Isolation and Complexation of the *cis* Isomer of the Pendant Arm Macrocycle 6,13-Dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine†

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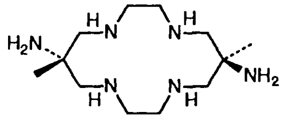
The *cis* isomer of the pendant arm macrocyclic hexaamine 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (L^2) has been isolated for the first time. The ligand has been complexed with cadmium(II) and characterised structurally. The complex $[CdL^2][ClO_4]_2$ crystallises in the monoclinic space group $P2_1/n$, $a = 10.238(1)$, $b = 16.445(2)$, $c = 13.106(2)$ Å, $\beta = 103.33(1)°$, and $Z = 4$. The Cd–N bond lengths are not unusual by comparison with those exhibited by typical CdN_6^{2+} complexes, compared with the generally short M–N bond lengths that have been observed in sexidentate co-ordinated complexes of the *trans* isomer L^1. Reaction of L^1 with cadmium(II) does not yield a hexaamine complex, instead the pendant primary amines are not co-ordinated and the four secondary amines encircle the metal centre.

In recent years we have pursued the co-ordination chemistry of the pendant arm macrocycle *trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (L^1).[1–4] Synthesis of the ligand is achieved *via* a metal-directed condensation of bis(ethane-1,2-diamine)copper(II) with nitroethane and formaldehyde, and subsequent reduction of the nitro groups to yield the hexaamine. It was initially anticipated that the reaction would generate two isomeric forms of the ligand, that is *trans* (L^1) and *cis* (L^2) isomers where the pendant amines lie on opposite sides or the same side of the macrocyclic ring respectively. The X-ray crystal structure of the copper(II) complex $[Cu(H_2L^1)][ClO_4]_4$ was reported[1] but the existence of L^2 was based only on subtle differences in the infrared spectra exhibited by the copper(II) complexes of L^1 and the putative L^2. In the absence of structural characterisation of $[Cu(H_2L^2)]^{4+}$ there remained some doubt as to whether the complex was as formulated or whether it was simply an N-based isomer of $[Cu(H_2L^1)]^{4+}$. Herein we report the identification and isolation of the ligand L^2, and the X-ray crystal structure of its cadmium(II) complex.

It has long been of interest to us to ascertain the point at which the metal ion becomes too large to allow sexidentate co-ordination of the *trans* isomer L^1. It was found that sexidentate co-ordination of L^1 to the relatively large zinc(II) ion could be achieved,[3] so the logical progression was to its larger, second-row relative cadmium(II). Contrasts between the cadmium(II) complexes of L^1 and L^2 will be illustrated, particularly in relation to the preferred modes of co-ordination exhibited by both isomers.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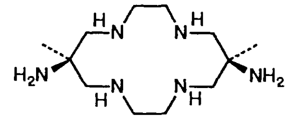
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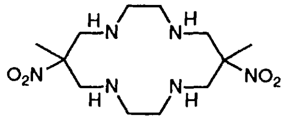
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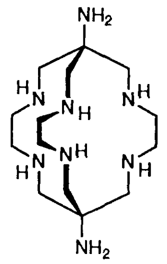
L^4

Experimental

Syntheses.—The complex (6,13-dimethyl-6,13-dinitro-1,4,8,11-tetraazacyclotetradecane)copper(II) perchlorate $[CuL^3][ClO_4]_2$ was prepared as previously described.[1]

cis-6,13-*Dimethyl*-1,4,8,11-*tetraazacyclotetradecane*-6,13-*diamine hexahydrochloride trihydrate* $L^2{\cdot}6HCl{\cdot}3H_2O$. *Synthesis of the mixture of* L^1 *and* L^2. To a solution of $[CuL^3][ClO_4]_2$ (8.0 g) in water (400 cm^3) was added hydrochloric acid (40 cm^3, 10 mol dm^{-3}) and excess of granulated zinc (*ca.* 16 g). The solution was stirred at 60 °C for 2 h or until no colour remained. Filtration of the solution removed copper and zinc residues and the filtrate was charged onto a column (15 × 3 cm) of Dowex 50W × 2 cation-exchange resin (200 mesh, H$^+$ form). The column was washed with dilute hydrochloric acid (1 mol dm^{-3}) in order to remove Zn^{2+} and unseparated bands of L^1 and L^2 followed by elution with 3 mol dm^{-3} hydrochloric acid. The eluate was evaporated to dryness, the residue suspended in diethyl ether and collected by filtration (6.0 g, 91%). This product was found to be a 4:1 mixture of $L^1 : L^2$ (both as their hexahydrochloride salts) from the ^{1}H and ^{13}C NMR spectra of the sample.

