Synthesis and Characterization of Dinickel(II) and Dipalladium(II) Complexes of the Macrocyclic Binucleating Ligand 3,13-Dimethyl-3,13-dinitro-1,5,11,15-tetra-azacycloeicosane-8,18-dithiol (L^5). Crystal Structure of the Complex $[Ni_2(L^5-2H)][NO_2]_2\cdot3.5H_2O$†

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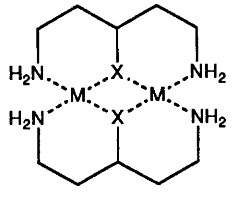
Condensation of the bis(1,5-diaminopentane-3-thiolato)dinickel(II) ion or the dipalladium(II) analogue with formaldehyde and nitroethane in basic methanol yields the dianion of the macromonocyclic ligand 3,13-dimethyl-3,13-dinitro-1,5,11,15-tetra-azacycloeicosane-8,18-dithiol (L^5) as the dimetal(II) complex. Spectroscopic properties of the diamagnetic complexes are reported, together with the crystal-structure analysis of the dinickel(II) complex. The nitrite salt of the latter crystallizes in the space group *Pbnm*, $a = 7.762(3)$, $b = 14.921(3)$, $c = 25.459(3)$ Å, $Z = 4$, $R = 0.057$ for 1 739 'observed' reflections. The complex is a *syn* isomer, the first time this geometry has been observed from this type of condensation reaction, with the two N_2NiS_2 planes folded slightly towards each other about the mirror plane through S ··· S in a 'butterfly' arrangement (interplanar angle 162.8°). Oxygen atoms of the pendant nitro groups form weak axial interactions, the six-membered rings at the 'ends' having skew-boat conformations.

Metal-directed condensation reactions of organic substrates to form acyclic and cyclic molecules of higher molecular weight and complexity have been developed, employing a number of strategies.[1-5] Syntheses of new polyamines, or mixed-heteroatom compounds including amines, commonly employ simpler molecules with terminal primary amines as building blocks.[1-6] Apart from building ligands which will complex a single metal ion, it has been possible to construct ligands which can accommodate two metal ions simultaneously.[4,7-10] Typical of these types are ligands formed *via* metal-ion template condensation of dialdehydes (or diketones) with two *cis*-disposed primary amines,[8,9] which produce ligands capable of complexing a range of metal ions in close proximity in two sites. Commonly, these reactions yield polyimine ligands initially, rather than saturated systems.

We have been pursuing in detail reactions of *cis*-disposed primary amines directed by labile metal ions such as Cu^{2+} and Ni^{2+} with formaldehyde and carbon acids (such as nitroethane). The chemistry has been largely pursued with bis(diamine) and tetra-amine complexes as precursors,[6,11] but evidently can be applied with aminoalkylpyridines,[12] aminoalcohols,[13] and amino acids,[14] provided two primary amines occupying *cis* sites are available. Given the success of this chemistry around a single metal-ion centre, the possibility of extending the chemistry to the synthesis of binucleating ligands has been receiving attention.

Simple potentially tridentate ligands such as L^1 and L^2 form binuclear complexes with Ni^{2+}, Pd^{2+}, and Cu^{2+}, the complexes $[M_2(L^1-H)_2]^{2+}$ and $[M_2(L^2-H)_2]^{2+}$ forming geometries of the type shown below ($X = S^-$ or O^-).[15,16] The potential for cyclization *via* reaction of the *cis*-disposed primary amines with formaldehyde and nitroalkanes has recently been demonstrated by condensation of $[Cu_2(L^1-H)_2]^{2+}$ to form $[Cu_2(L^3-2H)]^{2+}$.[17] This reaction proceeds in reasonable yield, despite the modest stability of the precursor, and yields the *anti* isomer. This chemistry parallels the chemistry involving stereospecific synthesis of *anti*-L^4 from $[Cu(en)_2]^{2+}$ (en = ethane-1,2-diamine); all such reactions characterized to date have yielded exclusively the *anti* geometry.



