Nickel Thioether Chemistry: Syntheses of Nickel(II) Complexes of Tetra- and Penta-thia Macrocyclic Ligands. The Single-crystal Structures of $[Ni([16]aneS_4)(OH_2)_2][BF_4]_2$ and $[Ni([15]aneS_5)][PF_6]_2$ ($[16]aneS_4$ =1,5,9,13-Tetrathiacyclohexadecane, $[15]aneS_5$ = 1,4,7,10,13-Pentathiacyclopentadecane)†

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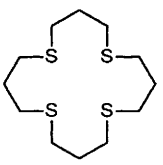
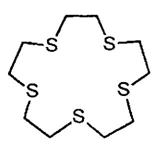
Treatment of $[Ni(OH_2)_6][BF_4]_2$ with 1 molar equivalent of $[12]aneS_4$ ($[12]aneS_4$ = 1,4,7,10-tetrathiacyclododecane) or $[16]aneS_4$ ($[16]aneS_4$ = 1,5,9,13-tetrathiacyclohexadecane) in $MeNO_2$ in the presence of acetic anhydride for 30 min affords blue solutions from which the complexes $[Ni([12]aneS_4)(OH_2)_2]^{2+}$ and $[Ni([16]aneS_4)(OH_2)_2]^{2+}$ can be isolated. The complex $[Ni([16]aneS_4)(OH_2)_2][BF_4]_2$ crystallises in the triclinic space group $P\bar{1}$, with the octahedral nickel atom lying on a crystallographic centre of symmetry, the aqua ligands mutually *trans*, Ni–S 2.4290(10), 2.4231(10), Ni–O 2.083(3) Å, and the macrocycle co-ordinated in the equatorial plane. Treatment of $[Ni(OH_2)_6][BF_4]_2$ or $[Ni(OH_2)_6][PF_6]_2$ with $[15]aneS_5$ in $MeNO_2$ in the presence of acetic anhydride affords purple solutions of the complex $[Ni([15]aneS_5)]^{2+}$. A single-crystal structure determination on $[Ni([15]aneS_5)][PF_6]_2$, which crystallises in the monoclinic space group $P2_1$, shows the cation to adopt a square-pyramidal geometry, $Ni–S_{apical}$ 2.413(5), $Ni–S_{basal}$ 2.146(7), 2.169(6), 2.177(6), 2.198(6) Å. The complex cation $[Ni([15]aneS_5)]^{2+}$ forms six-co-ordinate adducts with MeCN, pyridine and chloride.

The co-ordination chemistry of nickel with sulfur-containing ligands has recently been the subject of intense interest. Nickel(III) centres in hydrogenase and CO oxidoreductase enzymes are known to be co-ordinated in sulfur-rich environments,[1] and there has been considerable interest in the use of thiolate or thioether ligands to produce model compounds for these biological systems.[2] As part of our continuing studies on the co-ordination chemistry of polythia macrocyclic ligands,[3] we have undertaken an investigation of the complexation of Ni^{II} by the tetrathia crowns $[12]aneS_4$, $[14]aneS_4$ and $[16]aneS_4$, and the pentathia macrocycle $[15]aneS_5$.‡

The co-ordination chemistry of Ni^{II} with tetrathia macrocyclic ligands was first investigated by Rosen and Busch,[4] who reported the formation of the square-planar and octahedral complexes $[Ni([14]aneS_4)]^{2+}$ and $[Ni([14]aneS_4)X_2]$ (X = Cl, Br or I). A subsequent X-ray structural analysis confirmed that $[Ni([14]aneS_4)][BF_4]_2$ adopts a square-planar stereochemistry.[5] The reaction of $[Ni(OH_2)_6][BF_4]_2$ with $[12]aneS_4$ and $[13]aneS_4$ was reported to lead to the dimeric bi-octahedral species $[Ni_2([12]aneS_4)_3]^{4+}$ and $[Ni_2([13]aneS_4)_3]^{4+}$, although these species were not fully characterised.[6] The syntheses and single-crystal X-ray structures of the octahedral nickel(II) complexes $[Ni([9]aneS_3)_2]^{2+}$, $[Ni([12]aneS_3)_2]^{2+}$, $[Ni([18]aneS_6)]^{2+}$ and $[Ni([24]aneS_6)]^{2+}$ have been reported.[7,8] These complexes all show homoleptic NiS_6 co-ordination. Recently, we have investigated the synthesis and structures of the chloro-bridged dimeric species $[Ni_2L_2(\mu-Cl)_2]^{2+}$ (L = $[12]aneS_4$, $[14]aneS_4$ or $[16]aneS_4$) in which the macrocyclic ligands are bound in a *cis* fashion about the octahedral nickel centres.[9] With the tridentate macrocycle $[9]aneS_3$, the triply chloro bridged species $[Ni_2([9]aneS_3)_2(\mu-Cl)_3]^+$ can be isolated.[10] We were, therefore, interested in studying the co-ordination of these tetrathia ligands to Ni^{II} in the absence of co-ordinating anions such as halide.



$[16]aneS_4$



$[15]aneS_5$

Results and Discussion

Treatment of $[Ni(OH_2)_6][BF_4]_2$ with 1 molar equivalent of $[12]aneS_4$ or $[16]aneS_4$ at 293 K in $MeNO_2$ in the presence of a small amount of acetic anhydride (to remove excess water from the reaction mixture) afforded blue solutions. Filtration, reduction of solvent and addition of excess Et_2O gave pale blue solid products in 30–50% yield, which could be recrystallised from $MeNO_2$–Et_2O. These blue solids rapidly became intense purple on drying *in vacuo*. Fast atom bombardment (FAB) mass spectrometry and elemental analysis supported the formulation

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

‡ Ligand abbreviations used in text: $[12]aneS_4$ = 1,4,7,10-tetrathiacyclododecane; $[14]aneS_4$ = 1,4,8,11-tetrathiacyclotetradecane; $[16]aneS_4$ = 1,5,9,13-tetrathiacyclohexadecane; $[15]aneS_5$ = 1,4,7,10,13-pentathiacyclopentadecane; $[13]aneS_4$ = 1,4,7,11-tetrathiacyclotridecane; $[9]aneS_3$ = 1,4,7-trithiacyclononane; $[12]aneS_3$ = 1,5,9-trithiacyclododecane; $[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane; $[24]aneS_6$ = 1,5,9,13,17,21-hexathiacyclotetracosane; $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane and $[16]aneN_4$ = 1,5,9,13-tetraazacyclohexadecane.