Separation of L^1 *and* L^2. The above mixture (6.0 g) was dissolved in water (100 cm^3). To this solution was added copper(II) nitrate trihydrate (2.85 g) and the pH raised to 6 by addition of sodium hydroxide solution. The purple solution was

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

Table 1 Non-hydrogen positional parameters for $[CdL^2][ClO_4]_2$

Atom	*x*	*y*	*z*
Cd	−0.027 20(3)	0.110 98(2)	0.674 19(2)
N(1)	−0.203 6(4)	0.208 4(2)	0.677 5(3)
N(2)	0.011 5(4)	0.135 6(3)	0.860 1(3)
N(3)	−0.201 9(4)	0.045 1(3)	0.723 5(3)
N(4)	0.209 4(3)	0.088 8(2)	0.746 2(3)
N(5)	0.060 5(4)	0.243 5(2)	0.644 6(3)
N(6)	0.079 1(3)	0.087 1(2)	0.541 2(3)
C(1)	−0.279 4(6)	0.181 2(4)	0.753 4(5)
C(2)	−0.232 7(5)	0.097 7(3)	0.806 0(4)
C(3)	−0.105 6(6)	0.102 9(5)	0.894 2(4)
C(4)	0.140 9(5)	0.099 6(3)	0.911 8(4)
C(5)	0.247 1(5)	0.120 3(3)	0.853 2(4)
C(6)	−0.345 4(7)	0.063 5(5)	0.851 9(6)
C(7)	0.283 6(4)	0.122 1(3)	0.671 2(4)
C(8)	0.193 7(4)	0.145 1(3)	0.564 1(3)
C(9)	0.133 1(5)	0.230 8(3)	0.560 7(4)
C(10)	−0.051 9(6)	0.301 3(3)	0.620 1(5)
C(11)	−0.144 8(6)	0.289 6(3)	0.692 1(5)
C(12)	0.275 8(6)	0.141 4(4)	0.481 1(5)
Cl(1)	0.941 4(1)	0.126 1(1)	0.223 1(1)
O(11)	−0.024 9(4)	0.065 1(2)	0.303 1(3)
O(12)	−0.186 4(4)	0.104 9(3)	1.157 0(4)
O(13)	0.039 1(6)	0.121 0(4)	1.163 5(4)
O(14)	0.939 5(5)	0.202 2(2)	0.273 3(4)
Cl(2)	0.353 3(1)	0.888 0(1)	0.574 5(1)
O(21)	0.220 3(5)	−0.083 8(4)	0.539 1(5)
O(22)	0.413(1)	−0.074 8(6)	0.663 2(8)
O(23)	0.363 4(7)	−0.194 9(3)	0.579 3(6)
O(24)	0.412 2(6)	−0.088 1(5)	0.485 7(6)
O(21′)	0.404(3)	−0.176(2)	0.535(2)
O(22′)	0.287(4)	−0.172(2)	0.648(3)
O(23′)	0.264(3)	−0.069(2)	0.512(2)
O(24′)	0.464(3)	−0.074(2)	0.653(2)

Primes indicate minor contributors to disordered atoms.

charged on a column (100 × 3 cm) of Dowex 50W × 2 cation-exchange resin. Excess of Cu^{2+} was eluted with 1 mol dm^{-3} HCl solution. Four purple bands were eluted in the following order with the given eluents: 1 (2 mol dm^{-3} HCl), λ_{max} 528; 2 (3 mol dm^{-3} HCl), λ_{max} 538; 3 (3 mol dm^{-3} HCl), λ_{max} 528; and 4 (5 mol dm^{-3} HCl), λ_{max} 518 nm. The above solutions were reduced by reaction with zinc dust (*ca.* 4 g) at room temperature for 15 min. The reduced solutions were filtered, individually charged on cation-exchange columns and the free ligands were isolated as described above. The overall yield of the ligands, based on the above isomeric mixture, was quantitative. The ^1H NMR spectra of the isolated ligands revealed that bands 1, 2 and 4 all comprised $L^1{\cdot}6HCl$: NMR (^2H_2O, pH 1), ^1H, δ 0.95 (s, 6 H), 2.40 and 2.53 (AB, q, 8 H) and 2.64 (s, 8 H); ^{13}C, δ 20.5, 47.7, 53.7 and 55.4. Band 3 was identified as $L^2{\cdot}6HCl{\cdot}3H_2O$ (Found: C, 26.9; H, 7.7; Cl, 39.4; N, 16.0. Calc. for $C_{12}H_{42}Cl_6N_6O_3$: C, 27.1; H, 8.0; Cl, 40.0; N, 15.8%). NMR (^2H_2O, pH 1): ^1H, δ 0.90 (s, 6 H), 2.47 (s, 8 H), 2.58 and 2.62 (AB, q, 8 H); ^{13}C, δ 20.7, 47.0, 53.9 and 54.9.

