClO_4]_3$ led to complete removal of the macrocycle from the Ni^{2+}, indicating a greater lability for this sixteen-membered ring complex compared with the analogous fourteen-membered ring nickel(II) system studied previously.[2]

The complex $[Cu(L^1)][ClO_4]_2$ can be prepared from a 1:1 mixture of L^1 and $[Cu(H_2O)_6][ClO_4]_2$ in methanolic solution. It is blue and paramagnetic, and as with the nickel(II) complex, its visible spectrum shows little solvent dependence (Table 1). However, unlike the corresponding nickel complex, $[Cu(L^1)][ClO_4]_2$ can be selectively protonated with perchloric acid to give $[Cu(HL^1)][ClO_4]_3$. This protonation involves a change in geometry from trigonal bipyramidal (blue) to square planar (purple) and can be monitored by visible spectroscopy (Table 1).

The cobalt(II) complex of (L^1) also forms readily in methanolic solution to give $[Co(L^1)][ClO_4]_2$ as a red-brown solid. Magnetic susceptibility measurements confirm an oxidation state of +2 and indicate a high-spin electronic configuration (Table 1). The stability of $[Co(L^1)]^{2+}$ in air was unexpected, since it is well known that when Co^{2+} is co-ordinated to five ammonia molecules, ready uptake of O_2 occurs, to give μ-peroxo-bridged dicobalt(III) species. It is also known that low-spin $[Co(L^5)]^{2+}$ (L^5 = 1,4,8,11-tetra-azacyclotetradecane) and high-spin $[Co(L^6)]^{2+}$ (L^6 = 1,4,8,12-tetra-azacyclopentadecane) are oxygen sensitive,[8] whereas $[Co(L^7)]^{2+}$ (L^7 = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) is air-stable. The oxygen sensitivity of metal complexes including those of Co^{2+} has recently been reviewed.[9] It seems likely that $[Co(L^1)]^{2+}$ has a trigonal-bipyramidal geometry which would hinder O_2 uptake. As expected, attempts selectively to protonate the pendant arm in $[Co(L^1)][ClO_4]_2$ led only to decomposition.

The salts $[Zn(H_2O)_6][NO_3]_2$ and $[Cd(H_2O)_4][NO_3]_2$ both react with ligand L^1 in a 1:1 ratio to give products which analyse as $[M(L^1)][NO_3]_2$ (M = Zn or Cd). The zinc(II) complex consists of an approximately 1:1 mixture of two species, one symmetric the other asymmetric, as revealed by the ^{13}C n.m.r. spectrum (Table 3). This result is analogous to that previously described for the $Zn(NO_3)_2$ complex of 11-methyl-1,4,7,11-tetra-azacyclotetradecane.[2]

The ^{13}C n.m.r. spectrum of $[Cd(L^1)][NO_3]_2$ (Table 3) also reveals the presences of two major isomers in aqueous solution. These isomers are again symmetric and asymmetric. However, unlike the zinc(II) complex, traces of other isomers are visible and indeed $[Cd(L^1)][NO_3]_2$ is very similar to the previously reported cadmium(II) complex of 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexadecane.[3]

Attempts to prepare $[Hg(L^1)]X_2$ where $X^- = ClO_4^-$, NO_3^-, or O_2CMe^- led only to the rapid reduction of Hg^{II} to Hg^0. Even though mercury(II) ions are known to effect the oxidation of tertiary amines to imines, this result was somewhat surprising since the mercury(II) complex of 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexadecane has been reported previously.[3] This would tend to suggest that either the redox behaviour of Hg^{II} is significantly altered by complexation to L^1, or L^1 is more readily oxidised than 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexadecane. The organic oxidation products have not yet been characterised, but presumably oxidation of a tertiary amine to iminium perchlorate is involved, followed by solvolysis.

Experimental

Materials and Methods.—All chemicals used were of the highest available purity. Proton-decoupled, natural-abundance ^{13}C n.m.r. spectra were recorded either at 100.6 MHz using a Bruker WH400 Fourier-transform spectrometer, or at 22.63 MHz using a Bruker WH90 Fourier-transform spectrometer, with dioxane (δ = 67.4 p.p.m.) as internal reference. Proton n.m.r. spectra were recorded either using a Perkin-Elmer (model R34) 220-MHz spectrometer, or with a Bruker WH400 spectrometer with $SiMe_4$ as reference. Infrared spectra were recorded using a Perkin-Elmer (model 580B) spectrometer equipped with an internal reference, ultraviolet-visible spectra with a Shimadzu (model 365) spectrophotometer, and mass spectra with a Kratos (model MS80) instrument.

