Sexidentate Co-ordination of the Pendant-arm Macrocycle 6,13-Dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (L^1) to Zinc(II). Crystal Structure of $[ZnL^1][ClO_4]_2{\cdot}H_2O$†

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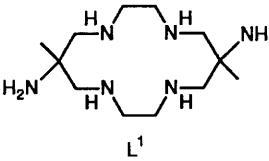
The pendant-arm macrocycle 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (L^1) co-ordinates as a sexidentate ligand to zinc(II) in neutral aqueous solution. The complex $[ZnL^1][ClO_4]_2{\cdot}H_2O$ crystallises in the monoclinic space group $P2_1/c$, $a = 9.488(4)$, $b = 14.736(9)$, $c = 16.037(4)$ Å, $\beta = 97.95(3)°$ and $Z = 4$. The Zn–N bond lengths in $[ZnL^1]^{2+}$ are, on average, the shortest known for a hexaaminezinc(II) complex. The stability constant for formation of $[ZnL^1]^{2+}$ was determined to be log K 15.0 ± 0.1, from potentiometric titrations. Five of the six successive protonation constants for the hexaamine L^1 were measured similarly and values pK_a 2.9, 5.5, 6.3, 9.9 and 11.0 found.

In earlier papers, we reported that sexidentate complexes of the pendant-arm macrocyclic hexaamine 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (L^1) with chromium(III),[1] iron(III),[2] cobalt(III),[3] rhodium(III)[4] and nickel(II)[5] exhibit the shortest metal–nitrogen bond lengths for a hexaamine complex of their particular series.



L^1

Although zinc(II) complexes are essentially 'silent' with respect to electronic, electrochemical and magnetic studies, structural properties obtained from their complexes can be quite informative. No ligand-field stabilisation energy is operative upon complexation of the d^{10} metal ion, and hence there is no particular preference for octahedral over tetrahedral geometry in zinc(II) complexes. This is evident from the existence of structures of both tetrahedral $[Zn(en)_2]^{2+}$ and octahedral $[Zn(en)_3]^{2+}$ (en = ethane-1,2-diamine) complexes in the literature.[6,7] The resultant geometry of the sexidentate zinc(II) complex of L^1 must therefore be dictated solely by steric factors. The sexidentate hexaamine complex of zinc(II) with the ligand L^1 is reported herein with its stability constant, which has been determined from a potentiometric titration of L^1 and zinc(II). The protonation constants of the free ligand are also reported.

Experimental

Syntheses.—The ligand 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine, as the hexahydrochloride salt ($L^1{\cdot}6HCl$), was prepared as described previously.[3]

(6,13-*Dimethyl*-1,4,8,11-*tetraazacyclotetradecane*-6,13-*diamine*)*zinc*(II) *perchlorate hydrate*, $[ZnL^1][ClO_4]_2{\cdot}H_2O$. A solution of anhydrous zinc(II) chloride (0.13 g) and $L^1{\cdot}6HCl$ (0.5 g) in sodium perchlorate solution (20 cm^3, 1 mol dm^3) was neutralised (pH 7–8) with dilute sodium hydroxide solution. On standing for 24 h, colourless crystals suitable for X-ray analysis formed which were collected by filtration and air dried. Several crops were obtained and the yield was quantitative. The product was not washed with ethanol since this resulted in dehydration and powdering of the crystals (Found: C, 26.8; H, 6.2; N, 15.5. Calc. for $C_{12}H_{32}Cl_2N_6O_9Zn$: C, 26.7; H, 6.0; N, 15.6%). NMR (D_2O): ^1H, δ 1.19 (s, 6 H); 2.50, 3.20 (q, 8 H); 2.60, 3.30 (q, 8 H); ^{13}C, δ 28.1, 54.5, 58.3 and 62.5 ppm.

