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Comparative study of the interaction of 'lop-sided' 14- to 17-membered tetraaza macrocycles containing fused dibenzo substituents with nickel(II) †

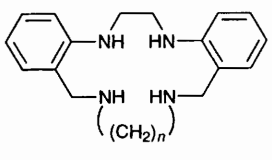
Ian M. Atkinson,[a] Philip J. Baillie,*[,b] Nick Choi,[b] Luigi Fabbrizzi,[c] Leonard F. Lindoy,[a] Mary McPartlin[b] and Peter A. Tasker *[,d]

[a] *Department of Chemistry & Biochemistry, James Cook University of North Queensland, Townsville, Queensland, 4811, Australia*
[b] *School of Applied Chemistry, The University of North London, Holloway, London N7 8DB, UK*
[c] *Istituto di Chimica Generale ed Inorganica, Universita di Pavia, 27100 Pavia, Italy*
[d] *Zeneca Specialties, PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS, UK*

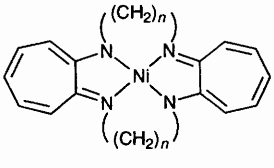
The effect of macrocyclic and chelate-ring size on the complexation behaviour of a series of dibenzo tetraaza macrocycles incorporating 14- to 17-membered inner rings has been investigated. Change in ring size along this 'lop-sided' series has been achieved solely by varying the number of methylene carbons that link adjacent benzyl nitrogen atoms. Several solid complexes of type $NiLX_2 \cdot xH_2O$ (L = macrocyclic ligand; x = 0 or 1; X = Cl, NCS or NO_3) with these rings have been isolated. The results of five X-ray crystallographic analyses, as well as molecular mechanics studies, have allowed comparison of the effect of change of ring size on the structures of the 14- to 17-membered ring complexes with X = NCS. All complexes have similar six-co-ordinate *trans*-isothiocyanato geometries in which the four donors of the macrocycle occupy the equatorial plane. For this series an inverse correlation between in-plane and axial bond lengths around the nickel atoms occurs for the 14- to 16-membered ring complexes; the correlation is less apparent in the case of the 17-membered species. The X-ray and molecular mechanics studies indicate that, as the number of methylene carbons linking adjacent benzylamino nitrogens increases, the corresponding bite angle at the metal increases, with the opposite bite angle decreasing in a (partial) compensatory manner. As a consequence, there is only a minor variation in the planarity of the macrocyclic donor plane along the series. The crystal structure of the 16-membered ring complex of nickel(II) nitrate is also reported, as is that of the 17-membered ring complex of nickel(II) chloride. The former contains an equal mixture of two (*trans*-octahedral) complexes of type $[NiL(NO_3)_2]$ and $[NiL(NO_3)(H_2O)]NO_3$. Cyclic voltammetry indicates that formation of the respective nickel(III) species is facilitated by the smaller-ring ligands; the oxidation of the 17-membered ring complex is non-reversible and probably ligand based.

In a previous paper,[2] a comparative X-ray structural investigation of the high- and low-spin complexes of nickel(II) with two tetraaza dibenzo-substituted macrocycles, incorporating 14-membered inner rings, was reported; the results obtained were also compared with those for the corresponding complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam). It was possible to undertake a detailed assessment of the effect of spin state and the presence of dibenzo substituents on the macrocyclic hole size and ring conformations adopted by individual complexes. From this and other prior work [3,4] it has become increasingly clear that macrocyclic ring size alone is but one factor influencing the 'fit' of a metal ion in a given macrocyclic cavity. Apart from more obvious parameters such as donor-atom radii and hybridisation type,[5] a range of other structural factors, including chelate-ring size, extent of ligand rigidity and the presence or absence of ring substituents, can all influence the geometry of the binding cavity, often in subtle ways.

In the present paper an investigation of the effect of increasing the macrocyclic ring size, within the dibenzo-substituted ligand series given by L^1–L^4,[1,6] on the complexation of nickel(II) is reported. Using this series, the influence on metal complexation of variation of one structural feature, namely the length of the alkyl bridge linking the benzyl nitrogen atoms, was investigated. Increasing the length of this bridge is expected to increase the 'lop-sidedness' of the N_4-donor set. Apart from its intrinsic interest, the information so obtained is of potential use for ligand design, an area that has received considerable attention from us in the past.[2,6,7] In particular, it was of interest to observe the effect of any build-up of ligand strain on the co-ordination geometry of the central metal. In other work it has been demonstrated that increasing the length of both alkyl linkages in the four-co-ordinate nickel(II) complexes of tropocoronands of type L^5–L^8 induces a gradual distortion of the co-ordination geometry from square planar to near tetrahedral.[8]



L^1 $n = 2$
L^2 $n = 3$
L^3 $n = 4$
L^4 $n = 5$



L^5 $n = 3$
L^6 $n = 4$
L^7 $n = 5$
L^8 $n = 6$

Experimental

Physical measurements were performed as described previously.[2,6] The syntheses of L^1–L^4 have also been reported previously.[1,6]

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† Macrocyclic Ligand Ring Size Effects. Part 4.[1]
Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

Metal complex synthesis

[NiL^1(NCS)$_2$]. This complex has been reported previously.[2] Electronic spectrum (acetonitrile); λ_{max}/nm (ε/m^2 mol^{-1}) 381 (sh), 427 (3.0), 510 (3.1), 700 (1.5), 805 (1.7) and 920 (1.9); μ_{eff} = 2.91 μ_B at 21 °C.