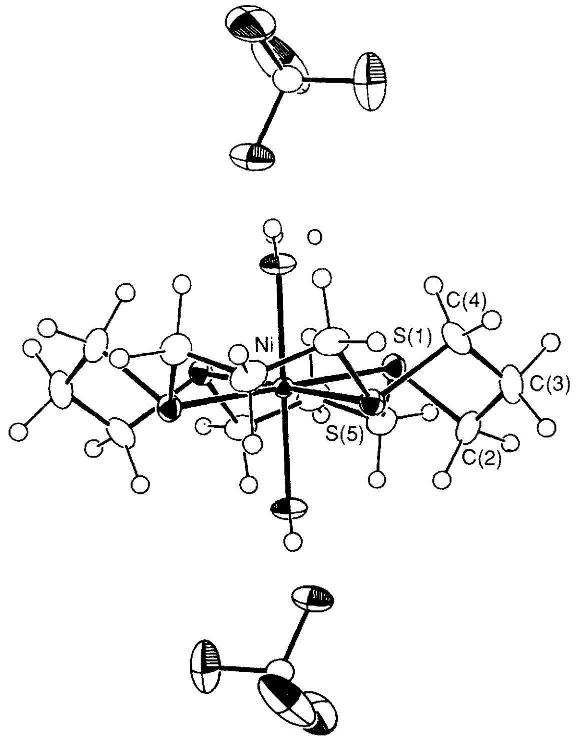

Fig. 1 Single-crystal X-ray structure of $[Ni([16]aneS_4)(OH_2)_2][BF_4]_2$ with numbering scheme adopted

of the final purple compounds as $[\{[NiL(OH_2)](BF_4)_2\}_n]$ (L = $[12]aneS_4$ or $[16]aneS_4$): it is unclear whether this corresponds to the formation of mononuclear five-co-ordinate species as observed for $[Cu([12]aneS_4)(OH_2)]^{2+}$ [11] or whether these compounds exist as dimeric octahedral species containing bridging aqua or hydroxo ligands, analogous to the complexes $[Ni_2L_2(\mu\text{-}Cl)_2]^{2+}$ (L = $[12]aneS_4$, $[14]aneS_4$ or $[16]aneS_4$).[9] In our hands, the dimeric complex $[Ni_2([12]aneS_4)_3]^{4+}$ obtained under similar reaction conditions by Rosen and Busch[6] was not observed. However, reaction of $[Ni(OH_2)_6][BF_4]_2$ with $[14]aneS_4$ does afford the known red species $[Ni([14]aneS_4)]^{2+}$ in agreement with Rosen and Busch.[4]

The purple mono-aqua species $[NiL(OH_2)][BF_4]_2$ (L = $[12]aneS_4$ or $[16]aneS_4$) regained their blue colouration on dissolution in $MeNO_2$ or MeCN. The electronic spectra of these solutions are typical of octahedrally co-ordinated nickel(II) centres[12] {for L = $[12]aneS_4$ in $MeNO_2$ solution, λ_{max} 1035 nm (ε_{max} 74 dm^3 mol^{-1} cm^{-1}), 951 (97) and 577 (33.3); in MeCN solution λ_{max} 1020 nm (sh), 943 (ε_{max} 13.8 dm^3 mol^{-1} cm^{-1}), 578 (8.1) and 306 (485); for L = $[16]aneS_4$ in $MeNO_2$ solution λ_{max} 1005 nm (sh), 928 (ε_{max} 35.3 dm^3 mol^{-1} cm^{-1}) and 580 (29.2); in MeCN solution λ_{max} 972 nm (ε_{max} 7.6 dm^3 mol^{-1} cm^{-1}), 580 (11.5) and 324 (440)}. Hence, these blue species are assigned as the six-co-ordinate complexes $[Ni([12]aneS_4)(solv)_2]^{2+}$ and $[Ni([16]aneS_4)(solv)_2]^{2+}$ (solv = H_2O, $MeNO_2$ or MeCN). The red square-planar complex $[Ni([14]aneS_4)]^{2+}$ forms a pale blue solution in MeCN, which shows d–d bands at λ_{max} 925 nm (ε_{max} 7.8 dm^3 mol^{-1} cm^{-1}) and 562 nm (10.3). This implies the formation of an octahedral species in this solvent, *via* the co-ordination of two axial solvent molecules to give $[Ni([14]aneS_4)(NCMe)_2]^{2+}$. Attempts to isolate this adduct were unsuccessful, however, giving a pale blue solid that rapidly turned red *in vacuo* and in air. It therefore appears that the aqua ligands in the complexes $[NiL(OH_2)_2]^{2+}$ are displaced by co-ordinating solvents such as MeCN to form species of the type $[NiL(NCMe)_2]^{2+}$.