1,5,9,13-Tetra-azacyclohexadecane (L^4) was synthesised as described in the literature[10] and its complexes with Ni^{II}, Cu^{II}, Co^{II} were prepared by mixing equimolar amounts of ligand (L^4) and metal perchlorate in ethanol followed by isolation of the solid product. The compound $Me_2NCH_2CH_2N(CH_2CH_2CH_2NHSO_2C_6H_4Me\text{-}p)_2$ was prepared as previously described.[1,2]

Preparations.—*Compound* (**1**). 3-Aminopropan-1-ol (25 g, 0.33 mol) was stirred at *ca.* 0 °C during the dropwise addition of methyl acrylate (28.65 g, 0.33 mol). The reaction was monitored to completion by ^1H n.m.r. spectroscopy. Any attempt to purify the compound at this stage leads only to decomposition to starting materials. The product was used, therefore, without further purification. ^1H N.m.r. ($CDCl_3$): δ 1.70 (2 H, quintet), 2.51 (2 H, t), 2.88 (4 H, m), 3.22 (2 H, br), 3.68 (3 H, s), and 3.75 p.p.m. (2 H, t).

Compound (**2**). Lithium aluminium hydride (12 g, 0.31 mol) was stirred in dry tetrahydrofuran (400 cm^3) under nitrogen during the dropwise addition of a 30% solution of compound (**1**) (50 g, 0.31 mol) in tetrahydrofuran. The resulting solution was stirred at room temperature for 30 min, then heated at reflux for 2 h. After cooling, water (10 cm^3) was added dropwise, followed by 15% NaOH (aqueous) (10 cm^3), and finally more water (20 cm^3). The resulting granular precipitate was filtered off, washed with dichloromethane, and the combined filtrates were evaporated to leave a colourless viscous oil. Fractional distillation gave 1,7-dihydroxy-4-azaheptane (**2**) (35 g, 0.26 mol), b.p. 145—150 °C (0.05 mmHg), in *ca.* 85% yield. ^1H N.m.r. ($CDCl_3$): δ 1.7 (4 H, quintet), 2.80 (4 H, t), 3.56 (3 H, br), and 3.75 p.p.m. (4 H, t). Mass spectrum (electron-impact, e.i.): M^+ at m/z 133.1105 (calc.: 133.1157).

Compound (**3**). Compound (**2**) (22.7 g, 0.17 mol) and triethylamine (80 g) were stirred in dichloromethane (500 cm^3) at *ca.* 0 °C during the dropwise addition of a solution of methanesulphonyl chloride (58.5 g, 0.51 mol) in dichloromethane (60 cm^3). After the addition was complete stirring was continued for 15 min. The precipitate of triethylammonium chloride was removed by filtration, and the filtrate was washed with 1 mol dm^{-3} HCl (aqueous) (100 cm^3), and distilled water (100 cm^3). Drying ($MgSO_4$), followed by filtration and evaporation, gave a viscous colourless oil which crystallised on standing. The product could be recrystallised from 10% dichloromethane in pentane to give (**3**) (50 g, 0.136 mol), m.p. 35—37 °C, in *ca.* 80% yield. ^1H N.m.r. ($CDCl_3$): δ 2.10 (4 H, quintet), 2.87 (3 H, s), 3.05 (6 H, s), 3.33 (4 H, t), and 4.30 p.p.m. (4 H, t).

Ligand L^1. Compound (**4**) (23.4 g, 45.8 mmol) was dissolved in dimethylformamide (dmf) and stirred under nitrogen during the addition of sodium hydride (2.2 g, 91.6 mmol). When gas evolution ceased the solution was heated to 100 °C and a solution of compound (**3**) (16.84 g, 45.8 mmol) in dmf (150 cm^3) was added dropwise over 2 h. The resulting solution was heated at 110 °C for 12 h and then poured into an equal volume of water. The whole of the solvent was then removed by evaporation to leave a viscous brown oil * which was then dissolved in concentrated H_2SO_4 (100 cm^3) and heated at 100 °C for 24 h. After cooling, the solution was poured into ethanol (200 cm^3) followed by addition of diethyl ether (500 cm^3). The resulting

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* Proton n.m.r. confirmed this oil as compound (**5**). Traces of dmf were removed by pumping overnight with a rotary pump at 60 °C.

dark brown precipitate was collected by decantation and dissolved in the minimum amount of distilled water. The solution was adjusted to *ca.* pH 10 with 2% NaOH (aqueous), followed by extraction with dichloromethane (5 × 100 cm^3). The combined extracts were dried ($MgSO_4$), filtered, and evaporated to leave a pale yellow oil. Fractional distillation (Kugelrohr apparatus) gave a colourless oil which could not be crystallised: L^1, 1-(2′-dimethylaminoethyl)-1,5,9,13-tetra-azacyclohexadecane (2.51 g, 8.4 mmol), b.p. 150—155 °C (0.05 mmHg), in *ca.* 18% yield. N.m.r.: ^{13}C (D_2O) δ (relative areas in parentheses) 28.2(2), 30.0(2), 46.2 (2 NCH_3), 48.1(2), 48.6(4), 52.8(2), 53.1(1), and 58.3(1) p.p.m.; ^1H ($CDCl_3$), δ 1.68 (8 H, m), 2.22 (6 H, s), 2.38 (2 H, m), 2.50 (6 H, m), and 2.71 p.p.m. (15 H, m). Mass spectrum (e.i.): M^+ at *m/z* 299.3031 (calc.: 299.3031). I.r. (thin film): 3 290 cm^{-1} (N–H).