[NiL^{2}Cl$_2$]. This complex has been reported previously.[2] Electronic spectrum (dichloromethane): λ_{max}/nm (ε/m^2 mol^{-1}) 375 (9), 520 (0.6), 585 (1.1), 800 (0.5), 855 (0.4) and 1140 (0.4); μ_{eff} = 3.19 μ_B at 21 °C.

[NiL^2(NCS)$_2$]. A solution of nickel(II) tetrafluoroborate (0.074 g, 0.275 mmol) in methanol (2 cm^3) was added to a solution of compound L^2 (0.053 g, 0.171 mmol) in methanol (15 cm^3). After 0.25 h a solution of potassium thiocyanate (0.15 g, 1.54 mmol) in methanol (2 cm^3) was added and the mixture allowed to stand for 48 h. The resultant violet crystals were filtered off, mixed with water (2 cm^3), refiltered then washed with water (3 × 3 cm^3) and diethyl ether (1 cm^3). They were dried at 110 °C for 2 h; yield 0.054 g, 0.111 mmol, 65% (Found: C, 51.7; H, 5.5; N, 17.3. Calc. for $C_{21}H_{26}N_6NiS_2$: C, 52.0; H, 5.4; N, 17.3%). Electronic spectrum (MeCN): λ_{max}/nm (ε/m^2 mol^{-1}) 380 (8.2), 545 (1.6), 760 (1.2) and 920 (1.3).

[NiL^{3}Cl$_2$]. Compound L^3 (0.40 g, 1.23 mmol) in warm methanol (40 cm^3) was added to a solution of nickel(II) chloride (0.50 g, 2.10 mmol) in methanol (25 cm^3). The solution was allowed to stand at room temperature overnight. The turquoise crystals which formed were washed with cold methanol (5 cm^3) then dried at 100 °C for 6 h; yield 0.45 g, 0.92 mmol, 75% (Found: C, 52.6; H, 6.2; N, 12.1. $C_{20}H_{28}Cl_2N_4Ni$ requires C, 52.9; H, 6.2: N, 12.3%). Electronic spectrum (CH$_2$Cl$_2$): λ_{max}/nm (ε/m^2 mol^{-1}) 393 (4.5), 635 (2.3), 695 (sh), 820 (1.5), 910 (1.7) and 1160 (0.9) μ_{eff} = 3.15 μ_B at 21 °C.

[NiL^3(NCS)$_2$]. Addition of a warm solution of L^3 (0.10 g, 0.31 mmol) in methanol (40 cm^3) to a solution of nickel(II) tetrafluoroborate (0.15 g, 0.56 mmol) in methanol (10 cm^3) produced a turquoise solution which faded to green after a few minutes. After the addition of a solution of potassium thiocyanate (0.30 g, 3.01 mmol) in methanol (10 cm^3) the mixture was allowed to stand for 4 d. The mixture of grey-green crystals and white powder that formed was filtered off and the latter removed by dissolution in boiling methanol followed by decantation (6 × 5 cm^3). The grey-green crystals which remained were filtered off and dried in air; yield 0.082 g, 0.16 mmol, 52% (Found: C, 53.1; H, 5.7; N, 16.9. $C_{22}H_{28}N_6NiS_2$ requires C, 52.9; H, 5.7; N, 16.8%). Electronic spectrum (MeCN): λ_{max}/nm (ε/m^2 mol^{-1}) 350 (22.8), 565 (5.8), 800 (4.5) and 910 (1.0). μ_{eff} = 3.25 μ_B at 21 °C.

[NiL^3(NO$_3$)(H$_2$O)]NO$_3$ and [NiL^3(NO$_3$)$_2$]. A mixture of nickel(II) nitrate (0.083 g, 0.28 mmol) and L^3 (0.083 g, 0.26 mmol) in methanol (50 cm^3) and chloroform (20 cm^3) was heated at reflux under nitrogen for 1 h. Evaporation of the deep green solution under reduced pressure followed by addition of acetone (5 cm^3) yielded a dark green powder which was filtered off, washed with a few drops of cold acetone and dried in air; yield 0.070 g (Found: C, 46.55; H, 5.50; N, 16.05. $C_{40}H_{58}N_{12}Ni_2O_{13}$ requires C, 46.55; H, 5.65; N, 16.30%). Electronic spectrum (MeCN): λ_{max}/nm 466, 548, 573, 664, 696, 790 and 813.

[NiL^4(NCS)$_2$]. A solution of L^4 (0.031 g, 0.09 mmol) in dichloromethane (15 cm^3) was added to a solution of nickel(II) tetrafluoroborate (0.035 g, 0.13 mmol) in methanol (15 cm^3), followed by potassium thiocyanate (0.10 g, 1.03 mmol) in methanol (20 cm^3). After 12 d at room temperature a mixture of large blue crystals and white powder had formed. This was filtered off then added to boiling water (2 × 10 cm^3) to dissolve the white powder. The insoluble blue crystals were again filtered off, washed with water (2 × 5 cm^3) then ether (5 cm^3) and dried in air; yield 0.045 g, 0.088 mmol, 92% (Found: C, 53.3; H, 5.8; N, 16.2. $C_{23}H_{30}N_6NiS_2$ requires C, 53.8; H, 5.9; N, 16.4%). Electronic spectrum (acetonitrile): λ_{max}/nm (ε/m^2 mol^{-1}) 370 (sh), 592 (1.4), 816 (0.7) and 975 (2.0).

