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A new class of mixed aza–thioether crown containing a 1,10-phenanthroline sub-unit †

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The new aza–thioether crowns [15]ane(phen $N_2)S_3$ and [19]ane(phen $N_2)S_4$ have been synthesised. Their complexation with nickel(II) salts afforded a range of octahedral complexes. The single crystal structures of [Ni{[15]ane(phen $N_2)S_3$}(NCMe)][BF_4]$_2$, [NiCl{[15]ane(phen $N_2)S_3$}]BF_4·dmf (dmf = dimethylformamide) and [NiI{[15]ane(phen $N_2)S_3$}][I_3] have been determined and confirm N_2S_3 donation of the aza–thioether crown in a folded conformation to Ni^{II} with the sixth co-ordination site taken up by MeCN, Cl^- and I^- respectively. The complex [Ni_2Cl_2{[19]ane(phen $N_2)S_4$}$_2$][BF_4]$_2$·3$MeNO_2$ shows a dichloro-bridged binuclear structure with the aza–thioether crown bound *via* only two S- and two N-donors, with two thioether S-donors unbound. A dichloro-bridged binuclear structure was found also for [Ni_2Cl_2{[12]ane(py N)S_3}$_2$][BF_4]$_2$·1.5$MeNO_2$. The redox properties of [Ni{[15]ane(phen $N_2)S_3$}(NCMe)][BF_4]$_2$ in MeCN have been examined.

Homoleptic thioether crowns are now well known to bind to a wide range of transition-metal ions to give complexes exhibiting unusual stereochemical and redox properties.[1] Mixed donor thioether–aza[2] and thioether–oxa[3] crowns are known, as well as those incorporating aryl[4] and/or heteroaryl[5,6] frameworks within the ring. There are no reports in the literature of mixed 1,10-phenanthroline (phen) thioether macrocycles. Although Lai *et al.*[7] have recently reported the coupling of phen units with single thioether S-linkers, their system does not allow co-ordination of both N- and S-donors to metal centres. Complexes of mixed aza–thioether ligands represent useful model compounds for metalloenzymes in biological systems.[2] In addition, it is well known that the N-donor heterocycles 2,2′-bipyridine (bipy) and 1,10-phenanthroline are excellent π acceptors and are also redox-active, the stabilisation of low-valent metal complexes and/or ligand-radical species having been reported.[8–10] Interest in complexes of substituted derivatives of bipy and phen is also based on their catalytic, redox and photoredox properties.[11] Although phen and bipy moieties have been incorporated into Schiff-base aza macrocycles,[8] crown ethers,[12] cryptands[13] and catenands,[9] no data are available on thioether crowns incorporating these fragments. We report herein the synthesis of the new mixed thia–phen crowns [15]ane(phen $N_2)S_3$ and [19]ane(phen $N_2)S_4$, and the preparation and characterisation of their nickel(II) complexes and that of [12]ane(py N)S_3.

Results and Discussion

The strategy adopted in the synthesis of [15]ane(phen $N_2)S_3$ and [19]ane(phen $N_2)S_4$ is outlined in Scheme 1, and involves the oxidation of 2,9-dimethyl-1,10-phenanthroline to the corresponding dialdehyde, followed by reduction of the latter to 2,9-bis(hydroxymethyl)-1,10-phenanthroline.[14] Subsequent chlorination followed by cyclisation with the appropriate dithiol in the presence of Cs_2CO_3[15,16] affords the required macrocycles.