In order unambiguously to identify the initial blue products from the above reactions, a single-crystal X-ray structural determination of the initial product of the complexation of $[Ni(H_2O)_6]^{2+}$ by $[16]aneS_4$ was carried out. Blue crystals of diffraction quality were obtained by the diffusion of diethyl ether vapour into a solution of the complex in $MeNO_2$. A single-crystal X-ray structure determination shows the complex to be the octahedral species *trans*-$[Ni([16]aneS_4)(OH_2)_2]^{2+}$. A view of the complex is shown in Fig. 1. The nickel atom lies on a crystallographic inversion centre, and is co-ordinated by a square plane of macrocyclic S donors, Ni–S(1) 2.4290(10), Ni–S(5) 2.4231(10) Å, with two axial aqua ligands, Ni–O 2.083(3) Å. The Ni–S and Ni–OH_2 bond lengths are within the ranges typically observed for octahedral nickel(II) complexes[7–9,13] confirming that this complex is a genuine octahedral nickel(II) species, rather than a square-planar nickel(II) complex with two very weakly interacting axial ligands. The nickel centre in *trans*-$[Ni([16]aneS_4)(OH_2)_2]^{2+}$ lies at the exact centre of the macrocyclic cavity due to the crystallographic symmetry, and the *cis* angles about the nickel centre are close to 90°, S(1)–Ni–S(5) 89.85(3), S(1)–Ni–O 92.85(8), S(5)–Ni–O 87.04(8)°. The $[16]aneS_4$ macrocycle exhibits a *CTCT* conformation analogous to that observed in the tetragonal complexes $[M([16]aneS_4)][ClO_4]_2$ (M = Cu,[11] Cd or Hg[14]). The BF_4^- counter ions are hydrogen-bonded to the co-ordinated aqua ligands, H(12)···F(1) 1.74(3) Å, O···H(12)···F(1) 173.9(3), H(12)···F(1)···B 116.30(10)°. Because of the smaller hole size of $[12]aneS_4$ compared to $[16]aneS_4$ it seems reasonable to assume that $[Ni([12]aneS_4)(OH_2)]^{2+}$ is a *cis* isomer, while both *cis* and *trans* isomers are possible for $[Ni([14]aneS_4)(solv)_2]^{2+}$. In the red cation $[Ni([14]aneS_4)]^{2+}$ the nickel(II) centre is essentially square planar with relatively shorter Ni–S bond lengths [2.175(1) and 2.177(1) Å[5]] compared with *trans*-$[Ni([16]aneS_4)(OH_2)_2]^{2+}$. This reflects the different co-ordination number in the two cations, six compared to four, but also the better match of metal ion radius and macrocyclic hole size between nickel(II) and $[14]aneS_4$ compared to that between Ni^{II} and the relatively large $[16]aneS_4$; $[Ni([14]aneS_4)X_2]$ shows the optimum metal ion/hole size match compared to the other tetrathia macrocycles (for $[Ni([14]aneS_4)]^{2+}$ the macrocyclic hole size R_A = 1.21 Å, *cf.* the ionic radius of low-spin Ni^{II} of 1.20 Å [15]). The equilibria between four-, five- and six-co-ordinate complexes of $[Ni([14]aneS_4)]^{2+}$ has been monitored in the presence of iodide;[4] similar equilibria appear to be relevant to the chemistry of the $[Ni([12]aneS_4)]^{2+}$ and $[Ni([16]aneS_4)]^{2+}$ fragments.

The formation of these aqua-containing complexes is surprising, given the known instability of nickel(II) complexes of tetrathia macrocycles towards hydrolysis by water and other O-donor solvents.[4,6] All the complexes described herein readily hydrolyse in water to give hydrated Ni^{II} and free ligand. This reflects the relatively weak ligand-field exerted on the nickel(II) ion by tetrathia ligands. Examination of the electronic spectra of these complexes in MeCN yields values for the ligand-field splitting parameter 10*Dq* of 10 600 cm^{-1} for $[Ni([12]aneS_4)(NCMe)_2]^{2+}$ and 10 290 cm^{-1} for $[Ni([16]aneS_4)(NCMe)_2]^{2+}$. This compares with the previously derived value of 10*Dq* of 10 700 cm^{-1} for $[Ni([14]aneS_4)X_2]$ (X = Cl or Br).[4] For the related tetraaza complexes $[NiL'X_2]$ (X = Cl or Br) the measured values of 10*Dq* are 14 800 cm^{-1} (L′ = $[14]aneN_4$) and 11 100 cm^{-1} (L′ = $[16]aneN_4$)[16] reflecting the higher ligand field imposed on Ni^{II} by N_4 compared with S_4-macrocycles, and the particularly good metal ion radius/macrocyclic hole size fit for Ni^{II} with 14-membered ring systems. The lower ligand-field splitting observed for the softer tetrathia ligands reflects the relatively weak σ donation of thioether S donors compared to N donors, and the increased organisational energy required to achieve *endo*-dentate co-ordination of thioether crowns.[17] Electronic spectral data for a range of thioether and aza macrocyclic nickel(II) complexes are listed in Table 1.

Treatment of $[Ni(OH_2)_6][BF_4]_2$ or $[Ni(OH_2)_6][PF_6]_2$ with 1 molar equivalent of $[15]aneS_5$ in $MeNO_2$ in the presence of acetic anhydride yielded intense purple solutions, from which a

Table 1 Electronic spectral data for octahedral nickel(II) complexes of polythia and polyaza macrocycles

	$10Dq$/cm^{-1}	Ref.
$[Ni([12]aneS_4)(NCMe)_2]^{2+}$	10 600	This work
$[Ni([14]aneS_4)(NCMe)_2]^{2+}$	10 810	This work
$[Ni([16]aneS_4)(NCMe)_2]^{2+}$	10 290	This work
$[Ni([14]aneS_4)X_2]$[a]	10 700	4
$[Ni([14]aneN_4)X_2]$[a]	14 800	16
$[Ni([16]aneN_4)X_2]$[a]	11 100	16
$[Ni([9]aneS_3)_2]^{2+}$	12 755	7, 18
$[Ni([12]aneS_3)_2]^{2+}$	11 240	8, 27
$[Ni([9]aneNS_2)_2]^{2+}$[b]	11 930	19
$[Ni([9]aneN_2S)_2]^{2+}$[c]	11 770	20, 21
$[Ni([9]aneN_3)_2]^{2+}$[d]	12 500	20–22
$[Ni([9]aneN_2O)_2]^{2+}$[e]	11 600	20, 21
$[Ni([15]aneS_5)(NCMe)]^{2+}$	11 090	This work
$[Ni([18]aneS_6)]^{2+}$	12 290	8, 23
$[Ni(Me_2[18]aneN_2S_4)]^{2+}$[f]	11 075	24
$[Ni([18]aneN_2S_4)]^{2+}$[g]	12 135	24
$[Ni([18]aneN_6)]^{2+}$[h]	11 200	8, 25, 26
$[Ni([24]aneS_6)]^{2+}$	11 050	23

[a] X = Cl or Br. [b] $[9]aneNS_2$ = 1,4-dithia-7-azacyclononane. [c] $[9]aneN_2S$ = 1-thia-4,7-diazacyclononane. [d] $[9]aneN_3$ = 1,4,7-triazacyclononane. [e] $[9]aneN_2O$ = 1-oxa-4,7-diazacyclononane. [f] $Me_2[18]aneN_2S_4$ = 7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclooctadecane. [g] $[18]aneN_2S_4$ = 1,4,10,13-tetrathia-7,16-diazacyclooctadecane. [h] $[18]aneN_6$ = 1,4,7,10,13,16-hexaazacyclooctadecane.