[NiL^4(NO$_3$)(H$_2$O)]NO$_3$. A mixture of nickel(II) nitrate (0.079 g, 0.27 mmol) and L^4 (0.084 g, 0.25 mmol) in methanol (60 cm^3) and chloroform (20 cm^3) was heated at reflux under nitrogen for 1 h. Evaporation of the deep green solution under reduced pressure followed by addition of acetone (5 cm^3) to the sticky residue yielded a grey-green powder which was filtered off, washed with a few drops of cold acetone and dried in air; yield 0.061 g, 0.11 mmol, 41% (Found: C, 47.10; H, 5.70; N, 16.05. $C_{21}H_{32}N_6NiO_7$ requires C, 46.75; H, 6.00; N, 15.60). Electronic spectrum (MeCN) λ_{max}/nm 463, 543, 570, 694, 797, 817 and 945.

[NiL^{4}Cl$_2$]. A mixture of nickel(II) chloride (0.20 g, 0.80 mmol) and L^4 (0.20 g, 0.60 mmol) in dry methanol (20 cm^3) was heated at reflux for 0.5 h. A blue-green flocculent precipitate formed which was filtered off, washed with cold methanol (3 × 5 cm^3) then dried at 100 °C for 6 h; yield 0.13 g, 0.30 mmol, 50%. Electronic spectrum (CH$_2$Cl$_2$): λ_{max}/nm (ε/m^2 mol^{-1}) 393 (sh), 642 (5.1), 830 (1.5), 902 (3.0) and 1130 (1.7). μ_{eff} = 3.17 μ_B at 21 °C.

Crystallography

Crystal data. [NiL^2(NCS)$_2$], $C_{21}H_{26}N_6NiS_2$, M = 485.3, monoclinic, space group $C2/c$, a = 15.225(3), b = 10.110(3), c = 15.544(3) Å, β = 108.92(2)°, U = 2263.34 Å^3, Z = 4, D_c = 1.424 g cm^{-3}, F(000) = 988, μ(Mo-Kα) = 9.88 cm^{-1}.

[NiL^3(NCS)$_2$], $C_{22}H_{28}N_6NiS_2$, M = 499.3, triclinic, space group $P\bar{1}$, a = 13.632(3), b = 9.378(2), c = 9.350(2) Å, α = 94.73(2), β = 90.55(2), γ = 89.40(2), U = 1191.13 Å^3, Z = 2, D_c = 1.392 g cm^{-3}, F(000) = 524, μ(Mo-Kα) = 9.42 cm^{-1}.

[NiL^4(NCS)$_2$], $C_{23}H_{30}N_6NiS_2$, M = 513.3, monoclinic, space group $P2_1/c$, a = 17.952(3), b = 8.344(2), c = 18.611(3) Å, β = 118.54(2)°, U = 2448.96 Å^3, Z = 4, D_c = 1.286 g cm^{-3}, F(000) = 1080, μ(Mo-Kα) = 9.17.

[NiL^{4}Cl$_2$], $C_{21}H_{30}Cl_2N_4Ni$, M = 468.1, triclinic, space group $P\bar{1}$, a = 11.757(3), b = 11.661(3), c = 8.803(2) Å, α = 111.44(2), β = 79.32(2), γ = 109.88(2)°, U = 1053.85 Å^3, Z = 2, D_c = 1.475 g cm^{-3}, F(000) = 492, μ(Mo-Kα) = 11.20 cm^{-1}.

[NiL^3(NO$_3$)$_2$]·[NiL^3(NO$_3$)(H$_2$O)]NO$_3$·MeOH, $C_{41}H_{60}N_{12}Ni_2O_{14}$, M = 1062.4, triclinic, space group $P\bar{1}$, a = 21.660(4), b = 11.965(3), c = 10.305(3) Å, α = 109.68(2), β = 103.56(2), γ = 82.14(2)°, U = 2439.69 Å^3, Z = 2, D_c = 1.446 g cm^{-3}, F(000) = 1120, μ(Mo-Kα) = 7.90 cm^{-1}.

Data were collected on a Philips PW1100 diffractometer in the range θ 3–25°, using crystals of dimensions and colours listed in Table 1. The method of data collection and calculation of reflection intensities was similar to that described previously.[9] Equivalent reflections were averaged to give the number of unique reflections with $I/\sigma(I) > 3$ listed in Table 1. Absorption corrections were applied to the isothiocyanato complexes.[10]

Structure solution and refinement. For each of the complexes the positions of the nickel atom and sulfur or chlorine, where appropriate, were deduced from a Patterson synthesis.[11] The remaining non-hydrogen atoms were located from subsequent Fourier and Fourier-difference syntheses. One of the carbon atoms [C(29b)] in the complex [NiL^3(NO$_3$)$_2$] was disordered over two sites in the ratio 0.6:0.4.