The reaction of $NiCl_2$·6H_2O with 1 molar equivalent of [15]ane(phen $N_2)S_3$ in refluxing MeCN–water followed by the addition of an excess of NH_4BF_4 and recrystallisation from MeCN–Et_2O afforded purple crystals of the species [Ni{[15]ane(phen $N_2)S_3$}(NCMe)][BF_4]$_2$ in good yield. A single-crystal structure determination was undertaken to ascertain the ligation and stereochemistry of this complex. Crystals of the complex were obtained in orthorhombic and monoclinic forms. The structure of the more stable monoclinic form confirms the formation of the [Ni{[15]ane(phen $N_2)S_3$}(NCMe)]$^{2+}$ cation (Fig. 1). Bond lengths and angles for the complex are summarised in Table 1. The nickel(II) ion is bound to the pentadentate macrocycle *via* two N-donors of the phen unit, Ni–N 2.025(2) and 2.013(2) Å, and three thioether S-donors of the thioether linker, Ni–S 2.4340(8), 2.4440(7) (*trans* to phen) and 2.4286(7) Å (*trans* to NCMe). The octahedral co-ordination sphere is completed by an MeCN molecule, Ni–N 2.070(2) Å.

Table 1 Selected bond distances (Å) and angles (°) for [Ni{[15]ane(phen $N_2)S_3$}(NCMe)][BF_4]$_2$

Ni–S(1)	2.4440(7)	Ni–N(1)	2.025(2)
Ni–S(2)	2.4340(8)	Ni–N(2)	2.013(2)
Ni–S(3)	2.4286(7)	Ni–N(3)	2.070(2)
S(1)–Ni–S(2)	115.85(3)	S(2)–Ni–N(3)	86.78(6)
S(1)–Ni–S(3)	86.96(2)	S(3)–Ni–N(1)	92.33(6)
S(1)–Ni–N(1)	81.13(6)	S(3)–Ni–N(2)	87.33(6)
S(1)–Ni–N(2)	160.59(6)	S(3)–Ni–N(3)	173.04(6)
S(1)–Ni–N(3)	93.91(7)	N(1)–Ni–N(2)	80.58(8)
S(2)–Ni–S(3)	86.63(3)	N(1)–Ni–N(3)	94.62(8)
S(2)–Ni–N(1)	162.86(6)	N(2)–Ni–N(3)	94.00(9)
S(2)–Ni–N(2)	82.28(6)		

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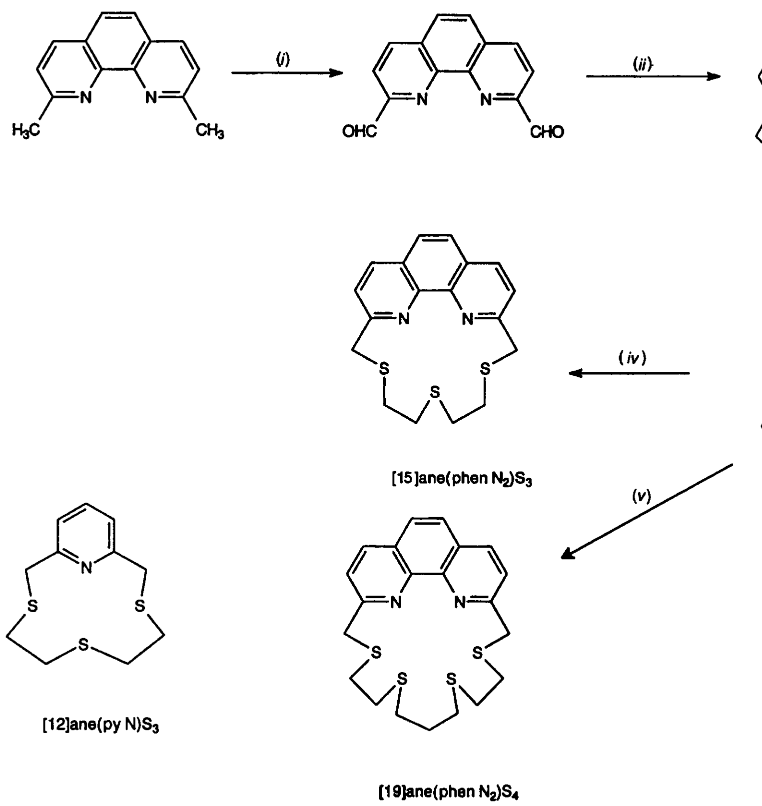
† Abbreviations used: [15]ane(phen $N_2)S_3$ = 2,5,8-trithia[9],(2,9)-1,10-phenanthrolinophane, [19]ane(phen $N_2)S_4$ = 2,5,9,12-tetrathia[13],(2,9)-1,10-phenanthrolinophane and [12]ane(py N)S_3 = 2,5,8-trithia[9],(2,6)pyridinophane.