Ligand L^2. Ligand L^1 (0.5 g, 1.67 mmol) was dissolved in 98% formic acid (10 cm^3) and formaldehyde (10 cm^3 of a 40% aqueous solution) was added. After heating at 90 °C for 12 h the reaction mixture was cooled in ice and basified (pH *ca.* 12) with 10% aqueous NaOH. Extraction with CH_2Cl_2 (5 × 25 cm^3), followed by drying ($MgSO_4$) of the combined extracts and removal of solvent *in vacuo*, gave a pale yellow oil. Distillation (Kugelrohr apparatus) gave 1-(2′-dimethylaminoethyl)-5,9,13-trimethyl-1,5,9,13-tetra-azacyclohexadecane (L^2) (0.51 g, 1.49 mmol), b.p. 130—135 °C (0.05 mmHg), as a colourless oil in *ca.* 89% yield. N.m.r.: ^{13}C ($CDCl_3$) δ 25.1(2), 25.3(2), 43.2 (2 NMe), 43.5 (1 NMe), 45.9 (NMe_2), 52.5(2), 53.5(1), 54.9(2), 55.0(2), 55.4(2), and 57.9(1) p.p.m.; ^1H ($CDCl_3$), 1.52 (8 H, quintet), 2.13 (6 H, s), 2.15 (3 H, s), 2.18 (6 H, s), 2.30 (16 H, m), and 2.40 p.p.m. (4 H, m). Mass spectrum (e.i.): M^+ at *m/z* 341.352 (calc.: 341.3541). I.r.: no N–H stretch.

$[Cu(L^1)][ClO_4]_2 \cdot H_2O$. The salt $[Cu(H_2O)_6][ClO_4]_2$ (61.86 mg, 0.16 mmol) was dissolved in ethanol and added to a solution of L^1 (50 mg, 0.16 mmol) in ethanol. The resulting turquoise-blue precipitate was removed by filtration, washed with a little cold ethanol and ether, and dried *in vacuo* to give $[Cu(L^1)][ClO_4]_2 \cdot H_2O$ (86 mg, 0.148 mmol) in *ca.* 92% yield (Found: C, 33.5; H, 6.45; N, 11.85. Calc. for $C_{16}H_{39}Cl_2CuN_5O_9$: C, 33.2; H, 6.80, N, 12.05%). I.r. (Nujol mull): 3 300, 3 260 (N–H), and 1 090 cm^{-1} (ClO_4^-).

$[Ni(L^1)][ClO_4]_2 \cdot H_2O$. The complex $[Ni(dmso)_6][ClO_4]_2$ (0.24 g, 0.33 mmol) was dissolved in ethanol and added to a solution of L^1 (0.1 g, 0.33 mmol) in ethanol. The resulting blue precipitate was treated as described above to give $[Ni(L^1)][ClO_4]_2$ (175 mg, 0.31 mmol) in *ca.* 94% yield (Found: C, 33.2; H, 6.80; N, 11.45. Calc. for $C_{16}H_{39}Cl_2N_5NiO_9$: C, 33.4; H, 6.85; N, 12.15%). I.r. (Nujol mull): 3 290, 3 260 (N–H), and 1 095 cm^{-1} (ClO_4^-).

$[Co(L^1)][ClO_4]_2 \cdot H_2O$. The salt $[Co(H_2O)_6][ClO_4]_2$ (122 mg, 0.33 mmol) was dissolved in ethanol and added to an equimolar solution of L^1 in ethanol. The resulting red-brown precipitate was collected by filtration, washed, and dried *in vacuo* to give $[Co(L^1)][ClO_4]_2 \cdot H_2O$ (162 mg, 0.29 mmol) in *ca.* 89% yield (Found: C, 33.25; H, 6.50; N, 11.45. Calc. for $C_{16}H_{39}Cl_2CoN_5O_9$: C, 33.4; H, 6.85; N, 12.15%). I.r. (Nujol mull): 3 280, 3 220 (N–H), and 1 100 cm^{-1} (ClO_4^-).

$[Cd(L^1)][NO_3]_2$. The salt $Cd(NO_3)_2 \cdot 4H_2O$ (0.31 g, 1.0 mmol) was dissolved in ethanol and added to a methanolic solution of L^1 (0.3 g, 1.0 mmol). The complex was precipitated as a white powder by addition of diethyl ether, filtered off, dried *in vacuo*, and recrystallised from the minimum amount of hot methanol to give $[Cd(L^1)][NO_3]_2$ (0.44 g, 0.82 mmol) as colourless crystals in *ca.* 81% yield (Found: C, 35.7; H, 7.10; N, 18.3. Calc. for $C_{16}H_{37}CdN_7O_6$: C, 35.85; H, 6.95; N, 18.1%).

$[Zn(L^1)][NO_3]_2$. The salt $Zn(NO_3)_2 \cdot 6H_2O$ (40 mg, 0.134 mmol) was dissolved in methanol and added to a methanolic solution of L^1 (41 mg, 0.137 mmol). The complex was precipitated as a white powder by addition of diethyl ether, filtered off, and dried *in vacuo* to give $[Zn(L^1)][NO_3]_2$ (62 mg, 0.127 mmol) in 94% yield.

Acknowledgements

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