In the final cycles of full-matrix least-squares refinement anisotropic thermal parameters were assigned to: the metal

Table 1 Details of the crystallographic data collection and refinement

	$[NiL^2(NCS)_2]$	$[NiL^3(NCS)_2]$	$[NiL^4(NCS)_2]$	$[NiL^3(NO_3)_2]\cdot[NiL^3(NO_3)(H_2O)]NO_3\cdot MeOH$	$[NiL^4Cl_2]$
Scan width/°	0.90	0.90	0.70	0.90	0.80
Crystal colour	Violet	Grey-green	Blue	Green	Blue-green
Dimensions/mm	0.10 × 0.25 × 0.45	0.15 × 0.15 × 0.50	0.15 × 0.30 × 0.35	0.25 × 0.28 × 0.18	0.19 × 0.34 × 0.29
Unique reflections with $I/\sigma(I) \geq 3$	703	1951	2100	3093	1622
R	0.0633	0.0842	0.0485	0.0642	0.0591
R'	0.0659	0.0857	0.0488	0.0590	0.0570

atom, the amine N atoms and the atoms of the thiocyanate ligands of $[NiL^2(NCS)_2]$; the metal atom and the thiocyanate ligands of $[NiL^3(NCS)_2]$; all the non-hydrogen atoms of $[NiL^4(NCS)_2]$; the metal atoms and the atoms of the nitrate groups in $[NiL^3(NO_3)_2]\cdot[NiL^3(NO_3)(H_2O)]NO_3$; and the metal and chlorine atoms, the amine N atoms and the C atoms of the five-carbon chain in $[NiL^4Cl_2]$. The respective refinements were based on F values using a weighting scheme of $w = 1/[\sigma^2(F_o)]$ and converged at the R and R' values given in Table 1.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/97.

Molecular mechanics calculations

These were carried out using the MOLMEC suite of programs written at James Cook University.[12] The procedure employed and the molecular mechanics force-field parameters for high-spin nickel(II) have been fully described previously;[13] no changes were made for the present study. Initial coordinates for the molecular mechanics refinements came from the crystal structures described herein {except for $[NiL^1(NCS)_2]$ the crystal structure[14] and molecular mechanics minimisation[13] of which have been reported earlier}.

Electrochemical studies

The redox behaviour of the nickel(II) chloride complexes of L^1–L^4 in dichloromethane was investigated by cyclic voltammetry using similar conditions to those reported in our previous study.[2]

Results and Discussion

Metal complex synthesis and characterisation

High-spin complexes of type $[NiL^1X_2]$ (X = Cl or NCS) and $[NiL^2Cl_2]$ have been characterised previously.[2,14,15] As an extension of these studies, the nickel(II) isothiocyanato complexes of compounds L^2–L^4 were obtained by reaction of the corresponding macrocycle in methanol or methanol–dichloromethane with nickel(II) tetrafluoroborate, followed by addition of potassium thiocyanate. The related dichloronickel(II) derivatives of L^3 and L^4 were obtained by direct reaction of the corresponding macrocycle with nickel(II) chloride in methanol. Reaction of nickel(II) nitrate hexahydrate with L^3 or L^4 in refluxing methanol–dichloromethane yielded $[NiL^3(NO_3)_2]\cdot[NiL^3(NO_3)(H_2O)]NO_3$ and $[NiL^4(NO_3)(H_2O)]NO_3$, respectively. The colours (purple to blue-green) and spectral data (see below) for the respective complexes suggested that each contained high-spin nickel(II) in a distorted-octahedral geometry, a geometry shown previously by X-ray analysis to be present in $[NiL^1(NCS)_2]$[14] and $[NiL^2Cl_2]$.[15] The infrared spectra of the thiocyanate-containing complexes in each case exhibit an intense band near the upper end of the range 2040–2080 cm^{-1} reported[16] for N-bonded thiocyanate: L^1, 2074; L^2, 2073; L^3, 2080; and L^4, 2085 cm^{-1}. In all cases the respective crystal structures (see later) confirm that only N-bonded thiocyanate is present in the solid state.

The visible spectra of the thiocyanato and chloro complexes were recorded in acetonitrile and dichloromethane, respectively. All contain between three and six peaks (see Experimental section) characteristic of octahedral nickel(II) with various degrees of distortion.[17] The dichloro and diisothiocyanato complexes of L^1 and L^2 both show splitting of the lowest-energy band, consistent with the presence of weak tetragonal distortion. For the thiocyanato complexes of the larger rings, L^3 and L^4, no detectable splitting was observed and the ligand field can be considered to be essentially octahedral.

In each case the infrared spectra of blue-green $[NiL^3(NO_3)_2]\cdot[NiL^3(NO_3)(H_2O)]NO_3$ and grey-green $[NiL^4(NO_3)(H_2O)]NO_3$ contained strong broad bands around 3400 cm^{-1} in accordance with the presence of co-ordinated or strongly hydrogen-bound water. The former species exhibits a strong NO stretch at 1385 cm^{-1} which is characteristic of the doubly degenerate stretch, ν_3, of the free nitrate ion.[18] Bands were also observed at 982 (ν_1), 1296 and 1420–1433 cm^{-1} which are in keeping with the additional presence of a monodentate nitrate ligand. The complex of L^4 exhibits similar characteristic bands for ν_3 at 1384 cm^{-1} (due to free nitrate) and at 1420 and 1298 cm^{-1} (due to monodentate nitrate); ν_1 occurs at 991 cm^{-1}. Both compounds yielded ligand-field spectra in acetonitrile (see Experimental section) which are somewhat more complex than those of the thiocyanato and chloro complexes but, nevertheless, are still consistent with the presence of distorted-octahedral co-ordination geometries.