Physical Methods.—NMR spectra were recorded on a JEOL FX90Q FT spectrometer, using sodium [$^2H_4$]trimethylsilylpropionate and 1,4-dioxane as internal standards for ^1H and ^{13}C spectra respectively, although ^{13}C chemical shifts are cited *versus* tetramethylsilane. Infrared spectra were recorded using an Hitachi 260-10 spectrophotometer with compounds being dispersed in potassium bromide discs. Potentiometric titrations were performed with a Metrohm 605 digital pH meter, a Metrohm 665 digital burette and Metrohm combined glass electrodes. All measurements were under the control of an IBM clone computer.[8] Titrations were performed at 298 K and an ionic strength of 0.5 mol dm^{-3} KCl. Acidic solutions of 0.6×10^{-3} mol dm^{-3} $L^1{\cdot}6HCl$ alone and in the presence of 0.9 equivalent of zinc(II) ion were titrated with 1×10^{-5} dm^{-3} increments of 0.4 mol dm^{-3} sodium hydroxide solution. Data reduction was performed using a TURBO BASIC version of the program TITFIT.[9]

Structure Determination.—*Crystal data.* $[ZnL^1][ClO_4]_2{\cdot}H_2O$, $C_{12}H_{32}Cl_2N_6O_9Zn$, $M = 540.6$, monoclinic, space group $P2_1/c$, $a = 9.488(4)$, $b = 14.736(9)$, $c = 16.037(4)$ Å, $\beta = 97.95(3)°$, $U = 2220.7$ Å^3, D_c ($Z = 4$) = 1.617 g cm^{-3}, $F(000) = 1128$, $\mu_{Mo} = 14.19$ cm^{-1}. Specimen: colourless prisms, $0.46 \times 0.21 \times 0.19$ mm. $A^*_{min,max}$ 0.74, 0.79; $N = 4153$, $N_o = 2446$, range of hkl −11 to 11, 0–17, 0–19. $R = 0.044$, $R' = 0.048$, $w = k/[\sigma^2(F_o) + gF_o{}^2]$ where k and g are 2.64 and 1.54×10^{-4}, residual extrema ±0.5 e Å^{-3}.

Data collection. Cell constants were determined by a least-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Non-hydrogen positional parameters (× 10^4) for [ZnL^1][ClO$_4$]$_2$·H$_2$O

Atom	*x*	*y*	*z*
Zn	2318(1)	7220(1)	4068(1)
N(1)	662(5)	6309(4)	4192(3)
N(2)	3905(5)	6290(3)	4531(3)
N(3)	2311(6)	6391(3)	2927(3)
N(4)	3991(5)	8115(3)	3914(3)
N(5)	739(5)	8195(4)	3685(3)
N(6)	2350(5)	8033(3)	5242(3)
C(1)	1051(7)	5442(5)	3823(5)
C(2)	2357(6)	5501(4)	3353(4)
C(3)	3778(8)	5504(4)	3955(4)
C(4)	5237(6)	6804(5)	4654(5)
C(5)	5282(6)	7544(5)	4015(5)
C(6)	2359(10)	4716(5)	2751(6)
C(7)	3887(7)	8888(5)	4477(5)
C(8)	2479(6)	8924(4)	4835(4)
C(9)	1190(8)	9049(5)	4153(5)
C(10)	−575(6)	7776(6)	3898(5)
C(11)	−608(6)	6773(6)	3732(5)
C(12)	2521(8)	9714(5)	5460(5)
Cl(1)	1501(2)	2138(1)	3780(1)
O(11)	276(5)	1623(4)	3652(4)
O(12)	1341(7)	2930(4)	4312(4)
O(13)	2564(7)	1603(5)	4217(5)
O(14)	1994(9)	2429(4)	3061(3)
Cl(2)	2843(2)	9159(1)	1739(1)
O(21)	2470(6)	9607(4)	985(3)
O(22)	3986(7)	8607(5)	1641(5)
O(23)	3265(11)	9726(6)	2379(4)
O(24)	1776(8)	8652(7)	1950(6)
O(3)	5034(10)	1529(8)	3059(5)