(cis-6,13-*Dimethyl*-1,4,8,11-*tetraazacyclotetradecane*-6,13-*diamine*)*cadmium*(II) *perchlorate* $[CdL^2][ClO_4]_2$. A solution of $L^2{\cdot}6HCl{\cdot}3H_2O$ (0.50 g), tricadmium sulfate octahydrate (0.24 g) and sodium perchlorate monohydrate (2.80 g) in water (20 cm^3) was raised to pH 6 with sodium hydroxide solution. Colourless crystals suitable for X-ray work formed upon slow evaporation of the solution at room temperature. The product was collected by filtration and air dried. Several crops were obtained and the yield was virtually quantitative (Found: C, 25.0; H, 5.3; Cl, 12.4; N, 14.8. Calc. for $C_{12}H_{30}CdCl_2N_6O_8$: C, 25.3; H, 5.3; Cl, 12.5; N, 14.8%). NMR (^2H_2O): ^1H, δ 0.35 (s, 6 H), ≈1.5 and ≈2.5 (AB, q, 8 H), 1.65 and 2.25 (AB, q, 4 H), 1.90 and 2.50 (AB, q, 4 H); ^{13}C, δ 26.7, 49.6, 51.3, 51.6, 54.9 and 57.6.

trans-(trans-13-*Ammonio*-6,13-*dimethyl*-1,4,8,11-*tetraazacyclotetradecane*-6-*amine*)*dichlorocadmium*(II) *perchlorate trihydrate* $[Cd(HL^1)Cl_2]ClO_4{\cdot}3H_2O$. This complex was prepared in an identical manner to $[CdL^2][ClO_4]_2$ except that $L^1{\cdot}6HCl{\cdot}2H_2O$ was substituted for $L^2{\cdot}6HCl{\cdot}3H_2O$. Colourless crystals of the complex precipitated within 2 d. These were collected by filtration and air dried. Several crops were obtained (Found: C, 24.0; H, 6.0; Cl, 18.6; N, 14.1. Calc. for $C_{12}H_{37}CdCl_3N_6O_7$: C, 24.2; H, 6.3; Cl, 17.8; N, 14.1%). NMR: ^1H (^2H_2O), δ 0.83 (s, 6 H), 2.35 and 2.50 (AB, q, 8 H) and 2.58 (s, 8 H); ^{13}C [$(CD_3)_2SO$], δ 22.4, 46.1, 51.7 and 55.1.

Physical Methods.—The NMR spectra were recorded using a Varian GEMINI 300 spectrometer at 75 (^{13}C) or 300 MHz (^1H), with 1,4-dioxane and sodium [$^2H_4$]-3-trimethylsilylpropionate being employed as the respective internal standards. All chemical shifts are cited *versus* tetramethylsilane. Infrared spectra of compounds dispersed as KBr discs were measured on a Perkin-Elmer 1600 FTIR spectrometer. Microanalyses were performed by CIBA-GEIGY, Basel.

Structure Determination of $[CdL^2][ClO_4]_2$.—*Crystal data.* $C_{12}H_{30}CdCl_2N_6O_8$, $M = 569.71$, monoclinic, space group $P2_1/n$, $a = 10.238(1)$, $b = 16.445(2)$, $c = 13.106(2)$ Å, $\beta = 103.33(1)°$, $U = 2146.9(5)$ Å^3, D_c ($Z = 4$) = 1.762 g cm^{-3}, $F(000) = 1160$, $\mu = 12.66$ cm^{-1}, λ(Mo-Kα) = 0.710 69 Å. Specimen: colourless prisms, 0.125 × 0.175 × 0.075 mm. $A^*_{min,max}$ 1.04, 1.22; $N = 4315$, $N_o = 3351$, *hkl* −13 to 13, 0–21, 0–18. $R = 0.033$, $R' = 0.037$, $w = 1.50/[\sigma^2(F) + 0.000\,29F^2]$. Residual extrema ±0.5 e Å^{-3}.