X-Ray diffraction studies

The crystal structures of the nickel(II) thiocyanate complexes of the 15- to 17-membered macrocycles (L^2–L^4) determined in the present study are illustrated in Fig. 1(*a*)–(*c*); the structure of the corresponding 14-membered ring (L^1) nickel thiocyanate complex has been reported previously.[14] In all four complexes the nickel atom is equatorially co-ordinated to all four macrocyclic donor nitrogens with two *trans*-axial, N-bonded thiocyanate ligands. The macrocyclic ligand adopts a 'step' configuration in which the benzo groups are directed to opposite sides of its co-ordination plane. Except for the complex of L^4, the amine hydrogens are disposed alternately above and below the donor plane so that the chiral nitrogen centres correspond to *S,S,S,S* (or *R,R,R,R*) configurations, as also observed previously for $[NiL^2Cl_2]$.[15] In contrast, for $[NiL^4(NCS)_2]$, the sequence is *S,R,R,S* (or *R,S,S,R*), with the anilino nitrogens, N(2a) and N(2b), having the opposite configuration from that of the benzylamino nitrogens, N(1a) and N(1b).

For the complexes of L^1–L^3 the increase in the in-plane Ni–N bond lengths, which occurs with increasing ring size, is accompanied by a decrease in the axial, Ni–X, bond lengths.

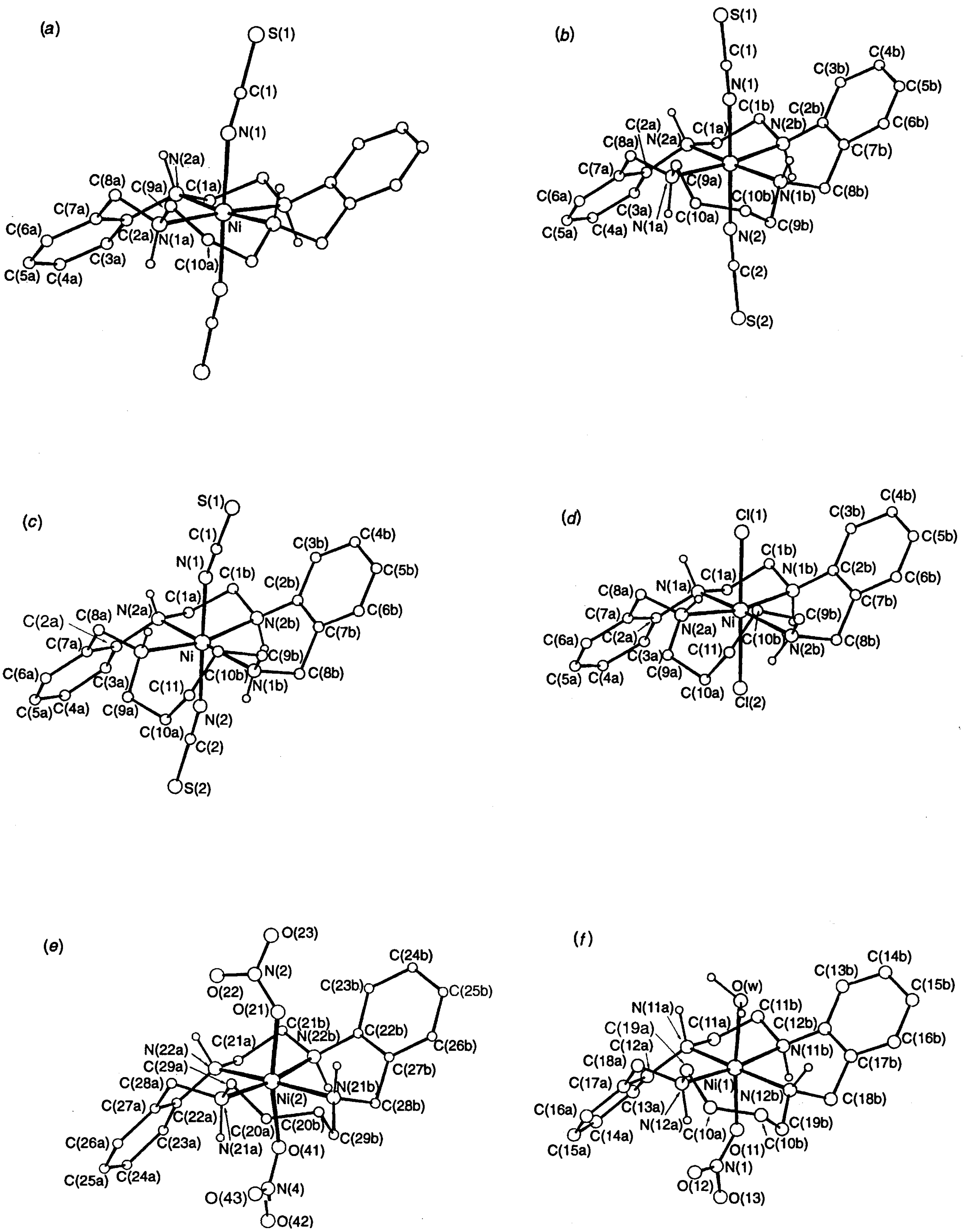

Fig. 1 Crystal structures of the complexes (*a*) [NiL^2(NCS)$_2$], (*b*) [NiL^3(NCS)$_2$], (*c*) [NiL^4(NCS)$_2$], (*d*) [NiL^{4}Cl$_2$], (*e*) [NiL^3(NO$_3$)$_2$] and (*f*) [NiL^3(NO$_3$)(H$_2$O)]NO$_3$·MeOH