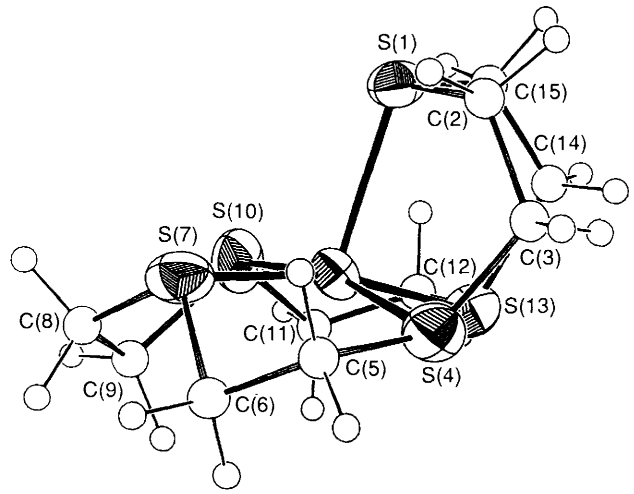

Fig. 2 Single-crystal X-ray structure of $[Ni([15]aneS_5)]^{2+}$ with numbering scheme adopted

purple solid could be isolated on addition of Et_2O. On the basis of elemental analysis and mass spectral data, the product was formulated as $[Ni([15]aneS_5)]X_2$ (X = BF_4 or PF_6). The electronic spectrum of purple $[Ni([15]aneS_5)][BF_4]_2$ in $MeNO_2$ solution was consistent with a high-spin, five-co-ordinate nickel(II) complex,[12] λ_{max} 1060 nm (sh), 823 (ε_{max} 81 dm^3 mol^{-1} cm^{-1}), 538 (118) and 475 (sh). However, dissolution of the complex in MeCN afforded a pale blue solution, which exhibited a different electronic spectrum consistent with the formation of a six-co-ordinate nickel(II) centre[12] in solution, λ_{max} 902 nm (ε_{max} 11.4 dm^3 mol^{-1} cm^{-1}), 572 (9.7), 312 (325), 283 (270) and 254 (1600). This implies the formation of an octahedral adduct $[Ni([15]aneS_5)(NCMe)_x]^{2+}$($x$ = 1 or 2) in MeCN. A similar blue solution is obtained when a solution of $[Ni([15]aneS_5)]^{2+}$ in $MeNO_2$ is treated with an excess of pyridine. Diffusion of Et_2O into solutions of $[Ni([15]aneS_5)(solv)]^{2+}$ (solv = MeCN or C_5H_5N) yielded pale blue crystals, which rapidly became purple on exposure to air presumably due to loss of the co-ordinated ligand (solv). However, reaction of $NiCl_2{\cdot}6H_2O$ with 1 equivalent of $TlPF_6$ followed by addition of $[15]aneS_5$ afforded the stable blue complex identified as the octahedral adduct $[NiCl([15]aneS_5)]PF_6$. No reaction was observed between purple $MeNO_2$ solutions of $[Ni([15]aneS_5)]^{2+}$ and O_2, CO or CO_2.

A single-crystal X-ray structure determination was undertaken to ascertain the stereochemistry of the $[Ni([15]aneS_5)]^{2+}$ complex cation. Crystals of $[Ni([15]aneS_5)][PF_6]_2$ were obtained by diffusion of Et_2O vapour into a solution of the complex in $MeNO_2$. The single-crystal X-ray structure of the complex shows (Fig. 2) a five-co-ordinate cation, with a distorted square-pyramidal geometry, Ni–S(1) 2.413(5), Ni–S(4) 2.177(6), Ni–S(7) 2.146(7), Ni–S(10) 2.169(6), Ni–S(13) 2.198(6) Å. The S–Ni–S angles within the basal S_4 plane are typical for a square-pyramidal structure: however, the apical S donor, S(1) is bent back by 6° from vertical, due to the constraints of the macrocyclic ligand, S(4)–Ni–S(10) 166.45(23), S(7)–Ni–S(13) 165.82(25)°; S(1)–Ni–S(4) 92.02(21), S(1)–Ni–S(7) 103.00(22), S(1)–Ni–S(10) 101.51(20), S(1)–Ni–S(13) 91.18(20)°. The nickel atom lies 0.26 Å above the least-squares S_4 basal plane of the cation. Significantly, there is no interaction with a potential sixth ligand. The $[Ni([15]aneS_5)]^{2+}$ complex exhibits similar structural features to the related five-co-ordinate nickel(II) compounds $[Ni([9]aneS_3)(L{-}L)]^{2+}$ (L–L = chelating diphosphine ligand),[27] as well as to the analogous pentathia complexes $[Cu([15]aneS_5)]^{2+}$ [28] and $[Pt([15]aneS_5)]^{2+}$ [3,29]

The cyclic voltammograms of the complexes $[NiL(NCMe)_2][BF_4]_2$ in MeCN–0.1 mol dm^{-3} NBu_4PF_6 at 293 K exhibit single irreversible reductions at E_{pc} −1.60 V *vs.* ferrocene–ferrocenium for $[12]aneS_4$, −1.18 V for $[14]aneS_4$ and −1.51 V for $[16]aneS_4$ at a scan rate of 400 mV s^{-1}, together with associated desorption spikes at $E_{pa} \approx 0$ V due to deposition of nickel metal onto the platinum working electrode. Cyclic voltammetry of $[Ni([15]aneS_5)(NCMe)][PF_6]_2$ under the same conditions showed an irreversible reduction at E_{pc} −1.26 V *vs.* ferrocene–ferrocenium (scan rate 400 mV s^{-1}), together with an associated desorption spike at $E_{pa} \approx 0$ V. Coulometric determinations of all of the above processes in MeCN–0.1 mol dm^{-3} NBu_4PF_6 at 293 K consistently gave values of between one and two electrons (typically $n \approx 1.6$), and resulted in deposition of nickel onto the platinum basket working electrode. In all cases, no current flow was observed on attempting to re-oxidise the reduced solutions, demonstrating the irreversibility of the reduction processes. No change in the electrochemical behaviour of any of the complexes described above was observed in the presence of CO or CO_2 reagent gases.