Subsequently, we have pursued reactions with the aminothiol L^2, employing the $[Ni_2(L^2-H)_2]^{2+}$ and $[Pd_2(L^2-H)_2]^{2+}$ complexes as precursors. Although condensation reactions of the type described have been reported around Cu^{2+} and Ni^{2+}, the use of Pd^{2+} as a templating metal in this chemistry has not been established previously.[6,11-14,18] Chemistry directed towards synthesis of the new binucleating eicosane macrocycle L^5 is described herein.‡

Experimental

CAUTION: Syntheses described below involve the use of perchlorate ion and isolation of complex cations as perchlorate salts. Such procedures may present an explosion hazard, and due care should be taken, although we encountered no problems.

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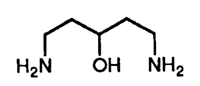
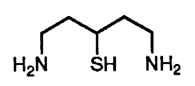
† (3,13-Dimethyl-3,13-dinitro-1κ*N*,2κ*N'*-1,5,11,15-tetra-aza-1κ$^2N^{1,5}$, 2κ$^2N^{11,15}$-cycloeicosane-8,18-dithiolato-1:2κ^2*S*; 1:2κ^2*S'*)dinickel(II) dinitrite—water (2/7).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

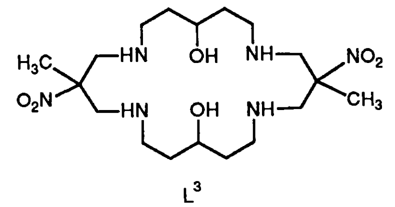
‡ Ligand nomenclature: L^1 = 1,5-diaminopentan-3-ol; L^2 = 1,5-diaminopentane-3-thiol; L^3 = 3,13-dimethyl-3,13-dinitro-1,5,11,15-tetra-azacycloeicosane-8,18-diol; L^4 = 6,13-dimethyl-6,13-dinitro-1,4,8,11-tetra-azacyclotetradecane; L^5 = 3,13-dimethyl-3,13-dinitro-1,5,11,15-tetra-azacycloeicosane-8,18-dithiol; L^6 = 3,13-diamino-3,13-dimethyl-1,5,11,15-tetra-azacycloeicosane-8,18-dithiol.



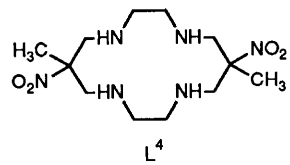
L^1



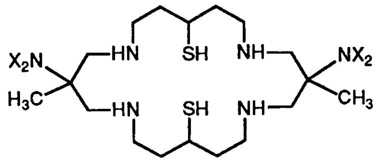
L^2



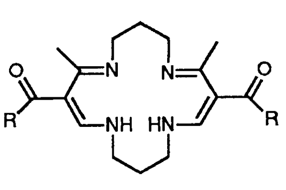
L^3



L^4



L^5 (X = O) L^6 (X = H)



L^7

Syntheses.—*Bis*(1,5-*diaminopentane*-3-*thiolato*)*dinickel*(II) *perchlorate*, $[Ni_2(L^2 - H)_2][ClO_4]_2$. This compound was prepared essentially as described,[16] from the reaction of $Ni(ClO_4)_2 \cdot 6H_2O$ and $L^2 \cdot 2HCl$ in warm water in the presence of triethylamine. The red-brown product was isolated in fair yield (43%). Electronic spectrum (water): $\lambda_{max.}$ 486 (ε 643), 364 (2 310), 299 (5 920), and 232 nm (18 960 $dm^3\ mol^{-1}\ cm^{-1}$). ^{13}C N.m.r. (D_2O): δ 35.9, 39.0, and 40.6 p.p.m.