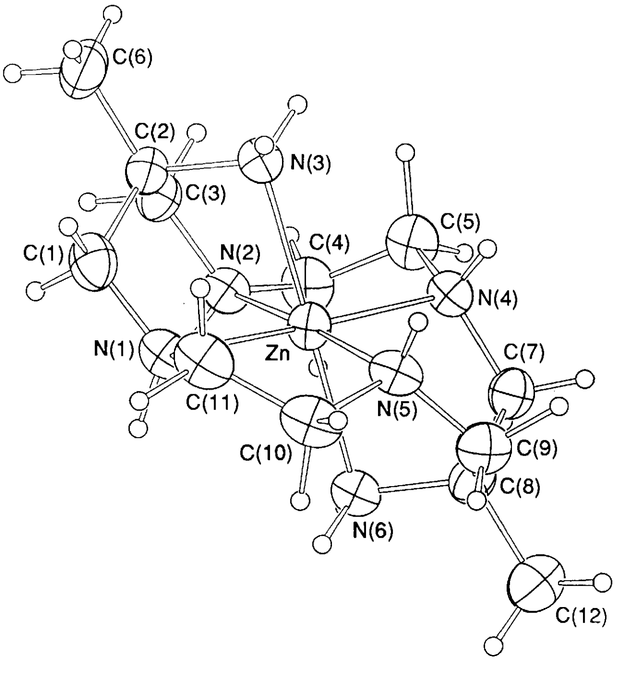


Fig. 1 ORTEP drawing of the [ZnL^1]$^{2+}$ cation

Table 2 Bond lengths (Å) and angles (°) for [ZnL^1][ClO$_4$]$_2$·H$_2$O

N(1)–Zn	2.097(5)	N(2)–Zn	2.095(4)
N(3)–Zn	2.200(5)	N(4)–Zn	2.104(5)
N(5)–Zn	2.105(5)	N(6)–Zn	2.228(4)
C(1)–N(1)	1.475(8)	C(11)–N(1)	1.491(8)
C(3)–N(2)	1.476(7)	C(4)–N(2)	1.464(7)
C(2)–N(3)	1.477(7)	C(5)–N(4)	1.477(7)
C(7)–N(4)	1.465(8)	C(9)–N(5)	1.497(9)
C(10)–N(5)	1.474(8)	C(8)–N(6)	1.480(7)
C(2)–C(1)	1.539(8)	C(3)–C(2)	1.545(8)
C(6)–C(2)	1.507(9)	C(5)–C(4)	1.501(9)
C(8)–C(7)	1.526(8)	C(9)–C(8)	1.535(8)
C(12)–C(8)	1.532(8)	C(11)–C(10)	1.500(10)
O(11)–Cl(1)	1.380(5)	O(12)–Cl(1)	1.466(5)
O(13)–Cl(1)	1.391(6)	O(14)–Cl(1)	1.371(6)
O(21)–Cl(2)	1.381(5)	O(22)–Cl(2)	1.382(6)
O(23)–Cl(2)	1.340(7)	O(24)–Cl(2)	1.339(7)

N(2)–Zn–N(1)	93.3(2)	N(3)–Zn–N(1)	78.9(2)
N(3)–Zn–N(2)	81.4(2)	N(4)–Zn–N(1)	178.4(2)
N(4)–Zn–N(2)	86.3(2)	N(4)–Zn–N(3)	99.6(2)
N(5)–Zn–N(1)	87.3(2)	N(5)–Zn–N(2)	176.1(2)
N(5)–Zn–N(3)	102.5(2)	N(5)–Zn–N(4)	93.2(2)
N(6)–Zn–N(1)	100.8(2)	N(6)–Zn–N(2)	97.3(2)
N(6)–Zn–N(3)	178.6(2)	N(6)–Zn–N(4)	80.8(2)
N(6)–Zn–N(5)	78.8(2)	C(1)–N(1)–Zn	106.5(3)
C(11)–N(1)–Zn	103.0(4)	C(11)–N(1)–C(1)	115.4(6)
C(3)–N(2)–Zn	107.4(3)	C(4)–N(2)–Zn	105.9(4)
C(4)–N(2)–C(3)	119.0(5)	C(2)–N(3)–Zn	96.4(3)
C(5)–N(4)–Zn	104.9(4)	C(7)–N(4)–Zn	107.4(4)
C(7)–N(4)–C(5)	120.1(5)	C(9)–N(5)–Zn	106.5(4)
C(10)–N(5)–Zn	103.8(4)	C(10)–N(5)–C(9)	115.4(5)
C(8)–N(6)–Zn	95.5(3)	C(2)–C(1)–N(1)	114.3(5)
C(1)–C(2)–N(3)	107.6(5)	C(3)–C(2)–N(3)	104.7(4)
C(3)–C(2)–C(1)	112.7(5)	C(6)–C(2)–N(3)	112.8(5)
C(6)–C(2)–C(1)	110.1(5)	C(6)–C(2)–C(3)	108.9(5)
C(2)–C(3)–N(2)	112.5(4)	C(5)–C(4)–N(2)	113.0(5)
C(4)–C(5)–N(4)	112.8(5)	C(8)–C(7)–N(4)	113.4(5)
C(7)–C(8)–N(6)	105.4(5)	C(9)–C(8)–N(6)	108.3(5)
C(9)–C(8)–C(7)	112.9(6)	C(12)–C(8)–N(6)	112.4(5)
C(12)–C(8)–C(7)	109.1(5)	C(12)–C(8)–C(9)	108.8(5)
C(8)–C(9)–N(5)	113.6(5)	C(11)–C(10)–N(5)	111.7(5)
C(10)–C(11)–N(1)	111.6(6)	O(12)–Cl(1)–O(11)	111.8(4)
O(13)–Cl(1)–O(11)	107.4(4)	O(13)–Cl(1)–O(12)	106.5(4)
O(14)–Cl(1)–O(11)	115.2(4)	O(14)–Cl(1)–O(12)	108.4(4)
O(14)–Cl(1)–O(13)	107.0(5)	O(22)–Cl(2)–O(21)	107.0(4)
O(23)–Cl(2)–O(21)	112.7(5)	O(23)–Cl(2)–O(22)	107.4(6)
O(24)–Cl(2)–O(21)	112.1(5)	O(24)–Cl(2)–O(22)	109.4(6)
O(24)–Cl(2)–O(23)	108.1(6)		