The instability of the reduced species $[NiL]^{+/0}$ (L = $[12]aneS_4$, $[14]aneS_4$ or $[16]aneS_4$) and $[Ni([15]aneS_5)]^{+/0}$ is disappointing given the known preference of Ni^I for four- or five-co-ordination and soft ligand donors;[30] however, this reflects again the poor binding ability of these polythia macrocycles compared to their polyaza analogues and to the related polythia ligands $[9]aneS_3$ and $[18]aneS_6$.[3] Significantly, the tri- and hexa-dentate crowns $[9]aneS_3$ and $[18]aneS_6$ readily form highly stable homoleptic complexes with Ni^{II}, the formation of $[Ni([9]aneS_3)_2]^{2+}$ and $[Ni([18]aneS_6)]^{2+}$ being very difficult to prevent with these ligands in the presence of Ni^{II}.

Experimental

Infrared spectra were run as KBr discs on a Perkin Elmer 598 spectrometer over the range 200–4000 cm^{-1}. Electronic spectra were recorded for solutions in 1 cm quartz cells using a Perkin Elmer Lambda 9 spectrophotometer. Fast-atom bombardment mass spectra were obtained on a Kratos MS 50TC spectrometer using a 3-nitrobenzyl alcohol matrix. Microanalyses were carried out by the University of Edinburgh Chemistry Department microanalytical service. Electrochemical measurements were obtained using a Bruker E310 Universal Modular Polarograph; for all readings a three electrode system in aceto-

Table 2 Bond lengths (Å) and angles and torsion angles (°) for [Ni-([16]aneS$_4$)(OH$_2$)$_2$][BF$_4$]$_2$

Ni–S(1)	2.4290(10)	C(3)–C(4)	1.524(6)
Ni–S(5)	2.4231(10)	C(4)–S(5)	1.828(5)
Ni–O	2.083(3)	S(5)–C(6)	1.817(4)
S(1)–C(2)	1.820(5)	C(6)–C(7)	1.526(6)
S(1′)–C(8)	1.821(4)	C(7)–C(8)	1.514(6)
C(2)–C(3)	1.532(6)		
S(1)–Ni–S(5)	89.85(3)	C(3)–C(4)–S(5)	111.3(3)
S(1)–Ni–O	92.85(8)	Ni–S(5)–C(4)	101.59(15)
S(5)–Ni–O	87.04(8)	Ni–S(5)–C(6)	110.32(14)
Ni–S(1)–C(2)	102.80(14)	C(4)–S(5)–C(6)	98.85(20)
Ni–S(1′)–C(8)	108.53(14)	S(5)–C(6)–C(7)	112.8(3)
C(8)–S(1′)–C(2′)	99.59(19)	C(6)–C(7)–C(8)	115.0(3)
S(1)–C(2)–C(3)	110.5(3)	S(1′)–C(8)–C(7)	112.1(3)
C(2)–C(3)–C(4)	115.1(4)		

C(2′)–S(1′)–C(8)–C(7)	173.0(3)
C(8)–S(1′)–C(2′)–C(3′)	166.2(3)
S(1)–C(2)–C(3)–C(4)	−46.2(5)
C(2)–C(3)–C(4)–S(5)	−45.4(5)
C(3)–C(4)–S(5)–C(6)	−163.4(3)
C(4)–S(5)–C(6)–C(7)	−167.4(3)
S(5)–C(6)–C(7)–C(8)	78.9(4)
C(6)–C(7)–C(8)–S(1′)	−81.9(4)

Table 3 Atomic coordinates for [Ni([16]aneS$_4$)(OH$_2$)$_2$][BF$_4$]$_2$

Atom	*x*	*y*	*z*
Ni	0.0	0.0	0.0
S(1)	0.046 25(12)	0.049 66(12)	0.226 20(10)
C(2)	0.281 7(5)	0.043 5(6)	0.196 7(5)
C(3)	0.289 6(6)	0.225 6(6)	0.085 8(5)
C(4)	0.178 6(6)	0.309 0(5)	−0.060 3(5)
S(5)	0.215 34(12)	0.14347(12)	−0.149 16(10)
C(6)	0.127 0(5)	0.295 9(5)	−0.339 9(4)
C(7)	0.098 0(5)	0.200 6(5)	−0.435 6(4)
C(8)	−0.075 0(5)	0.155 9(5)	−0.394 0(4)
O	0.221 3(3)	−0.242 5(3)	0.049 2(3)
B	0.523 7(6)	−0.631 0(6)	0.316 1(5)
F(1)	0.334 2(3)	−0.533 0(3)	0.307 88(25)
F(2)	0.613 8(4)	−0.546 8(4)	0.353 4(3)
F(3)	0.584 0(4)	−0.630 9(6)	0.168 9(4)
F(4)	0.551 4(4)	−0.794 6(4)	0.423 3(5)

nitrile containing 0.1 mol dm^{-3} NBu$_4$PF$_6$ as supporting electrolyte was employed. Cyclic voltammetric measurements were performed with a double platinum electrode and a Ag–AgCl reference electrode. Potentials are quoted *versus* ferrocene–ferrocenium.