Bis(1,5-*diaminopentane*-3-*thiolato*)*dipalladium*(II) *perchlorate*, $[Pd_2(L^2 - H)_2][ClO_4]_2$. This was prepared as described from the reaction of $K_2[PdCl_4]$ and $L^2 \cdot 2HCl$ in water in the presence of triethylamine,[16] except that $NaClO_4$ was added in excess to facilitate precipitation of the yellow product in excellent yield (97%). Electronic spectrum (water): $\lambda_{max.}$ 328 (ε 2 040), 285(sh), 254 (14 150), and 209 nm (15 830 $dm^3\ mol^{-1}\ cm^{-1}$). ^{13}C N.m.r. (D_2O): δ 39.65, 41.7, and 42.1 p.p.m.

(3,13-*Dimethyl*-3,13-*dinitro*-1,5,11,15-*tetra-azacycloeicosane*-8,18-*dithiolato*)*dinickel*(II) *perchlorate*, $[Ni_2(L^5 - 2H)][ClO_4]_2$. A mixture of $[Ni_2(L^2 - H)_2][ClO_4]_2$ (1.5 g, 2.6 mmol), nitroethane (0.8 cm^3, 11 mmol), and aqueous formaldehyde (4 cm^3, 52 mmol) in AR methanol (80 cm^3) was treated with triethylamine (0.5 cm^3) and heated at reflux for 4 h, then left to stand overnight. The yellow-green product which precipitated was collected, and the red solution refluxed for a further 7 h, yielding further product on cooling. This latter procedure was repeated three more times, yielding successively less product. Overall yield (0.85 g, 42%) was fair. Refluxing the reaction mixture for extended periods did not significantly improve the isolated yield (Found: C, 27.4; H, 4.6; N, 10.4. $C_{18}H_{36}Cl_2N_6Ni_2O_{12}S_2$ requires C, 27.7; H, 4.65; N, 10.75%). Electronic spectrum (water): $\lambda_{max.}$ 478 (ε 130), 360 (530), and 313 (1 780 $dm^3\ mol^{-1}\ cm^{-1}$). N.m.r.: ^{13}C, δ 23.8, 34.3, 36.6, 36.7, 42.6, 50.3, 51.9, 53.0, 54.9, and 89.4 p.p.m.; ^1H, δ 1.57 (s, 3 H), and 2.0—4.0 (m, 14 H).

(3,13-*Dimethyl*-3,13-*dinitro*-1,5,11,15-*tetra-azacycloeicosane*-8,18-*dithiolato*)*dipalladium*(II) *perchlorate dihydrate*, $[Pd_2(L^5 - 2H)][ClO_4]_2 \cdot 2H_2O$. To a suspension of $[Pd_2(L^2 - H)_2][ClO_4]_2$ (0.86 g, 1.25 mmol) in methanol (150 cm^3) was added nitroethane (1.0 cm^3, 14 mmol), aqueous formaldehyde (10 cm^3, 130 mmol), and triethylamine (1 cm^3). The mixture was heated and stirred for 6 h, then left to stir at room temperature for 2 d. After this time some undissolved starting material was still visible, so heating was resumed for 9 h. The resultant yellow solution was concentrated to a small volume, and product precipitated upon addition of an equivalent amount of water (0.12 g recovered). Chromatography of the filtrate on SP Sephadex C-25 cation-exchange resin, using 0.2 mol dm^{-3} $NaClO_4$ as eluant, produced a major yellow band which yielded further product on concentration and standing (overall yield 0.45 g, 40%). Variation of the reaction time did not significantly alter the yield (Found: C, 23.7; H, 4.1; N, 9.1. $C_{18}H_{40}Cl_2N_6O_{14}Pd_2S_2$ requires C, 23.7; H, 4.4; N, 9.2%). Electronic spectrum (water): $\lambda_{max.}$ 333 (ε 4 530), 264 (22 970), and 214 nm (29 010 $dm^3\ mol^{-1}\ cm^{-1}$). ^1H N.m.r. spectrum [D_2O–$(CD_3)_2SO$]: δ 1.67 (s, 3 H) and 2.0—4.0 (m, 14 H).