Non-SI units employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, eV $\approx 1.60 \times 10^{-19}$ J.



Scheme 1 Synthesis of macrocyles. (*i*) SeO_2, 1,4-dioxane, 4 h, reflux; (*ii*) $NaBH_4$, EtOH, reflux; (*iii*) $SOCl_2$; (*iv*) $HS(CH_2)_2S(CH_2)_2SH$, Cs_2CO_3, dimethylformamide (dmf), 328 K; (*v*) $HS(CH_2)_2S(CH_2)_3S(CH_2)_2SH$, Cs_2CO_3, dmf, 328 K

The phenanthroline moiety and the two adjacent sulfur atoms S(1) and S(2) of the pentadentate ring lie approximately in an equatorial plane of the octahedron, with the third sulfur atom S(3) and the MeCN molecule occupying the two apical positions, S(3)–Ni–N(3) 173.04(6)°.

Monomeric nickel(II) complexes of 1,10-phenanthroline ligands bearing bulky substituents in the 2,9 positions of the heterocycle are often tetrahedral or pseudo-tetrahedral as a consequence of the steric hindrance of the substituents.[17,18] In the present case the macrocycle [15]ane(phen N_2)S_3 encapsulates the nickel(II) ion within a cavity having a square-based pyramidal stereochemistry, with the sixth co-ordination position occupied by other donating molecules. The Ni–N bond lengths are similar to those found in other nickel(II) complexes of phen derivatives.[19] The three Ni–S lengths [2.4286(7)–2.4440(7) Å] are slightly longer than those normally observed in complexes of aliphatic thia- and mixed thia–aza-crown ethers[1,2] such as $[Ni([18]aneN_2S_4)]^{2+}$ ($[18]aneN_2S_4$ = 1,10-dithia-4,7,13,16-tetraazacyclohexadecane)[2] [Ni–S 2.403(6)–2.416(7) Å] and are indicative of uncompressed Ni–S bonds (*cf.* the sum of the ionic radii of Ni^{2+} and S^{2-}, 2.44 Å).

The electronic spectrum of $[Ni\{[15]ane(phen\ N_2)S_3\}(NCMe)][BF_4]_2$ measured in MeCN solution shows two charge-transfer transitions at λ_{max} = 274 (ε_{max} = 25 700) and 228 (30 830) with shoulders at 298 (10 390) and 206 (23 130), and two weak d–d transitions at 858 (ε_{max} = 61) and 542 (36) with shoulders at 970 (31) and 588 nm (27 $dm^3\ mol^{-1}\ cm^{-1}$). This spectrum is indicative of a low symmetry at Ni^{II} as shown by the structure determination.* The ligand-field strength, 10*Dq*, has been evaluated approximately from the lowest-energy transition to be 11 655 cm^{-1}; this value is intermediate between that of $[Ni([18]aneN_6)]^{2+}$ and $[Ni([18]aneS_6)]^{2+}$ ([18]ane-N_6 and -S_6 = 1,4,7,10,13,16-hexaaza- and 1,4,7,10,13,16-hexathiacyclooctadecane) (11 200 and 12 290 cm^{-1} respectively)[2] and between that of $[Ni(phen)_3]^{2+}$ and $[Ni(NCMe)_6]^{2+}$ (12 400 and 10 650 cm^{-1}).[20] It is comparable with those of other thia–aza crown ether complexes of Ni^{II} [2] and interestingly higher than those observed for $[NiL(NCMe)_x]^{2+}$ {10 290–11 090 cm^{-1}; L = $[12]aneS_4$ (1,4,7,10-tetrathiacyclododecane), $[14]aneS_4$ (1,4,8,11-tetrathiacyclotetradecane) or $[16]aneS_4$ (1,5,9,13-tetrathiacyclohexadecane) for $x = 2$ and $[15]aneS_5$ (1,4,7,10,13-pentathiacyclopentadecane) for $x = 1$}.[21] The magnetic susceptibility obeys the Curie law from 4 to 300 K with μ_{eff} = 3.09 μ_B.