Syntheses.—[Ni([12]aneS$_4$)(OH$_2$)][BF$_4$]$_2$. Reaction of [Ni(OH$_2$)$_6$][BF$_4$]$_2$ (0.053 g, 1.5 × 10^{-4} mol) with [12]aneS$_4$ (0.036 g, 1.5 × 10^{-4} mol) in MeNO$_2$ (4 cm^3) and acetic anhydride (1 drop) at 293 K yielded a deep blue solution, which was filtered, reduced to 1 cm^3, and the blue solid product crystallised by addition of Et$_2$O. The complex was recrystallised from MeNO$_2$–Et$_2$O (yield 0.042 g, 56%) (Found: C, 19.8; H, 3.8. Calc. for [C$_8$H$_{18}$NiOS$_4$][BF$_4$]$_2$: C, 19.6; H, 3.7%). FAB mass spectrum: *m/z* 404 {[^{58}Ni([12]aneS$_4$)(OH$_3$)(^{11}BF$_4$)]$^+$}, 385 {[^{58}Ni([12]aneS$_4$)(^{11}BF$_4$)]$^+$}, 317 {[^{58}Ni([12]aneS$_4$)(OH$_3$)]$^+$} and 298 {[^{58}Ni([12]aneS$_4$)]$^+$} with correct isotopic distributions. Electronic spectra: (in MeNO$_2$) λ_{max} 1035 nm (ε_{max} 74 dm^3 mol^{-1} cm^{-1}), 951 (97) and 577 (33.3); (in MeCN) λ_{max} 1020 nm (sh), 943 (ε_{max} 13.8 dm^3 mol^{-1} cm^{-1}), 578 (8.1) and 306 (485). IR spectrum: 2980w, 2960w, 2920w, 1430s, 1410s, 1380w, 1305m, 1285w, 1255m, 1190w, 1060vs, 950w, 930w, 910m, 890m, 855s, 840m, 820w, 770m, 740w, 705w, 690m, 675m, 655w, 615m, 525s, 430m, 415w and 330w cm^{-1}.

[Ni([16]aneS$_4$)(OH$_2$)$_2$][BF$_4$]$_2$. Method as above, using [16]aneS$_4$ (0.044 g, 1.5 × 10^{-4} mol). The product was a pale blue microcrystalline solid, which rapidly became purple when dried *in vacuo* (yield 0.027 g, 32%) (Found: C, 26.7; H, 4.7. Calc. for [C$_{12}$H$_{26}$NiOS$_4$][BF$_4$]$_2$: C, 26.4; H, 4.8%). FAB mass spectrum: *m/z* 459 {[^{58}Ni([16]aneS$_4$)(OH$_2$)(^{11}BF$_4$)]$^+$}, 373 {[^{58}Ni([16]aneS$_4$)(OH$_3$)]$^+$} and 354 {[^{58}Ni([16]aneS$_4$)]$^+$} with correct isotopic distribution. Electronic spectra: (in MeNO$_2$) λ_{max} 1005 nm (sh), 928 (ε_{max} 35.3 dm^3 mol^{-1} cm^{-1}) and 580 (29.2); (in MeCN) λ_{max} 972 nm (ε_{max} 7.6 dm^3 mol^{-1} cm^{-1}), 580 (11.5) and 324 (440). IR spectrum: 2940w, 2900m, 2840w, 1440s, 1420s, 1300m, 1290s, 1250m, 1060vs, 990w, 950w, 925m, 875m, 860s, 845m, 795w, 770s, 755w, 745s, 720w, 695w, 645w, 525s and 455m cm^{-1}.

[Ni([15]aneS$_5$)][BF$_4$]$_2$. The salt [Ni(OH$_2$)$_6$][BF$_4$]$_2$ (0.045 g, 1.7 × 10^{-4} mol) was dissolved in MeNO$_2$ (4 cm^3) with acetic anhydride (1 drop) at 293 K. Addition of [15]aneS$_5$ (0.040 g, 1.7 × 10^{-4} mol) immediately afforded a purple solution, which was filtered and reduced in volume, to 1 cm^3. Addition of excess Et$_2$O gave a purple solid product, which was recrystallised from MeNO$_2$–Et$_2$O (yield 0.052 g, 73%) (Found: C, 22.4; H, 3.8. Calc. for [C$_{10}$H$_{20}$NiS$_5$][BF$_4$]$_2$: C, 22.6; H, 3.8%). FAB mass spectrum: *m/z* 444 {[^{58}Ni([15]aneS$_5$ − H)(^{11}BF$_4$)]$^+$} and 358 {[^{58}Ni([15]aneS$_5$)]$^+$} with correct isotopic distribution. Electronic spectra: (in MeNO$_2$) λ_{max} 1060 nm (sh), 823 (ε_{max} 81 dm^3 mol^{-1} cm^{-1}), 538 (118) and 475(sh); (in MeCN) λ_{max} 902 nm (ε_{max} 11.4 dm^3 mol^{-1} cm^{-1}), 572 (9.7), 312 (325), 283, (270) and 254 (1600). IR spectrum: 2990m, 2940m, 2840w, 1430s, 1285m, 1260w, 1060vs, 945w, 930w, 900w, 860m, 825w, 810w, 680w, 620w, 525s and 410w cm^{-1}.

[Ni([15]aneS$_5$)][PF$_6$]$_2$. A solution of [Ni(OH$_2$)$_6$][PF$_6$]$_2$ was generated by stirring NiCl$_2$·6H$_2$O (0.032 g, 1.33 × 10^{-4} mol) with an excess of TlPF$_6$ in MeNO$_2$ (4 cm^3) with acetic anhydride (1 drop) at 293 K for 30 min. This solution was filtered, and treated as above. The product was a purple microcrystalline solid (yield 0.070 g, 80%) (Found: C, 18.6; H, 3.1. Calc. for [C$_{10}$H$_{20}$NiS$_5$][PF$_6$]$_2$: C, 18.5; H, 3.1%).

[Ni([15]aneS$_5$)Cl][PF$_6$]. Reaction of NiCl$_2$ (0.022 g, 1.7 × 10^{-4} mol) with TlPF$_6$ (0.058 g, 1.7 × 10^{-4} mol) in MeNO$_2$ (4 cm^3) yielded a pale green solution and a white TlCl precipitate. The solution was filtered, and [15]aneS$_5$ (0.050 g, 1.7 × 10^{-4} mol) added to the filtrate. The resultant blue solution was stirred for 30 min, filtered, and the blue microcrystalline product crystallised by addition of Et$_2$O. The complex was recrystallised from MeNO$_2$–Et$_2$O (yield 0.065 g, 72%) (Found: C, 22.4; H, 3.7. Calc. for [C$_{10}$H$_{20}$ClNiS$_5$][PF$_6$]: C, 22.3; H, 3.7%). FAB mass spectrum: *m/z* 392 {[^{58}Ni^{35}Cl([15]aneS$_5$ − H)]$^+$} and 358 {[^{58}Ni([15]aneS$_5$)]$^+$} with correct isotopic distribution. Electronic spectrum (in MeCN) λ_{max} 920 nm (ε_{max} 59 dm^3 mol^{-1} cm^{-1}), 582 (43.8), 334 (87), 312 (3100) and 227 (7450). IR spectrum: 3000w, 2940m, 2860w, 1460s, 1410m, 1390w, 1310w, 1290m, 1260s, 1250w, 1220w, 1200w, 1180w, 1160w, 1145w, 1120m, 1060w, 1025w, 990w, 970w, 945s, 930w, 880w, 840vs, 780w, 740m, 700w, 685m, 650w, 630w, 610w, 555s, 530m, 485w, 460w and 425 cm^{-1}.