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, $\lambda = 0.710\,69$ Å, graphite monochromator, and operating in the ω–θ scan mode. Independent reflections with $I > 2.5\sigma(I)$ were considered observed and used for solution of the structure. Data were reduced and Lorentz, polarisation and decomposition corrections were applied using the Enraf-Nonius Structure Determination Package.

Structure solution. The structure was solved by Patterson techniques and refined by full-matrix least-squares analysis with SHELX 76.[10] 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 Zn were taken from ref. 11 and for all other atoms the values supplied in SHELX 76 were used. Absorption correction was by numerical integration.[12] Non-hydrogen atom coordinates are listed in Table 1. The atomic nomenclature is defined in Fig. 1, drawn with ORTEP.[13] A list of non-hydrogen interatomic distances appears in Table 2.

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

Results and Discussion

Complexation of zinc(II) by L^1 was found to be facile and was achieved rapidly by neutralising an aqueous solution of equimolar quantities of zinc(II) and ligand, followed by crystallisation as the perchlorate salt. The infrared spectrum of [ZnL^1][ClO$_4$]$_2$ displayed resonances common to other sexidentate complexes of L^1,[1–5] with a strong primary amine vibration

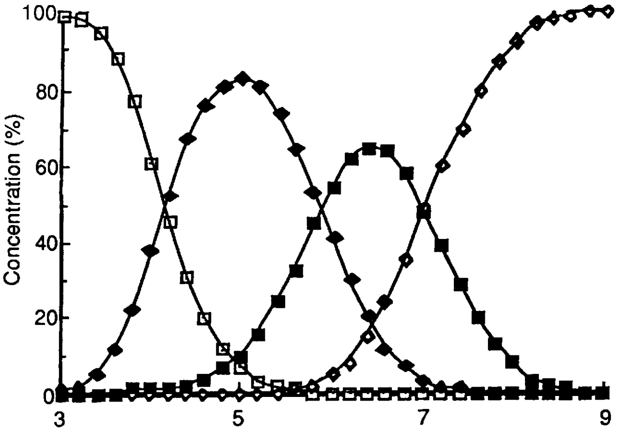
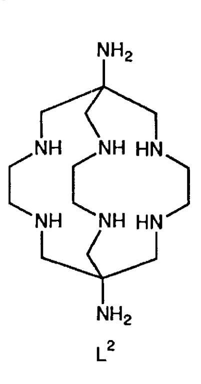


Fig. 2 Calculated distribution of the species Zn^{2+} (□), $[Zn(H_2L^1)(OH_2)_2]^{4+}$ (◆), $[Zn(HL^1)(OH_2)]^{3+}$ (■) and $[ZnL^1]^{2+}$ (◇) as a function of pH

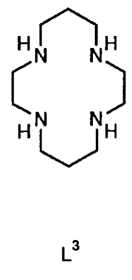
$[\delta(NH_2)]$ appearing at 1600 cm^{-1} being indicative of co-ordination by both pendant groups. This is in contrast to the spectrum of *trans*-$[Zn(H_2L^1)(OSO_2SO_3)_2]$, where protonation of both pendant amines was defined by the appearance of resonances at 1630 and 1500 cm^{-1} characteristic of primary ammonium groups.[14] The ^1H NMR spectrum of $[ZnL^1]^{2+}$ displayed two overlapping AB quartets and a low-field singlet corresponding to the two sets of methylene protons (in the five- and six-membered rings of the macrocycle) and the equivalent methyl groups respectively. The proton-decoupled ^{13}C NMR spectrum of $[ZnL^1]^{2+}$ displayed four resonances consistent with the anticipated C_{2h} geometry of the complex cation. Although strong evidence for sexidentate co-ordination of L^1 to zinc(II) was obtained from the NMR and IR spectra, conclusive proof was provided by the X-ray crystal structure of $[ZnL^1][ClO_4]_2 \cdot H_2O$.