Data collection. Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections. Data were measured on an Enraf-Nonius CAD4-F diffractometer within the limit $1 < \theta < 25°$, with Mo-Kα radiation, λ = 0.710 69 Å, graphite monochromator, and operating in the ω–θ scan mode. 3351 Independent reflections with $I > 2.5\sigma(I)$ were considered observed and used for solution of the structure. Data were reduced and Lorentz, absorption, polarisation and decomposition corrections were applied using the Enraf-Nonius Structure Determination Package.[5]

Structure solution. The structure was solved by Patterson techniques and refined by full-matrix least-squares analysis with SHELX 76.[6] All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were located and refined with isotropic thermal parameters. Scattering factors and anomalous dispersion coefficients for Cd were taken from the literature[7] and for all other atoms the values supplied in SHELX 76 were used. Non-hydrogen atom coordinates are listed in Table 1. The atomic nomenclature is defined in Fig. 2, drawn with ORTEP.[8] A list of non-hydrogen interatomic distances and angles appears in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Although the *trans* isomer L^1 has been known for some time, the existence of L^2 has, until now, remained equivocal. Selective crystallisation of $L^1{\cdot}6HCl$ from a mixture of L^1 and L^2 is an efficient procedure for obtaining L^1 in an isomerically pure form, and this method has been employed in earlier studies of complexes of L^1. Evaporation of a mixture of both ligands to dryness is necessary in order to precipitate the more soluble isomer, $L^2{\cdot}6HCl$. Therefore, fractional crystallisation of L^2 from an isomeric mixture of the ligands was not viable and chromatographic separation of the ligands was necessary. Direct separation of the free ligands on Dowex cation-exchange resin was not facile. It should be said, however, that a genuine evaluation of the separation was not possible. The ultraviolet absorbance of the hydrochloric acid eluent was much greater than that of the ligands so spectrophotometric detection of the eluate was not possible.

Table 2 Bond lengths (Å) and angles (°) for $[CdL^2][ClO_4]_2$

N(1)–Cd	2.423(4)	C(3)–C(2)	1.530(7)
N(2)–Cd	2.410(4)	C(5)–C(4)	1.507(8)
N(3)–Cd	2.308(4)	C(8)–C(7)	1.537(6)
N(4)–Cd	2.416(3)	C(9)–C(8)	1.536(6)
N(5)–Cd	2.422(4)	C(12)–C(8)	1.521(8)
N(6)–Cd	2.292(4)	C(11)–C(10)	1.499(9)
C(1)–N(1)	1.465(9)	O(11)–Cl(1)	1.434(3)
C(11)–N(1)	1.460(6)	O(12)–Cl(1)	1.437(4)
C(3)–N(2)	1.475(8)	O(13)–Cl(1)	1.406(7)
C(4)–N(2)	1.467(6)	O(14)–Cl(1)	1.417(4)
C(2)–N(3)	1.474(7)	O(21)–Cl(2)	1.411(5)
C(5)–N(4)	1.461(6)	O(22)–Cl(2)	1.33(1)
C(7)–N(4)	1.479(7)	O(23)–Cl(2)	1.370(5)
C(9)–N(5)	1.477(8)	O(24)–Cl(2)	1.482(8)
C(10)–N(5)	1.470(7)	O(21′)–Cl(2)	1.33(3)
C(8)–N(6)	1.488(5)	O(22′)–Cl(2)	1.63(4)
C(6)–C(2)	1.53(1)	O(23′)–Cl(2)	1.29(3)
C(2)–C(1)	1.561(8)	O(24′)–Cl(2)	1.48(3)
N(2)–Cd–N(1)	79.6(1)	N(3)–Cd–N(1)	71.0(1)
N(3)–Cd–N(2)	75.7(1)	N(4)–Cd–N(1)	141.1(1)
N(4)–Cd–N(2)	73.4(1)	N(4)–Cd–N(3)	126.3(1)
N(5)–Cd–N(1)	73.4(1)	N(5)–Cd–N(2)	91.7(1)
N(5)–Cd–N(3)	143.8(1)	N(5)–Cd–N(4)	79.8(1)
N(6)–Cd–N(1)	127.9(1)	N(6)–Cd–N(2)	143.3(1)
N(6)–Cd–N(3)	131.9(1)	N(6)–Cd–N(4)	70.2(1)
N(6)–Cd–N(5)	76.9(1)	C(1)–N(1)–Cd	108.9(3)
C(11)–N(1)–Cd	108.7(3)	C(11)–N(1)–C(1)	117.2(5)
C(3)–N(2)–Cd	106.8(3)	C(4)–N(2)–Cd	108.6(3)
C(4)–N(2)–C(3)	115.1(4)	C(2)–N(3)–Cd	103.9(3)
C(5)–N(4)–Cd	109.9(3)	C(7)–N(4)–Cd	107.8(2)
C(7)–N(4)–C(5)	116.3(4)	C(9)–N(5)–Cd	105.1(3)
C(10)–N(5)–Cd	108.4(3)	C(10)–N(5)–C(9)	115.6(4)
C(8)–N(6)–Cd	103.1(3)	C(2)–C(1)–N(1)	114.3(5)
C(1)–C(2)–N(3)	106.7(4)	C(3)–C(2)–N(3)	107.4(4)
C(3)–C(2)–C(1)	113.9(5)	C(6)–C(2)–N(3)	112.4(5)
C(6)–C(2)–C(1)	108.4(5)	C(6)–C(2)–C(3)	108.2(5)
C(2)–C(3)–N(2)	113.6(4)	C(5)–C(4)–N(2)	110.8(4)
C(4)–C(5)–N(4)	110.3(4)	C(8)–C(7)–N(4)	114.0(3)
C(7)–C(8)–N(6)	107.8(3)	C(9)–C(8)–N(6)	106.8(3)
C(9)–C(8)–C(7)	113.9(4)	C(12)–C(8)–N(6)	111.7(4)
C(12)–C(8)–C(7)	109.2(4)	C(12)–C(8)–C(9)	107.6(4)
C(8)–C(9)–N(5)	112.2(4)	C(11)–C(10)–N(5)	111.0(4)
C(10)–C(11)–N(1)	109.7(4)	O(12)–Cl(1)–O(11)	107.6(2)
O(13)–Cl(1)–O(11)	106.5(3)	O(13)–Cl(1)–O(12)	108.4(3)
O(14)–Cl(1)–O(11)	107.7(3)	O(14)–Cl(1)–O(12)	112.7(3)
O(14)–Cl(1)–O(13)	113.5(4)	O(22)–Cl(2)–O(21)	110.7(5)
O(23)–Cl(2)–O(21)	113.5(4)	O(23)–Cl(2)–O(22)	113.7(5)
O(24)–Cl(2)–O(21)	101.0(4)	O(24)–Cl(2)–O(22)	112.0(6)
O(24)–Cl(2)–O(23)	105.0(5)	O(21′)–Cl(2)–O(21)	124.2(9)
O(22′)–Cl(2)–O(21′)	90(2)	O(23′)–Cl(2)–O(21′)	118(2)
O(23′)–Cl(2)–O(22′)	112(2)	O(24′)–Cl(2)–O(21′)	107(2)
O(24′)–Cl(2)–O(22′)	101(2)	O(24′)–Cl(2)–O(23′)	121(2)