X-Ray Structure Determination of [Ni([16]aneS$_4$)(OH$_2$)$_2$][BF$_4$]$_2$.—A blue tablet (0.95 × 0.82 × 0.51 mm) suitable for X-ray analysis was obtained by diffusion of Et$_2$O vapour into a solution of the complex in MeNO$_2$. The crystal was coated in oil, mounted on a glass fibre, and cooled to 150 K in the cold stream of an Oxford Cryosystems low-temperature device.[31]

Crystal data. C$_{12}$H$_{28}$NiO$_2$S$_4{}^{2+}$·2BF$_4{}^-$, *M* 581.2, triclinic, space group $P\bar{1}$ (no. 2) with $a = 7.927(4)$, $b = 8.657(5)$, $c = 9.351(5)$ Å, $\alpha = 67.106(20)$, $\beta = 79.764(23)$, $\gamma = 66.898(24)°$, $U = 543.5$ Å^3, $D_c = 1.775$ g cm^{-3} [from 2θ values of 38 reflections measured at $\pm\omega$ ($31 < 2\theta < 32°$, $\lambda = 0.710\,73$ Å)], $Z = 1$, μ(Mo-Kα) = 1.354 nm^{-1}, $F(000) = 298$.

Data collection and processing. Stoë STADI-4 four circle diffractometer, ω–2θ scan mode with ω scan width (0.99 + 0.347 tanθ)°, graphite-monochromated Mo-Kα radiation, 1427 reflect-

Table 4 Bond lengths (Å) and angles and torsion angles (°) for [Ni([15]aneS$_5$)][PF$_6$]$_2$

Ni–S(1)	2.413(5)	C(5)–C(6)	1.498(18)
Ni–S(4)	2.177(6)	C(6)–S(7)	1.801(14)
Ni–S(7)	2.146(7)	S(7)–C(8)	1.842(15)
Ni–S(10)	2.169(6)	C(8)–C(9)	1.511(19)
Ni–S(13)	2.198(6)	C(9)–S(10)	1.730(15)
S(1)–C(2)	1.697(14)	S(10)–C(11)	1.781(14)
S(1)–C(15)	1.856(13)	C(11)–C(12)	1.490(19)
C(2)–C(3)	1.440(19)	C(12)–S(13)	1.835(15)
C(3)–S(4)	1.883(15)	S(13)–C(14)	1.723(13)
S(4)–C(5)	1.792(14)	C(14)–C(15)	1.556(17)
S(1)–Ni–S(4)	92.02(21)	S(4)–C(5)–C(6)	106.6(9)
S(1)–Ni–S(7)	103.00(22)	C(5)–C(6)–S(7)	109.2(9)
S(1)–Ni–S(10)	101.51(20)	Ni–S(7)–C(6)	102.8(5)
S(1)–Ni–S(13)	91.18(20)	Ni–S(7)–C(8)	99.7(5)
S(4)–Ni–S(7)	89.46(25)	C(6)–S(7)–C(8)	102.8(7)
S(4)–Ni–S(10)	166.45(23)	S(7)–C(8)–C(9)	105.2(9)
S(4)–Ni–S(13)	90.42(23)	C(8)–C(9)–S(10)	116.4(10)
S(7)–Ni–S(10)	86.82(24)	Ni–S(10)–C(9)	104.9(5)
S(7)–Ni–S(13)	165.82(25)	Ni–S(10)–C(11)	99.0(5)
S(10)–Ni–S(13)	90.03(23)	C(9)–S(10)–C(11)	104.9(7)
Ni–S(1)–C(2)	98.7(5)	S(10)–C(11)–C(12)	101.9(9)
Ni–S(1)–C(15)	98.8(4)	C(11)–C(12)–S(13)	109.6(9)
C(2)–S(1)–C(15)	105.5(6)	Ni–S(13)–C(12)	100.0(5)
S(1)–C(2)–C(3)	118.6(10)	Ni–S(13)–C(14)	106.6(5)
C(2)–C(3)–S(4)	115.7(10)	C(12)–S(13)–C(14)	114.5(7)
Ni–S(4)–C(3)	101.4(5)	S(13)–C(14)–C(15)	115.2(9)
Ni–S(4)–C(5)	106.0(5)	S(1)–C(15)–C(14)	115.4(8)
C(3)–S(4)–C(5)	97.4(6)		

C(15)–S(1)–C(2)–C(3)	66.8(12)
C(2)–S(1)–C(15)–C(14)	−76.3(10)
S(1)–C(2)–C(3)–S(4)	44.8(14)
C(2)–C(3)–S(4)–C(5)	81.2(11)
C(3)–S(4)–C(5)–C(6)	−140.6(9)
S(4)–C(5)–C(6)–S(7)	55.0(10)
C(5)–C(6)–S(7)–C(8)	−151.5(9)
C(6)–S(7)–C(8)–C(9)	158.6(9)
S(7)–C(8)–C(9)–S(10)	−37.2(12)
C(8)–C(9)–S(10)–C(11)	−99.9(11)
C(9)–S(10)–C(11)–C(12)	169.4(9)
S(10)–C(11)–C(12)–S(13)	−64.4(10)
C(11)–C(12)–S(13)–C(14)	148.8(9)
C(12)–S(13)–C(14)–C(15)	−74.5(11)
S(13)–C(14)–C(15)–S(1)	−42.1(12)

ions measured ($2\theta_{max} = 45°$, h −8 to 8, k −8 to 9, l 0 to 10) giving 1393 with $F > 4\sigma(F)$. Linear isotropic decay ($\approx 8\%$) corrected for during data reduction, no absorption correction.