The Cl^- adduct $[NiCl\{[15]ane(phen\ N_2)S_3\}]^+$ can be isolated as a green solid from the reaction of $NiCl_2\cdot6H_2O$ with [15]ane(phen N_2)S_3, while the black iodide adduct $[NiI\{[15]ane(phen\ N_2)S_3\}][I_3]$ can be prepared by addition of I_3^- to a solution of $[Ni\{[15]ane(phen\ N_2)S_3\}(NCMe)]^{2+}$. Addition of Cl^- and I^- to solutions of $[Ni\{[15]ane(phen\ N_2)S_3\}(NCMe)]^{2+}$ shows isosbestic conversion into the corresponding halogeno adducts. Electronic spectroscopy of these products in dmf solution gave 10*Dq* values of 10 920 and 10 970 cm^{-1} for $[NiX\{[15]ane(phen\ N_2)S_3\}]^+$ (X = Cl or I) compared to a value of 11 220 cm^{-1} for the MeCN adduct. The single-crystal structures of the Cl^- and I^- adducts were determined (Figs. 2 and 3); bond lengths and angles are summarised in Tables 2 and 3. The structures of $[NiCl\{[15]ane(phen\ N_2)S_3\}]^+$ and $[NiI\{[15]ane(phen\ N_2)S_3\}]^+$ confirm six-co-ordination at Ni^{II} in each case with Ni–S 2.4364(10)–2.4392(9), Ni–Cl 2.3605(8), Ni–N 2.024(2) and 2.027(2) Å for the Cl^- adduct, and Ni–S 2.411(3)–2.452(4), Ni–I 2.761(2) Å, Ni–N 1.999(10) and 2.021(10) Å for the I^- adduct. As for the MeCN adduct, both Cl^- and I^- adducts show the macrocyclic ligand adopting a square-based pyramidal geometry at the Ni^{II}.

We wished to monitor the effect of increasing the number of thioether S-donor centres within the N/S crown upon the

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* In O_h symmetry for a nickel(II) ion three d–d transitions are expected; while two d–d bands are present, the highest-energy absorption $[^3A_{2g} \rightarrow {}^3T_{1g}(P)$ in O_h symmetry] is often hidden by charge-transfer bands. By considering the three Ni–N and the three Ni–S bond lengths, an approximate local C_{3v} symmetry can be attributed to the complex; this is consistent with the splitting seen for the two observed d–d transitions.