This trend, however, is not continued for [NiL^4(NCS)$_2$]. An inverse relationship of this type has been previously demonstrated for complexes of type [NiLX$_2$] {L = 1,4,8,11-tetraazacyclotetradecane ([14]aneN$_4$), 1,4,8,12-tetraazacyclopentadecane ([15]aneN$_4$) and 1,5,9,13-tetraazacyclohexadecane ([16]aneN$_4$); X = Cl or NCS}.[19]

As the length of the methylene chain linking the benzyl nitrogens increases in the nickel thiocyanate complexes of L^1–L^4, the dihedral angles between the donor plane and the benzo rings increase: from 35° for both rings of [NiL^1(NCS)$_2$], to 40° for both rings of [NiL^2(NCS)$_2$], to 46° for both rings of [NiL^3(NCS)$_2$], up to 55 and 50° for the a and b rings of [NiL^4(NCS)$_2$]. In each case the tendency for the nickel to promote octahedral co-ordination (that is, with orthogonal metal–ligand bond directions) results in the N(1a)···N(1b) distance decreasing on co-ordination relative to the distance

Table 2 Bond lengths (Å) in the co-ordination spheres of the complexes

		$[NiL^2(NCS)_2]$		$[NiL^4(NCS)_2]$	
	$[NiL^2(NCS)_2]$	a half	b half	a half	b half
Ni–N(1)	2.075(10)	2.136(10)	2.010(11)	2.147(6)	2.138(5)
Ni–N(2)	2.138(9)	2.168(8)	2.179(8)	2.166(6)	2.200(6)
Ni–N	2.093(10)	2.010(11)	2.054(11)	2.072(6)	2.049(5)

	$[NiL^3(NO_3)_2]$		$[NiL^3(NO_3)(H_2O)]NO_3$		$[NiL^4Cl_2]$	
	a half	b half	a half	b half	a half	b half
Ni–N(1)	2.104(9)	2.114(8)	2.096(9)	2.124(8)	2.140(11)	2.137(6)
Ni–N(2)	2.125(8)	2.124(9)	2.157(7)	2.156(9)	2.156(7)	2.176(10)
Ni–X	2.108(8)	2.135(7)	2.088(7)	2.109(6)	2.261(3)	2.437(3)
X =	O(21)	O(41)	O(11)	O(w)	Cl(1)	Cl(2)

Table 3 Interbond angles (°) in the co-ordination spheres of the complexes

	$[NiL^2(NCS)_2]$	$[NiL^3(NCS)_2]$	$[NiL^4(NCS)_2]$
N(1a)–Ni–N(1b)	91.7(5)	97.9(4)	100.4(2)
N(1a)–Ni–N(2a)	92.5(4)	90.4(3)	89.2(2)
N(1a)–Ni–N(2b)	174.1(4)	171.3(4)	166.5(2)
N(1b)–Ni–N(2a)	174.1(4)	171.6(3)	168.9(2)
N(1b)–Ni–N(2b)	92.5(4)	90.4(3)	90.3(2)
N(2a)–Ni–N(2b)	83.7(5)	81.4(3)	81.1(2)
N(1a)–Ni–N(1)	89.2(4)	88.8(4)	85.2(2)
N(1b)–Ni–N(1)	94.9(4)	91.8(4)	94.7(2)
N(2a)–Ni–N(1)	89.3(4)	89.9(4)	91.5(2)
N(2b)–Ni–N(1)	86.3(4)	88.3(4)	85.7(2)
N(1a)–Ni–N(2)	94.9(4)	92.6(4)	97.0(2)
N(1b)–Ni–N(2)	89.2(4)	90.3(4)	85.8(2)
N(2a)–Ni–N(2)	86.3(4)	87.8(4)	87.6(2)
N(2b)–Ni–N(2)	89.3(4)	90.0(4)	91.9(2)
X(1)–Ni–N(2)	174.1(4)	177.3(4)	177.6(3)
	$[NiL^3(NO_3)_2]$	$[NiL^3(NO_3)(H_2O)]^+$	$[NiL^4Cl_2]$
N(1a)–Ni–N(1b)	96.7(4)	97.7(3)	100.9(3)
N(1a)–Ni–N(2a)	90.9(3)	90.8(3)	89.8(3)
N(1a)–Ni–N(2b)	171.6(3)	172.1(3)	166.5(3)
N(1b)–Ni–N(2a)	171.0(3)	170.8(4)	167.1(4)
N(1b)–Ni–N(2b)	90.9(4)	89.8(3)	89.9(3)
N(2a)–Ni–N(2b)	81.9(3)	81.8(3)	80.7(3)
N(1a)–Ni–X(1)	90.5(3)	97.4(3)	82.7(2)
N(1b)–Ni–X(1)	86.6(3)	89.1(3)	96.3(2)
N(2a)–Ni–X(1)	98.4(3)	86.3(3)	92.2(2)
N(2b)–Ni–X(1)	86.3(3)	84.8(3)	88.2(2)
X(1) =	O(21)	O(11)	Cl(1)
N(1a)–Ni–X(2)	101.5(3)	93.0(3)	97.8(2)
N(1b)–Ni–X(2)	88.9(3)	92.9(3)	83.1(2)
N(2a)–Ni–X(2)	84.6(3)	90.1(3)	88.3(2)
N(2b)–Ni–X(2)	82.3(3)	84.5(3)	91.5(2)
X(1)–Ni–X(2)	167.6(3)	169.0(3)	179.3(1)
X(2) =	O(41)	O(w)	Cl(2)