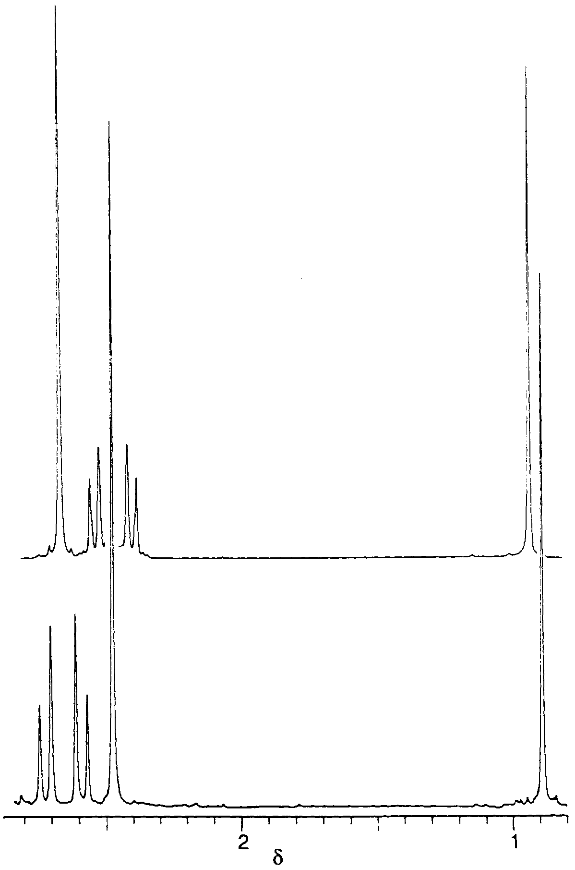
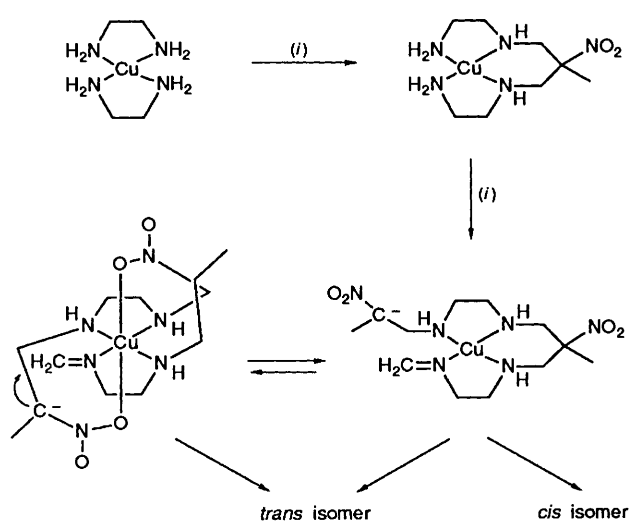