Structure solution and refinement. Consideration of the observed unit-cell volume, together with the assumed cell contents, implied that the nickel atom must lie on a crystallographic inversion centre. This assumption was confirmed as the structure was developed using iterative cycles of least-squares refinement and Fourier difference synthesis.[32] Anisotropic thermal parameters were refined for all non-hydrogen atoms: a common isotropic thermal parameter (U_{iso} 0.040 Å^2) was also refined for the hydrogen atoms, which were included in fixed, calculated positions.[32] The fixed weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,10F^2$ gave satisfactory agreement analyses. At convergence R, R' = 0.0381 and 0.0488 respectively, S = 1.366 for 140 independent parameters. The final ΔF synthesis exhibited maximum and minimum residuals of 0.86 and −0.75 e Å^{-3} respectively. Bond lengths, angles and torsion angles, and atomic coordinates are listed in Tables 2 and 3.

X-Ray Structure Determination of [Ni([15]aneS$_5$)][PF$_6$]$_2$.—A purple needle (0.08 × 0.10 × 0.5 mm) suitable for an X-ray diffraction study was obtained by diffusion of Et$_2$O vapour into a solution of the complex in MeNO$_2$.

Table 5 Atomic coordinates for [Ni([15]aneS$_5$)][PF$_6$]$_2$

Atom	x	y	z
Ni	0.039 67(22)	0.0	0.750 08(6)
S(1)	−0.173 0(4)	0.002 5(8)	0.624 26(14)
C(2)	−0.070 2(16)	−0.137 8(14)	0.588 1(9)
C(3)	0.162 2(16)	−0.171 5(14)	0.609 7(9)
S(4)	0.264 3(9)	−0.152 8(6)	0.715 2(4)
C(5)	0.156 5(16)	−0.305 5(13)	0.747 6(8)
C(6)	0.068 7(16)	−0.277 9(13)	0.823 5(8)
S(7)	−0.132 7(10)	−0.145 5(7)	0.811 4(4)
C(8)	−0.108 8(17)	−0.068 9(13)	0.907 9(9)
C(9)	−0.199 6(17)	0.069 2(14)	0.894 8(9)
S(10)	−0.137 8(9)	0.146 8(6)	0.811 1(4)
C(11)	0.092 6(16)	0.253 1(13)	0.840 8(8)
C(12)	0.164 8(18)	0.295 9(14)	0.765 3(9)
S(13)	0.267 9(9)	0.153 2(6)	0.714 7(4)
C(14)	0.223 5(15)	0.162 6(12)	0.615 4(8)
C(15)	−0.023 9(16)	0.139 2(13)	0.580 3(8)
P(1)	−0.598 8(5)	−0.000 1(9)	0.066 83(18)
F(11)	−0.579 9(17)	0.074 8(14)	0.144 6(10)
F(11′)	−0.597 0(17)	−0.002 2(19)	0.154 1(9)
F(12)	−0.662 8(18)	0.131 3(16)	0.033 8(12)
F(12′)	−0.603 5(18)	0.160 7(15)	0.077 7(10)
F(13)	−0.606 7(17)	−0.084 8(14)	−0.009 6(9)
F(13′)	−0.612 3(15)	0.028 2(12)	0.975 7(7)
F(14)	−0.575 0(19)	−0.145 0(16)	0.110 9(11)
F(14′)	−0.5242(20)	−0.142 5(18)	0.041 0(14)
F(15)	−0.857 0(12)	−0.016 7(15)	0.062 2(5)
F(16)	−0.338 4(11)	0.007 6(16)	0.073 1(5)
P(2)	0.600 0(4)	0.501 5(8)	0.603 51(15)
F(21)	0.572 9(15)	0.388 8(10)	0.537 7(6)
F(22)	0.637 3(16)	0.393 8(10)	0.664 6(7)
F(23)	0.625 7(14)	0.612 8(12)	0.666 2(10)
F(24)	0.558 6(15)	0.607 0(12)	0.545 1(8)
F(25)	0.338 8(10)	0.500 8(15)	0.610 1(5)
F(26)	0.856 4(10)	0.500 5(16)	0.595 5(5)

Crystal data. $C_{10}H_{20}NiS_5^{2+}\cdot 2PF_6^-$, M = 649.08, monoclinic, space group $P2_1$ (no. 4), with a = 5.968(3), b = 10.146(7), c = 17.402(9) Å, β = 96.04(4)°, U = 1048 Å^3, D_c = 2.06 g cm^{-3} [from 2θ values of 10 reflections measured at $\pm\omega$ ($26 < 2\theta < 28°$, λ = 0.710 73 Å)], Z = 2, μ(Mo-Kα) = 1.659 mm^{-1}, $F(000)$ = 652.

Data collection and processing. Stoë STADI-4 four-circle diffractometer, ω–2θ scan mode with ω scan-width (0.66 + 0.347 tanθ)°, graphite-monochromated Mo-Kα radiation, 1485 reflections measured ($2\theta_{max}$ = 45°, h −6 to 6, k 0–10, l 0–18), giving 1233 with $F > 2\sigma(F)$. Correction for isotropic crystal decay (2%) applied during data reduction. No absorption correction.

Structure analysis and refinement. The nickel position was located from a Patterson synthesis, and iterative cycles of least-squares refinement and Fourier difference syntheses[32] located all other non-hydrogen atoms. During refinement, one PF$_6^-$ anion was found to be disordered over two equally occupied orientations by rotation about one F–P–F axis. Anisotropic thermal parameters were refined for the nickel and sulfur atoms of the cation, and for the phosphorus and wholly occupied fluorine atoms of the PF$_6^-$ anions. Hydrogen atoms were included in fixed, calculated positions.[32] The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,382F^2$ gave satisfactory agreement analyses. At convergence R = 0.059 9, R' = 0.0720, S = 1.623 for 216 parameters. The maximum and minimum residuals in the final ΔF synthesis were 0.87 and −0.56 e Å^{-3} respectively. Bond lengths, angles and torsion angles, and atomic coordinates are listed in Tables 4 and 5. The illustrations were prepared using ORTEP,[33] molecular geometry calculations were performed using CALC,[34] and scattering factor data were taken from ref. 35.

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

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