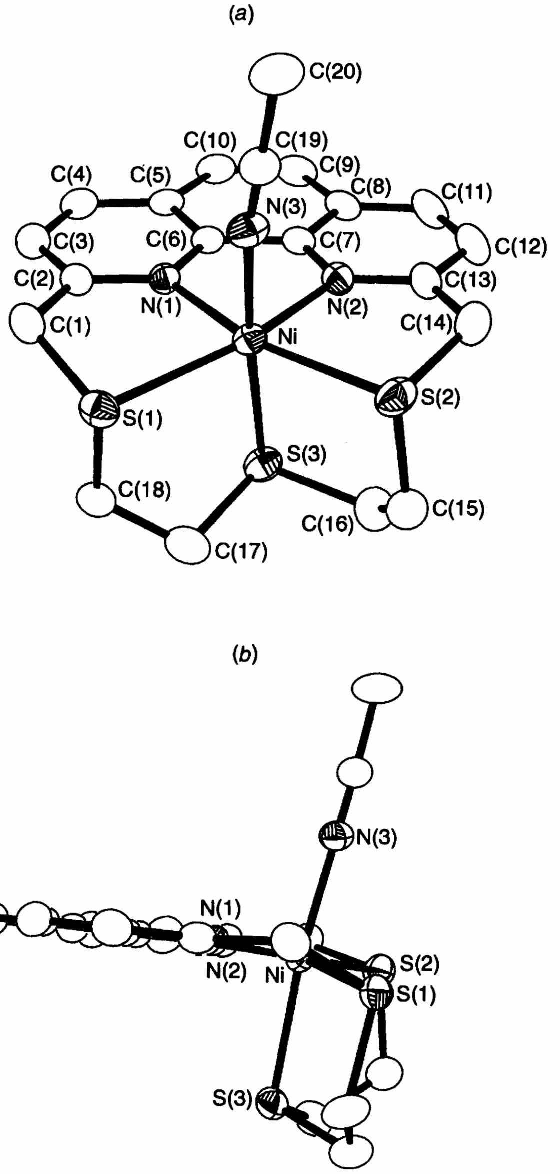

Fig. 1 Two views (*a*) and (*b*) of the [Ni{[15]ane(phen N_2)S_3}(NCMe)]$^{2+}$ cation with numbering scheme adopted. Thermal ellipsoids are drawn at 30% probability

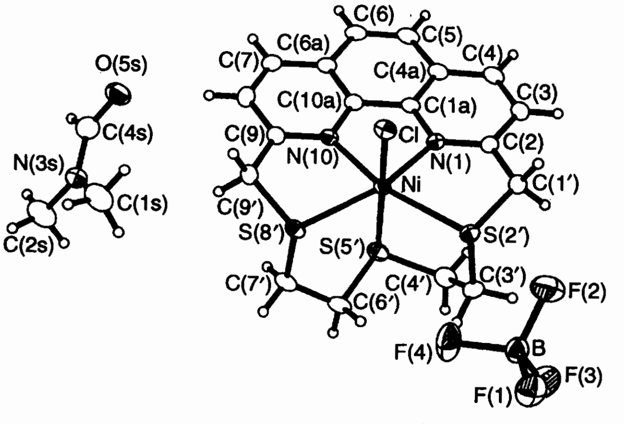

Fig. 2 View of [NiCl{[15]ane(phen N_2)S_3}]$^+$ with the numbering scheme adopted. Thermal ellipsoids are drawn at 30% probability

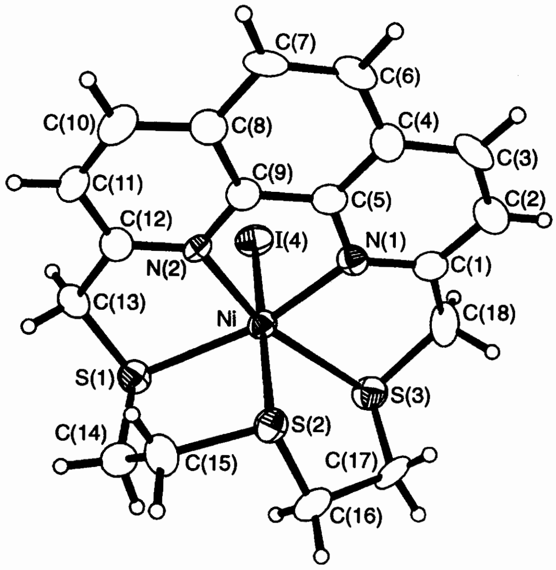

Fig. 3 View of [NiI{[15]ane(phen N_2)S_3}]$^+$ with the numbering scheme adopted. Thermal ellipsoids are drawn at 30% probability

Table 2 Selected bond lengths (Å), angles and torsions (°) for [NiCl{[15]ane(phen N_2)S_3}]BF_4·dmf