Fig. 1 Proton NMR spectra of L^1 (top) and L^2 in ^2H_2O (pH 1)

Column chromatography of the copper(II) complexes of L^1 and L^2 on a strongly acidic cation-exchange resin was found to be a successful method for separation of the ligands. The colour of the complexes allowed visual detection of the bands, and also imparted different chromatographic behaviour to ligands L^1 and L^2. This technique is quite unusual for the separation of copper(II) complexes since their lability generally dictates that chromatography be performed at, or around, neutral pH. The high stability, and inertness, of fourteen-membered tetraaza macrocyclic complexes of copper(II) in particular dictates that the ligands remain co-ordinated at acid concentrations as high as 5 mol dm^{-3} for several weeks. Three bands were observed as a result of N-based isomerism of the copper(II) complexes of L^1, an observation which has been noted previously for other related fourteen-membered tetraaza macrocyclic complexes of copper(II).[9–12] The three isomers displayed quite different visible maxima (518, 528 and 538 nm). Further discussion of the absolute configuration of these three isomers is not offered, since none of the complexes was isolated as a solid. The copper(II) complex of L^2 formed but one isomer, exhibiting an electronic maximum at 528 nm, which suggests a configuration the same as that found for the second $[Cu(H_2L^1)]^{4+}$ band. Removal of copper(II) was achieved by reduction with zinc in hydrochloric acid and the reduced solutions were again chromatographed to separate the isomerically pure ligands from Zn^{2+}. The ^1H NMR spectra of the ligands L^1 and L^2 are shown in Fig. 1. There is a reversal in the chemical shifts of the AB quartet and the accompanying singlet. The quartets in both spectra are due to geminal coupling between the methylene hydrogens adjacent to the pendant methyl and amino groups, whereas the protons contained in the ethylene residues result in singlets. The resonances due to the pendant methyl groups in the two spectra also exhibit slightly different chemical shifts. The proton-decoupled ^{13}C NMR spectra of L^1 and L^2 are very similar, with the pairs of matching resonances being within 1 ppm of each other.

It is appropriate at this point to discuss the origins of the stereoselectivity in formation of L^1 in preference to L^2. One must return to the precursor dinitro-substituted complex $[CuL^3]^{2+}$, since the ratio of *trans* to *cis* isomers of L^3 is necessarily the same as that found for L^1 to L^2 in the absence of any carbon–carbon or carbon–nitrogen bond rearrangements in the reduction step. It is apparent that the original template synthesis of L^3 must be the source of the stereoselectivity. The two isomers of L^3 (and for that matter L^1 and L^2) are equally likely if one considers the relative stabilities of their copper(II) complexes. There is no significant difference between the steric bulk of a nitro group and that of a methyl group, so whether the nitro groups are on the same side or on opposite sides of the macrocyclic ring is immaterial when the relative strain energies of the two complexes are considered. It is then clear that the



Scheme 1 (*i*) $EtNO_2$–CH_2O

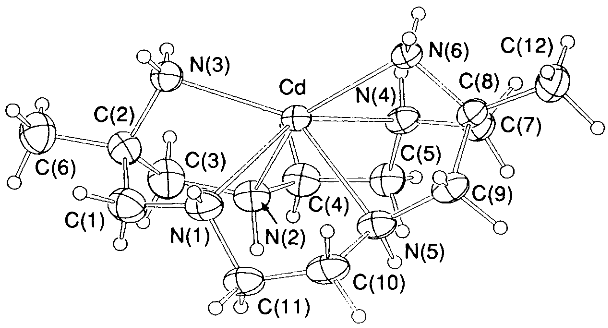


Fig. 2 An ORTEP drawing of the $[CdL^2]^{2+}$ cation (perchlorate anions have been omitted for clarity)

observed isomer ratio is a result of kinetic control, *i.e.* there is an intermediate step which favours the formation of the *trans* isomer of L^3. The proposed mechanism is illustrated in Scheme 1.