observed in the crystal structure of the corresponding free macrocycle.[1,6,14] The decreases are: L^1, 2.90 to 2.79; L^3, 3.76 to 3.23; and L^4, 5.38 to 3.29 Å. In other words, the requirement of the nickel to approach a regular co-ordination geometry enforces a reduction in the 'lop-sidedness' of the ligand in each case. Despite this, however, the bite angle N(1a)–Ni–N(1b), of the five- to eight-membered chelate rings increases progressively with ring size from 86.1(1)° in $[NiL^1(NCS)_2]$ to 100.4(2)° in $[NiL^4(NCS)_2]$.

In the above complexes of L^1 and L^2 the nickel atom lies exactly in the respective mean planes of the macrocyclic donor sets, in accordance with the crystallographic two-fold symmetry found for these systems. In the complex of L^3 it is virtually in the plane (deviation 0.005 Å) while, for the complex of L^4, the nickel lies 0.025 Å from the mean plane.

Recrystallisation of $[NiL^4Cl_2]$ from methanol–dichloromethane yielded crystals suitable for X-ray analysis. The structure of the complex is shown in Fig. 1(*d*) and it can be seen that, as in the thiocyanato complexes, all four nitrogen donors of the macrocycle are equatorially co-ordinated to the nickel atom, with chlorides filling the apical sites. In common with the other nickel(II) complexes, $[NiL^4Cl_2]$ has an overall step shape [Fig. 1(*d*)] with the phenylene rings inclined to either side of the macrocycle donor plane (53° for the a ring, 51° for the b ring).

There is a slight tetrahedral distortion of the macrocyclic donor set in $[NiL^4Cl_2]$ (deviations of up to 0.17 Å from its co-ordination plane) which is more pronounced than occurs in $[NiL^2Cl_2]$ (maximum deviation 0.062 Å).[15] Although the donor atoms become less coplanar as the ring size is increased from fifteen to seventeen, the deviation of the nickel atom from the plane is reduced, from 0.017 Å in $[NiL^2Cl_2]$ to 0.008 Å in $[NiL^4Cl_2]$.

The complex $[NiL^4Cl_2]$ exhibits a similar degree of trapezoidal distortion to that of $[NiL^4(NCS)_2]$; the angle

Table 4 Ligand bonding cavity radii (R_a) for the complexes of type [NiX(Y)L]

L	X	Y	R_a[a]/Å	R_a/R_p[b]
L^1	NCS	NCS	1.35 (1.35)	0.97
L^2	Cl	Cl	1.39	1.00
L^2	NCS	NCS	1.39 (1.40)	1.00
L^3	NCS	NCS	1.43 (1.43)	1.03
L^3	NO_3	NO_3	1.39	1.00
L^3	NO_3	H_2O	1.41	1.01
L^4	NCS	NCS	1.43 (1.44)	1.03
L^4	Cl	Cl	1.43	1.03

[a] Hole size (mean of centroid to donor distance) minus the appropriate donor radius (0.72 Å for secondary amine donors).[3,14] The figures in parentheses are calculated from structures after molecular mechanics minimisation. [b] R_p is the Pauling covalent radius for high-spin nickel(II) (1.39 Å).

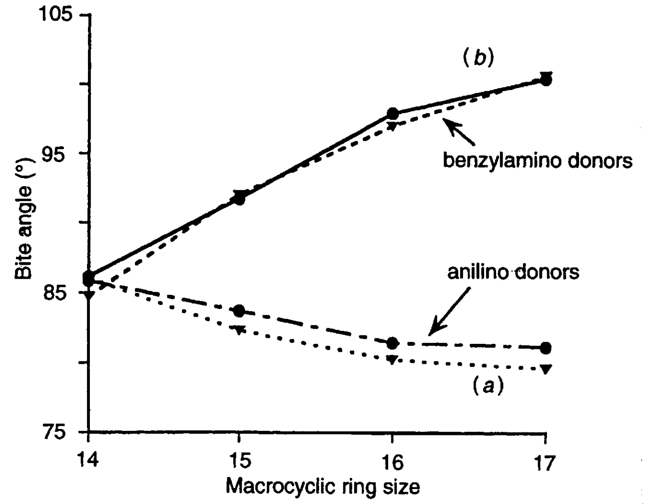

Fig. 2 Comparison of calculated (▼) and observed (●) (X-ray) chelate-ring bite angles for the nickel(II) thiocyanate complexes of L^1–L^4: (a) five-membered ring incorporating two anilino nitrogen donors; (b) six- to eight-membered rings incorporating two benzylamino nitrogen donors

Table 5 The $E_{\frac{1}{2}}$ values for the nickel-(II) to -(III) conversion in dichloromethane relative to the ferrocenium–ferrocene couple[a]