Unlike all other sexidentate complexes of L^1, the $[ZnL^1]^{2+}$ cation was not located on a crystallographic centre of symmetry, but instead was found on a general site, as were the two perchlorate anions and a single water molecule. The five-membered ethylenediamine chelate rings adopt like conformations (both δ), which removes the centre of symmetry at the metal, which has otherwise been found to exist in all other structures of sexidentate complexes of L^1. The *trans* axial Zn–N(primary) bond lengths are inequivalent, but both are more than 0.1 Å longer than the equatorial Zn–N bonds. This is by far the largest axial elongation of M–N bond lengths in the $[ML^1]^{n+}$ series so far. There is not a large amount of data available for comparison with $[ZnL^1]^{2+}$ but it is clear that the Zn–N bond lengths, particularly the equatorial Zn–N (secondary) bonds (Table 2), are much shorter than those reported for other hexaaminezinc(II) complexes. For comparison, the average Zn–N bond lengths in $[Zn(en)_3]^{2+}$ and $[Zn(H_2L^2)]^{4+}$ were found to be 2.22 and 2.19 Å respectively.[7,15]

Examination of Table 2 shows considerable distortion of the ZnN_6 octahedron, with the N(3)–Zn–N(6) axis being tilted toward the atoms C(2) and C(8). That is, the N–Zn–N angles in the five-membered rings formed by co-ordination of the pendant amines are all close to 80°. There is considerable strain in the angles C(3)–N(2)–C(4) and C(5)–N(4)–C(7), both being close to 120°. It can be seen that this is a direct result of co-ordination of the pendant primary amines which 'pulls' the C(3) and C(7) atoms toward the metal centre and hence opens the angles at the co-ordinated secondary amines. There is less strain in the opposite five-membered chelate ring, which adopts a different conformation with respect to the rest of the molecule (although it is also a δ conformer). The angles formed at the pendant primary amines, C(2)–N(3)–Zn, 96.4(3)°, and C(8)–N(6)–Zn, 95.5(3)°, are both quite small compared with an ideal tetrahedral geometry. To relieve this strain, either the axial Zn–N bond must be shortened or the N(3)–Zn–N(1,2) and N(6)–Zn–N(4,5) angles contracted even more than they already have been. It is well known that bond compression requires more energy than bond angle deformation and that intraligand non-bonded interactions may dominate both of these factors.[16] In this case it is apparent that deformation of the C(2)–N(3)–Zn and C(8)–N(6)–Zn angles results in the smallest increase in strain energy, although it appears that this strain is also shared to some degree by a reduction of the *cis* N–Zn–N angles.



L^2



L^3

The metal centre and the four secondary amine nitrogens are not coplanar. Calculation of the least-squares plane defined by these atoms indicates that one pair of *trans* secondary amine nitrogens [N(1) and N(4)] lies on the opposite side of the least-squares plane to the atoms N(2) and N(5). This is related to the staggered conformations of the ethylenediamine chelates, which distort the ZnN_4 plane. The metal centre lies on the same side of the plane as the N(1) and N(4) pair, as does N(3), which indicates why the Zn–N(3) bond length is shorter than the Zn–N(4) bond. It is also worth noting that the single water molecule in the structure links complex cations *via* hydrogen bonds with the amine hydrogens on N(3) and N(6). The water oxygen, O(3), approaches N(3) somewhat more closely [HN(3) ··· O(3) 2.23 Å] than the *trans* amine hydrogens [HN(6) ··· O(3) 2.68 Å]. This may also be entwined with the discrepancy between the Zn–N(3) and Zn–N(6) bond lengths.