Physical Methods.—Electronic spectra were recorded using Hitachi 220A or 150-20 spectrophotometers, i.r. spectra of compounds dispersed in KBr discs using a Nicolet MX-1 Fourier-transform spectrometer, and n.m.r. spectra using a JEOL FX-90Q spectrometer, with shifts cited *versus* tetramethylsilane. Voltammetry experiments were performed as previously described,[11] with aqueous solutions.

Structure Determination.—*Crystal data.* $C_{18}H_{36}N_8Ni_2O_8S_2 \cdot 3.5H_2O$, $M = 739.1$, orthorhombic, space group *Pbnm* (variant of *Pnma*, D_{2h}^{16}, No. 62), $a = 7.762(3)$, $b = 14.921(3)$, $c = 25.459(3)$ Å, $U = 2\,949(1)$ Å^3, D_c ($Z = 4$) = 1.66 g cm^{-3}, $F(000) = 1\,548$, $\mu_{Mo} = 14.1\ cm^{-1}$. Specimen: $0.45 \times 0.25 \times 0.47$ mm. $A^*_{min.,max.} = 1.38, 1.51$. $R = 0.057$, $R' = 0.068$, $n_v = 211$.

A unique data set was measured for $[Ni_2(L^5 - 2H)][NO_2]_2 \cdot 3.5H_2O$ (crystallized by slow concentration of a $NaNO_2$ solution of the perchlorate salt) at *ca.* 295 K on a Syntex $P2_1$ diffractometer within the limits $2\theta_{max.} = 50°$, with monochromatic Mo-K_α radiation, $\lambda = 0.710\,69$ Å, graphite monochromator, and operating in the ω—2θ scan mode. Of the 2 618 independent reflections obtained, 1 739 with $I > 3\sigma(I)$ were considered observed and used in the full-matrix least-squares refinement after Gaussian absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were constrained at estimated values. Residuals at convergence R, R' on $|F|$ are quoted, with statistical weights derived from $\sigma^2(I) = \sigma^2(I)_{diff.} + 0.0001\sigma^4(I)_{diff.}$. Neutral-atom complex scattering factors were used;[19] computation used the XTAL system implemented by S. R. Hall on a Perkin-Elmer 3240 computer.[20] Pertinent results and atom numbering are given in the two parts of the Figure and in Tables 1 and 2.

Abnormal features. The nitrite anion was modelled in terms of the oxygen atoms disordered equally over two sets of sites with high thermal motion, and its geometries are therefore un-

Table 1. Non-hydrogen atom co-ordinates for $[Ni_2(L^5 - 2H)][NO_2]_2 \cdot 3.5H_2O$

	Part A			Part B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Cation						
Ni	0.035 3(1)	0.129 08(7)	0.187 50(4)			
C(1)	0.095(1)	0.153 7(7)	0.063 1(4)			
N(1)	0.262(1)	0.195 8(7)	0.083 9(4)			
O(1)	0.262(1)	0.237 2(6)	0.123 4(4)	0.394(1)	0.175 8(9)	0.063 4(5)
C(11)	0.098(2)	0.158 4(8)	0.003 0(4)			
C(2)	−0.057(1)	0.204 0(7)	0.085 2(4)	0.099(1)	0.053 8(6)	0.081 8(4)
N(3)	−0.127 9(10)	0.171 5(5)	0.134 7(3)	0.132 7(10)	0.041 2(5)	0.137 8(3)
C(4)	−0.264(1)	0.234 2(7)	0.150 2(4)	0.099(1)	−0.054 1(6)	0.149 9(4)
C(5)	−0.354(1)	0.204 2(7)	0.200 4(5)	0.187(2)	−0.084 9(7)	0.200 3(4)
C(6)	−0.272(2)	0.241 7(10)	$\frac{1}{4}$	0.133(2)	−0.039 8(8)	$\frac{1}{4}$
S(7)	−0.034 8(5)	−0.221 6(2)	$\frac{1}{4}$	0.199 3(4)	0.077 8(2)	$\frac{1}{4}$
Anion (oxygen-atom populations 0.5)						
N	−0.407(4)	−0.021(2)	0.113(2)			
O(1)	−0.306(5)	0.003(3)	0.118(3)	−0.466(5)	0.018(3)	0.138(1)
O(2)	−0.492(5)	−0.049(4)	0.101(3)	−0.346(7)	−0.011(4)	0.078(1)
Solvent [O(B) population 0.75]						
O	0.151(1)	0.398 9(7)	0.014 2(5)	−0.310(2)	−0.033(1)	$\frac{1}{4}$