The critical step is the introduction of the second nitroethane residue into the acyclic mononitro complex. The orientation of the nitro group at the time that cyclisation of the second six-membered chelate ring occurs determines whether the *trans* or *cis* isomer is formed. For there to be a preference (4 : 1) of *trans* to *cis* it is proposed that co-ordination of both nitro groups (necessarily in *trans* sites) is the factor which results in the observed ratio of products. It is clear that although this mechanism explains the formation of L^1 it does not account for the formation of L^2. In an analogous mechanism, two nitro groups cannot co-ordinate in the same axial site during formation of the *cis* isomer of L^3, so the minor isomer must have been formed in the absence of axial co-ordination by at least one of the two nitro groups. Statistically, an equal amount of the *trans* isomer of L^3 would also be formed while both nitro groups are not co-ordinated. Recent studies concerning the copper(II)-directed condensations of racemic amino acids with nitroethane and formaldehyde have also indicated that co-ordination of the nitroethane residue during the reaction is an important factor in determining the resultant isomer distribution.[13,14] Indeed, the stereoselectivity has been as high as 100% in some cases. Although axial co-ordination of nitro groups to the copper(II) metal centre has not been positively identified in solution, it has been observed in crystal structures of copper(II) complexes bearing pendant nitro groups.[15] Despite the tenuous connections between solid-state and solution behaviour of co-ordination compounds, the existence of such interactions in the crystal lattice does add weight to the proposed mechanism.

Co-ordination of L^1 and L^2 to Cd^{II} was achieved simply by neutralising an equimolar ratio of metal ion and ligand in aqueous solution. The ^1H NMR spectrum of $[CdL^2]^{2+}$ revealed a complex pattern of four sets of overlapping AB quartets corresponding to the methylene hydrogens, plus a singlet at low field from the pendant methyl groups. The ^{13}C NMR spectrum gave a clearer picture of the symmetry of the complex. Six resonances were observed indicative of C_2 symmetry of the complex cation. That is, the spectrum indicated that the ligand had folded into a non-planar arrangement of the four secondary amines. This is in contrast to the ^{13}C NMR spectra of sexidentate co-ordinated complexes of L^1 where four resonances have been observed consistent with C_{2h} symmetry.[2,3,16] However, the ^{13}C NMR spectrum of $[Cd(HL^1)Cl_2]ClO_4{\cdot}3H_2O$ displayed four resonances. The ^1H NMR spectrum revealed that the ligand L^1, in addition to encircling the metal ion, had co-ordinated in a quadridentate manner *via* the four secondary amines, not as a sexidentate co-ordinated ligand. Previous ^1H NMR spectra of sexidentate co-ordinated complexes of L^1 have shown that two sets of AB quartets are observed, from geminal coupling between the methylene hydrogens in both the five- and six-membered chelate rings.[2,3,16] However, the ^1H NMR spectrum of $[Cd(HL^1)Cl_2]ClO_4{\cdot}3H_2O$ exhibited but one AB quartet whereas the other quartet collapsed into a singlet. This is typical of the spectra of other[2,16] quadridentate co-ordinated complexes of L^1, where the observation of this singlet is due to the greater conformational flexibility of the five-membered chelate rings in the absence of co-ordination by the pendant primary amines. Protonation of one pendant primary amine was indicated by infrared resonances (H–N–H bending) at 1618 and 1501 cm^{-1} ($-NH_3^+$) and 1570 ($-NH_2$) compared with the single sharp maximum at 1590 cm^{-1} in the spectrum of $[CdL^2][ClO_4]_2$, and consistent with a co-ordinated primary amine. Within the given formulation of $[Cd(HL^1)Cl_2]ClO_4{\cdot}3H_2O$ there exist several possible isomeric forms depending on whether the water molecules or anions are contained within or situated outside the co-ordination sphere. It is always difficult to distinguish between co-ordinated and anionic chloride in labile species such as the present complex. The compound could also conceivably be written as $[Cd(HL^1)(OH_2)_2][ClO_4]Cl_2{\cdot}H_2O$, but the present techniques could not unequivocally discriminate between the two forms.

The crystal structure of $[CdL^2][ClO_4]_2$ confirmed sexidentate co-ordination of L^2 (Fig. 2). The macrocyclic moiety of L^2 is folded and the pendant primary amines occupy *cis* positions within the co-ordination sphere. The configuration of the four secondary amine nitrogens is *RRRR*, which is the most common arrangement for folded fourteen-membered macrocycles. The Cd–N bonds to the macrocyclic secondary amines (2.410–2.423 Å) are significantly longer than the corresponding Cd–N bonds to the pendant primary amines [2.292(4) and 2.308(4) Å]. There are relatively weak bonds between one oxygen of each perchlorate anion and the metal centre [Cd–O(11) 2.947(3), Cd–O(21) 3.059(5) Å]. There are no intermolecular interactions between $[CdL^2][ClO_4]_2$ units. Hydrogen bonding between the perchlorate oxygens and the amine hydrogens is also apparent. In addition to the weak bond formed with the metal centre, O(11) makes contacts with the amine hydrogens on N(3), N(4) and N(6) (2.59, 2.52 and 2.24 Å respectively). The geometry of the $Cd^{II}N_6O_2$ co-ordination sphere is approximately square antiprismatic but in the absence of the perchlorate ions is best described as distorted trigonal prismatic (twist angle 21.3°: *cf.* 0° for trigonal prismatic and 60° for octahedral geometry), with an approximate C_2 axis bisecting the N(3)–Cd–N(6) angle. There is minimal deviation of the intraligand bond lengths or angles from their ideal values, suggesting that the ligand may readily accommodate other comparatively large metal ions. The average Cd–N bond length in $[CdL^2]^{2+}$ (2.38 Å) is longer than that found in the structure of the macrobicyclic cage complex $[Cd(H_2L^4)]^{4+}$ (average 2.30 Å),[17] and comparable with $[Cd(en)_3]^{2+}$ (2.38 Å, en = ethane-