A potentiometric titration of the ligand $(H_6L^1)^{6+}$ identified five of the six successive amine protonation constants: pK_a 2.9, 5.5, 6.3, 9.9 and 11.0. The first deprotonation step was not able to be determined ($pK_a < 2$). The pK_a values of 5.5 and 6.3 are assigned to the deprotonation of the pendant amines and the remaining values to deprotonation of the macrocycle nitrogens. The deprotonation steps of the secondary amines compare well with those determined for L^3 (pK_a 1.5, 10.5 and 11.49).[17] The order of titration was confirmed by the recent isolation and X-ray crystal structure of $L^1 \cdot 2HClO_4 \cdot 2H_2O$, where the sites of protonation were found to be a pair of *trans* secondary-amine nitrogens.[18] An earlier structure[14] of the tetraprotonated ligand $L^1 \cdot 4HClO_4 \cdot 6H_2O$, revealed that the four protonated sites were a pair of *trans* secondary-amine nitrogens and the pair of pendant primary amines. Titration of an acidic solution of zinc(II) and L^1 yielded a stability constant for complex formation log *K* of 15.0 ± 0.1 which is comparable with the value reported for $[ZnL^3]^{2+}$ (log *K* 15.34).[17] A further observation was the stepwise deprotonation and co-ordination of the pendant primary amines following insertion of the metal ion into the macrocyclic cavity. A distribution of the three complexed species $[Zn(H_2L^1)(OH_2)_2]^{4+}$ (both pendants unco-ordinated), $[Zn(HL^1)(OH_2)]^{3+}$ (one pendant co-ordinated) and $[ZnL^1]^{2+}$ as a function of pH is shown in Fig. 2. Intersections on the $[Zn(HL^1)(OH_2)]^{3+}$ curve yield pK_a values of 5.9 and 7.0 for the two primary amine groups, compared with corresponding values of 5.5 and 6.3 from titration of the free ligand. It is apparent that the slight differences in pK_a values determined from the two titrations are the result of a weaker inductive effect of the dipositive metal centre in $[Zn(H_2L^1)(OH_2)_2]^{4+}$ on the protonated pendant amine groups compared with the two additional protons bound to the secondary amines in $(H_4L^1)^{4+}$.

It is clear that sexidentate co-ordination of the macrocycle L^1 to zinc(II) results in particularly short Zn–N bond lengths when compared with other hexaaminezinc(II) complexes that have been structurally characterised. However, it is most important to realise that the Zn–N bond lengths in $[ZnL^1]^{2+}$ are not exceptionally short by comparison with, for example, diacidotetraaminezinc(II) complexes. To illustrate this, the crystal structure of *trans*-$[Zn(H_2L^1)(OSO_2SO_3)_2]$ revealed Zn–N bond lengths of 2.096(1) and 2.082(2) Å,[14] similar bond lengths were reported for the structure of *trans*-$[ZnL^3(NCS)_2]$.[19] The necessity of comparing similar systems (hexaamine complexes) is then seen. A similar observation was made when the structures of $[NiL^1]^{2+}$ and *trans*-$[NiL^1(NCS)_2]$ were compared.[5] The Ni–N bond lengths in the sexidentate nickel(II) complex, although the shortest for a hexaaminenickel(II) ion, were not shorter than those found in *trans*-$[NiL^1(NCS)_2]$. The origins of these apparent anomalies may be found by examining the relative conformations of sexidentate and quadridentate complexes of L^1. When the macrocycle coordinates as a sexidentate, the six-membered chelate rings must form boat conformers, rather than the less strained chair conformers. Quadridentate co-ordination of the ligand allows the six-membered rings to adopt their most sterically favourable orientation, and in all quadridentate complexes of L^1 reported so far, this has indeed been the chair conformer.[14,20–22] The additional steric strain introduced by the boat conformer in $[ZnL^1]^{2+}$ compared with *trans*-$[Zn(H_2L^1)(OSO_2SO_3)_2]$ evidently results in an extension of the Zn–N(secondary) bond lengths. Perhaps related to this, intramolecular non-bonded H ··· H interactions in the sexidentate complex are necessarily greater than in the quadridentate complex. The more severe interactions are expected to occur between the pendant amine hydrogens and the methylene hydrogens in the 'ethylenediamine' residues. These interactions are obviously unimportant in structures such as *trans*-$[Zn(H_2L^1)(OSO_2SO_3)_2]$ and the Zn–N bond lengths may be shorter in the absence of axial amino groups. The axial dithionato ligands in *trans*-$[Zn(H_2L^1)(OSO_2SO_3)_2]$ are more sterically efficient donors than primary amines, and may also pivot about the Zn–O axis so as to minimise steric clashes with the macrocycle hydrogens. The chelated pendant amines clearly do not enjoy the same freedom of movement.

Acknowledgements

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