Table 2. Core geometry (distances in Å, angles in °) (parts A and B)

Ni–N(3)	1.954(8), 1.973(8)
Ni–S(7)	2.176(2), 2.177(2)
Ni···Ni	3.182(2)
S(7A)···S(7B)	2.813(5)
N(3)–Ni–N(3′)	91.3(3)
S(7)–Ni–S(7′)	80.5(1)
N(3)–Ni–S(7)	97.8(2), 90.6(2)
N(3)–Ni–S(7′)	175.3(2), 170.6(2)
Ni–S(7)–Ni	94.0(1), 93.9(1)
Ni–S(7)–C(6)	110.4(3), 100.0(3)

reliable. Difference-map artefacts were modelled as water molecules, populations 1 and 0.75 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Reaction of the bis(1,5-diaminopentane-3-thiolato)-dinickel(II) or -dipalladium(II) complexes with formaldehyde and nitroethane in basic methanol produced complexes of the substituted macrocycle L^5 in good yield. The diamagnetic complexes were readily characterized spectroscopically. The nitro groups on the introduced six-membered rings are signalled by strong i.r. resonances at 1 550 and 1 350 cm^{-1}, and an irreversible, multielectron reduction in the aqueous voltammetry near −1.05 V (*versus* Ag–AgCl) for both the dinickel(II) and dipalladium(II) compounds. The introduced methyl groups are clearly defined by singlets in the ^1H n.m.r. at δ 1.57 (Ni) and 1.67 (Pd). Clearly, the condensation proceeds in a like manner to that established for mononuclear systems with *cis*-disposed primary amines reacting,[6,11–14,18] and like that observed for the dicopper(II) complex of the analogue L^1.[17] Preservation of the binuclear nature of the precursor is also inferred from the two-electron (by wave-height comparisons with known compounds) irreversible oxidation observed at +0.67 V (*versus* Ag–AgCl) for the nickel complex, and assigned to Ni^{II}–Ni^{III} oxidations of both metal centres. Confirmation of macrocyclization came from an *X*-ray crystal structure study of the dinickel(II) complex.

The $[Ni_2(L^5 - 2H)]^{2+}$ complex cation contains two nickel(II) ions, each bound by two secondary nitrogen and two (bridging) thiolate donors in essentially planar *cis*-NiN_2S_2 geometries, the donors being part of a 20-membered macrocyclic ring. Non-hydrogen atomic co-ordinates appear in Table 1, with the core geometry of the cation given in Table 2. Views of the molecular cation from two directions approximately at right angles appear in the Figure. There are several important observations to be made regarding the structural study. First, it identifies the complex as a *syn* isomer, rather than the *anti* isomer found with the analogue $[Cu_2(L^3 - 2H)]^{2+}$, and found exclusively with syntheses of L^4. This represents the first example of this geometry for this type of condensation. Secondly, and perhaps related to the first observation, is the fact that the two N_2NiS_2 units are not coplanar, but are hinged at the bridging thiolates located on a crystallographic mirror plane, bending down away from the side of the ring where the nitro groups reside (Figure). The interplane angle is reduced from 180°, as found for $[Cu_2(L^3 - 2H)]^{2+}$, to 162.8° in this case, and the carbon atoms of the original six-membered rings lie below the metal-donor planes. The six-membered rings introduced with nitro substituents during macrocyclization adopt skew-boat conformations, with one oxygen of each nitro interacting axially with a nickel ion, distances being quite long at 2.89(1) Å. This type of interaction has been observed earlier with (3-methyl-3-nitro-1,5,9,13-tetra-azacyclohexadecane)copper(II) (2.703 Å) and (10-methyl-10-nitro-1,4,8.12-tetra-azacyclopentadecane)copper(II) (2.443 Å) ions.[11] The Ni–N [1.954(8) and 1.973(8) Å] and Ni–S [2.176(2) and 2.177(2) Å] distances are a little shorter than in a range of mononuclear nickel(II) structures, perhaps a consequence of the relatively small macrocycle accommodating two metal ions. The Ni···Ni separation is 3.182(2) Å, with the cross-ring S(7A)···S(7B) separation 2.813(5) Å, the Ni–S–Ni angle opened to 94.0(1)°, and the S–Ni–S angle contracted to 80.5(1)°. Strain in the framework is indicated by non-ideal tetrahedral angles.