Complex	$E_{\frac{1}{2}}$/V	Complex	$E_{\frac{1}{2}}$/V
$[NiL^1Cl_2]$	0.30	$[NiL^3Cl_2]$	0.58
$[NiL^2Cl_2]$	0.50	$[NiL^4Cl_2]$	b

[a] Supporting electrolyte $[NBu_4][ClO_4]$ (0.1 mol dm^{-3}) in each case. [b] Irreversible oxidation at ≈0.6 V.

subtended at the nickel atom by the anilino donors is 80.7(3)° (Table 3), 20° less than that by the benzylamino donors [100.9(3)°], undoubtedly reflecting the strain caused by the inclusion of the C_5 chain between the latter. In $[NiL^2Cl_2]$, with its C_3 chain between the benzylamino donors, the latter bite angle is only 92.5(4)°.

Slow recrystallisation of the nickel(II) nitrate complex of L^3 from methanol yielded crystals of the methanol solvate which were suitable for X-ray analysis. The crystal contains an equal mixture of two separate complexes $[NiL^3(NO_3)_2]$ and $[NiL^3(NO_3)(H_2O)]NO_3$, with the macrocycle being co-ordinated equatorially and yielding a near-planar donor set in each case. Both complexes contain the nickel atom in a distorted-octahedral environment and the co-ordinated nitrate groups are all monodentate. The metal atom is very close to the best plane in each case [Ni(1) is displaced 0.012 Å towards the co-ordinated water molecule, while Ni(2) is displaced 0.011 Å towards O(21)].

The nickel-to-donor bond lengths and selected angles at the nickel atoms are presented in Tables 2 and 3. The Ni–N bond lengths in both complexes all fall within the range of 2.03–2.16 Å observed previously for co-ordinate bonds from neutral sp^3-hybridised nitrogen atoms in high-spin nickel(II) complexes of macrocyclic ligands.[14,15,19,20]

The Ni–O bond length to the co-ordinated water in the cationic complex is 2.109(6) Å, near the upper end of the range previously observed for nickel(II) complexes containing two or three aqua ligands and monodentate nitrate ligands (range 2.037–2.111; mean of seven bonds 2.070 Å).[21]

The seven-membered chelate ring in the cationic complex adopts a twist-chair or skew conformation with a virtual two-fold rotation axis between Ni(1) and the midpoint of the C(10a)–C(10b) bond. As mentioned, in the neutral complex one carbon atom of this chelate ring is disordered such that two conformational isomers are present in a 60:40 random arrangement throughout the crystal. The major component has C(29b) in the position required for the skew conformation, but the alternative position of this atom gives the chelate ring a chair conformation.

The combinations of chelate-ring conformations and consequent amine hydrogen-atom configurations impart an overall step shape to both complexes. The aromatic a and b rings are inclined to the donor plane at 50 and 48°, respectively, in the cationic complex and at 55 and 48° in the neutral complex.

Macrocyclic hole-size calculations

Using the procedure described previously,[3,14] the X-ray data for the complexes investigated in the present study have been used to estimate the 'apparent bonding cavity' (R_a) for each complex. The results are shown in Table 4 along with the corresponding R_a/R_p ratios [R_p is the Pauling covalent radius for high-spin nickel(II)]. This ratio gives an indication of the 'fit' of the metal ion for the macrocyclic cavity in the respective complexes. Overall, the data suggest that the 15- and 16-membered rings best match the radius of the nickel(II) ion; such a result is in keeping with previous findings.[3]

Molecular mechanics calculations

The results of the molecular mechanics minimisations show that the previously reported force field for high-spin nickel(II)[13] is quite successful in reproducing the crystal structures of the nickel thiocyanate complexes of L^1–L^4. In particular, a significant result from this study is the observation that the force field is successful in modelling the large increase in N–Ni–N bite angle (Fig. 2) associated with increasing chelate-ring size along the series. Furthermore, the ligand bonding cavity radii (Table 4) calculated from the minimised structures match closely those observed in the crystal structures.

Electrochemical studies

As an extension of an earlier study,[2] the redox behaviour of the nickel(II) chloride complexes of L^1–L^4 in dichloromethane was investigated by cyclic voltammetry. A summary of the results obtained is given in Table 5. Reversible oxidation to nickel(III) was observed for the complexes of L^1–L^3 while that of L^4 showed irreversible oxidation (at about 600 mV). The relatively facile oxidation of the nickel(II) complex of L^1 perhaps reflects the observation based on the crystal structure of this complex (see Table 4) that this ring is slightly smaller than is ideal for nickel(II). It is apparent from the data in Table 5 that, as the ring size is increased, oxidation to the smaller nickel(III) is progressively disfavoured, the trivalent ion fitting best in the smallest cavity.

Conclusion

Electronic spectra, crystal structure determinations and molecular mechanics calculations on the current series of complexes all indicate that the tendency for nickel(II) to favour octahedral co-ordination (that is with orthogonal metal–ligand bond directions) promotes changes in ligand conformation which reduce the 'lop-sidedness' of the N_4-donor set. The planarity of the N_4-donor set is maintained in the nickel complexes, but the distortion to a trapezoidal arrangement of the donors increases steadily as the length of the methylene bridge between the benzyl nitrogen atoms is increased.

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