1,2-diamine).[18] This is notable since all crystal structures of complexes of the sexidentate co-ordinated *trans* isomer L^1 have revealed shorter than average M–N bonds, indeed they have generally been the shortest known for a hexaamine complex. Obviously this has not occurred in the case of $[CdL^2]^{2+}$.

A molecular mechanics study of the sexidentate co-ordinated complexes of L^1 and L^2 has recently been completed.[19] Briefly, it is apparent that L^1 shows a distinct preference for small metal ions whereas the *cis* isomer L^2 co-ordinates to large or small metal ions without favour. The apparent inability of L^1 to co-ordinate to the large cadmium(II) ion as a sexidentate ligand is consistent with this. It has been found that the axial elongation of M–N(pendant) bonds relative to the equatorial M–N(secondary) increases with increasing metal-ion size throughout the series of sexidentate co-ordinated complexes of L^1. In addition the N(pendant)–M–N(secondary) bite angle becomes increasingly acute as the metal ion becomes larger. It can be seen that this concomitant elongation and lateral displacement of the M–N(pendant) bond must eventually result in its breaking. Given the results presented herein, the metal-ion size limit to sexidentate co-ordination of L^1 lies between zinc(II) and cadmium(II).

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References

1 P. Comba, N. F. Curtis, G. A. Lawrance, A. M. Sargeson, B. W. Skelton and A. H. White, *Inorg. Chem.*, 1986, **25**, 4260.

2 P. V. Bernhardt, T. W. Hambley and G. A. Lawrance, *J. Chem. Soc., Dalton Trans.*, 1989, 1059.

3 P. V. Bernhardt, G. A. Lawrance, M. Maeder, M. Rossignoli and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1991, 1167.

4 P. V. Bernhardt, P. Comba, T. W. Hambley and G. A. Lawrance, *Inorg. Chem.*, 1991, **30**, 942.

5 Enraf-Nonius Structure Determinaton Package, Enraf-Nonius, Delft, 1985.

6 G. M. Sheldrick, SHELX 76, A Program for X-Ray Crystal Structure Determination, University of Cambridge, 1976.

7 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, vol. 4.

8 C. K. Johnson, ORTEP, A Thermal Ellipsoid Plotting Program, Oak Ridge National Laboratory, TN, 1965.

9 D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc.*, 1970, **92**, 2151.

10 R. A. Bauer, W. R. Robinson and D. W. Margerum, *J. Chem. Soc., Chem. Commun.*, 1973, 289.

11 R. Clay, J. Murray-Rust and P. Murray-Rust, *J. Chem. Soc., Dalton Trans.*, 1979, 1135.

12 B. F. Liang and C. S. Chung, *J. Chem. Soc., Dalton Trans.*, 1980, 1349.

13 P. Comba, T. W. Hambley, G. A. Lawrance, L. L. Martin, P. Renold and K. Várnagy, *J. Chem. Soc., Dalton Trans.*, 1991, 277.

14 P. V. Bernhardt, P. Comba, T. W. Hambley, R. Schmidlin and K. Várnagy, unpublished work.

15 P. Comba, N. F. Curtis, G. A. Lawrance, M. A. O'Leary, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1988, 2145.

16 P. V. Bernhardt, G. A. Lawrance and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1990, 983.

17 P. Comba, A. M. Sargeson, L. M. Engelhardt, J. M. Harrowfield, A. H. White, E. Horn and M. R. Snow, *Inorg. Chem.*, 1985, **24**, 2325.

18 C. Mahadevan, M. Seshasayee, S. Sastry and C. Subrahmanyan, *Z. Kristallogr.*, 1985, **171**, 173.

19 P. V. Bernhardt and P. Comba, *Helv. Chim. Acta*, in the press.

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