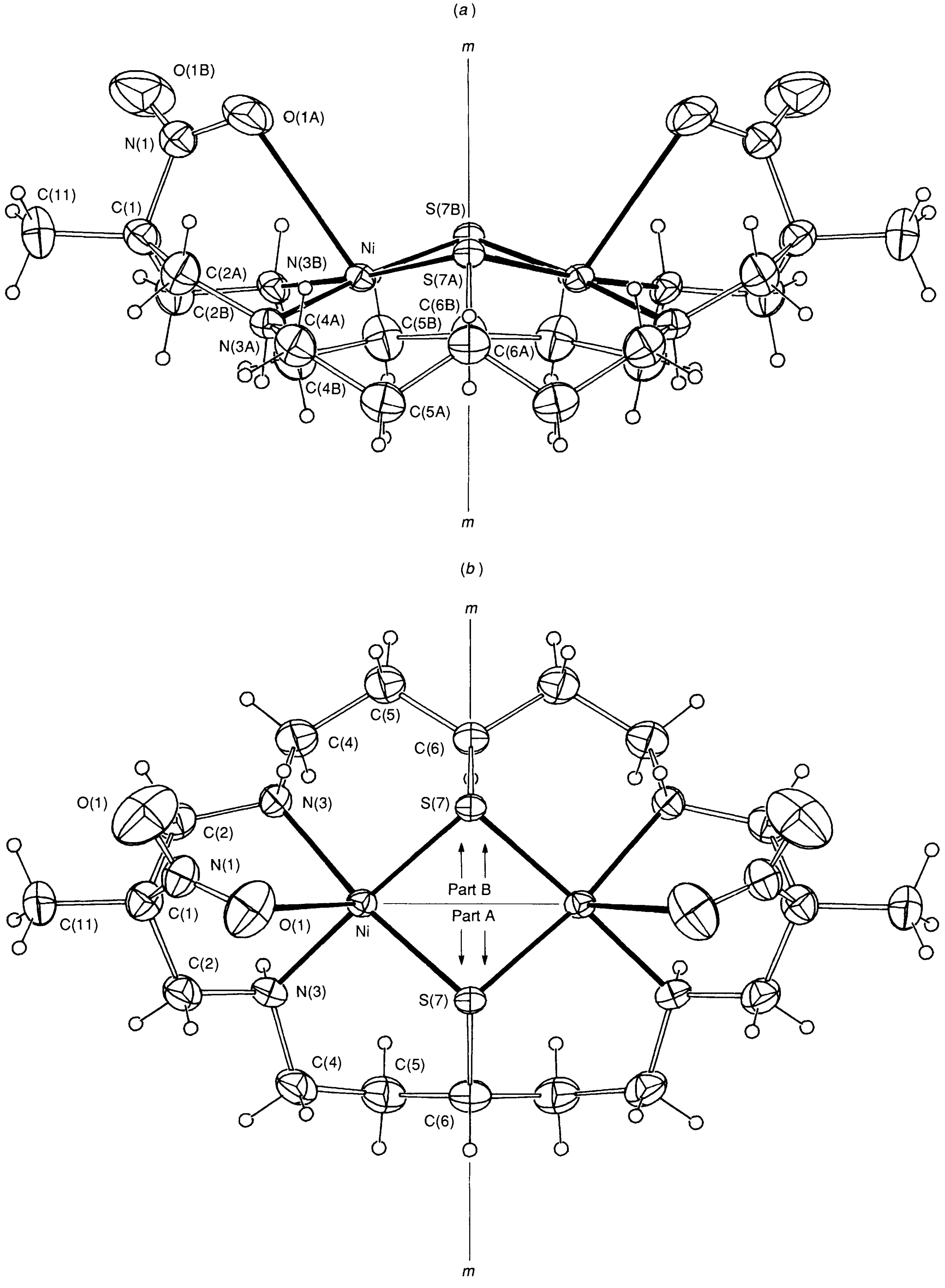


Figure. Views of the molecular cation $[Ni_2(L^5 - 2H)]^{2+}$, (*a*) approximately side-on to the metal-donor planes, and (*b*) from above the metal-donor planes. The folding about the S $\cdots$ S axis is clear in the former view, and the dissymmetry in the half-molecule obvious in the latter view

Although there is a mirror plane bisecting the molecular cation in one direction, there is no such plane in the other direction (Figure), the two halves of each ring having different conformations, so that all ten carbons in one half of the molecule are in different environments. Surprisingly, this observation carries through to solution, since ^{13}C (^{1}H-decoupled) n.m.r. spectroscopy showed ten non-equivalent resonances, ranging from the CH_3 at 23.8 p.p.m. to the nitro-substituted tertiary C at 89.4 p.p.m., suggesting that the molecule retains a conformational rigidity in solution. Unfortunately, the low solubility of the dipalladium(II) complex prevented us recording a reasonable ^{13}C n.m.r. spectrum, for comparison; indeed, we have been unable to obtain single crystals of this compound, and hence the *syn* geometry in that case can only be inferred from the complex ^{1}H n.m.r. spectrum and by extrapolation from the dinickel(II) case.

The 'butterfly' folding in the structure involving the two donor planes is somewhat reminiscent of the folding in the nickel(II) complexes of derivatives of L^7,[21] where the ligand folds up at each end.[22] The nickel(II) complex of L^7 serves as a starting point for building 'straps' between the extremities, creating a cavity above the metal ion.[22–24] This has been achieved, for example, by reaction of the complex of L^7 with a linear diamine.[24] The ability of the nitro groups in L^4, for example, to be reduced to primary amines[6] suggests that similar chemistry could be available in this case. Preliminary study of the Zn/H^+ reduction of $[Ni_2(L^5-2H)]^{2+}$ in aqueous solution apparently yielded the complex of the diamino-substituted macrocycle L^6. Loss of the NO_2 group is clear from i.r. spectroscopy and voltammetry, whereas preservation of the macrocycle is indicated by stability of the complex in strong acid for long periods, and from n.m.r. spectroscopy. Since the primary amines will reside on the same side of the donor planes, the prospect of linking the two by reaction with dialdehydes or diacids (the latter in the presence of a carbodi-imide promoter) to generate a cavity above the metal ions exists, and is being addressed. The two nitro-group nitrogens in $[Ni_2(L^5-2H)]^{2+}$ are separated by 6.45 Å, somewhat similar to the separation of the aldehyde residues in derivatives of $[Ni_2(L^7-2H)]$ (*ca.* 7 Å).[22–24] Should introduction of a strap prove successful, the prospect of trapping small molecules in the vicinity of two metal ions will exist. While this chemistry remains unproven, the ability to generate a saturated, binucleating macrocyclic ligand by metal-directed condensation in a facile manner has been demonstrated here.

Acknowledgements

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