Ni–Cl	2.3605(8)	Ni–S(2′)	2.4392(9)
Ni–N(1)	2.024(2)	Ni–S(5′)	2.4377(9)
Ni–N(10)	2.027 (2)	Ni–S(8′)	2.4364(10)
Cl–Ni–N(1)	95.60(6)	N(1)–Ni–S(8′)	161.88(6)
Cl–Ni–N(10)	93.13(6)	N(10)–Ni–S(2′)	162.44(6)
Cl–Ni–S(2′)	89.69(3)	N(10)–Ni–S(5′)	92.42(6)
Cl–Ni–S(5′)	171.66(2)	N(10)–Ni–S(8′)	81.57(6)
Cl–Ni–S(8′)	89.42(3)	S(2′)–Ni–S(5′)	86.88(3)
N(1)–Ni–N(10)	80.78(8)	S(2′)–Ni–S(8′)	115.80(3)
N(1)–Ni–S(2′)	81.70(6)	S(5′)–Ni–S(8′)	85.25(3)
N(1)–Ni–S(5′)	91.43(6)		

N(1)–C(2)–C(1′)–S(2′)	11.2(3)
C(3)–C(2)–C(1′)–S(2′)	−172.0(2)
C(2)–C(1′)–S(2′)–C(3′)	93.3(2)
C(1′)–S(2′)–C(3′)–C(4′)	−71.5(2)
S(2′)–C(3′)–C(4′)–S(5′)	−49.6(2)
C(3′)–C(4′)–S(5′)–C(6′)	−61.5(2)
C(4′)–S(5′)–C(6′)–C(7′)	160.5(2)
S(5′)–C(6′)–C(7′)–S(8′)	−62.2(2)
C(6′)–C(7′)–S(8′)–C(9′)	133.8(2)
N(10)–C(9)–C(9′)–S(8′)	−10.8(3)
C(8)–C(9)–C(9′)–S(8′)	173.4(2)
C(7′)–S(8′)–C(9′)–C(9)	−91.1(2)

Table 3 Selected bond lengths (Å) and angles (°) for [NiI{[15]ane(phen N_2)S_3}][I_3]

Ni–N(1)	1.999(10)	Ni–S(3)	2.452(4)
Ni–N(2)	2.021(10)	Ni–I(4)	2.761(2)
Ni–S(2)	2.411(3)	I(1)–I(3)	2.9184(14)
Ni–S(1)	2.434(4)	I(1)–I(2)	2.919(2)
N(1)–Ni–N(2)	80.3(4)	S(2)–Ni–S(3)	85.45(12)
N(1)–Ni–S(2)	92.2(3)	S(1)–Ni–S(3)	115.48(14)
N(2)–Ni–S(2)	92.0(3)	N(1)–Ni–I(4)	93.1(3)
N(1)–Ni–S(1)	162.8(3)	N(2)–Ni–I(4)	95.1(3)
N(2)–Ni–S(1)	82.5(3)	S(2)–Ni–I(4)	171.78(11)
S(2)–Ni–S(1)	86.82(11)	S(1)–Ni–I(4)	89.89(9)
N(1)–Ni–S(3)	81.6(3)	S(3)–Ni–I(4)	89.19(9)
N(2)–Ni–S(3)	161.6(3)	I(3)–I(1)–I(2)	174.36(5)

resultant co-ordination to Ni^{II}. Reaction of [19]ane(phen N_2)S_4 with $NiCl_2$·$6H_2O$ in MeCN–water afforded a green product which can be recrystallised from $MeNO_2$–Et_2O. The structure of the complex confirms the formation of the binuclear species [Ni_2Cl_2{[19]ane(phen N_2)S_4}$_2$][BF_4]$_2$·3$MeNO_2$ (Fig. 4, Table 4). Interestingly, the macrocycle in this complex is four-co-ordinate, being bound by two N-donors of the phen moiety, Ni–N (*trans* to Cl^-) 2.023(12), 2.024(12), Ni–N (*trans* to S) 2.150(11), 2.14(2) Å, and only two S-donors

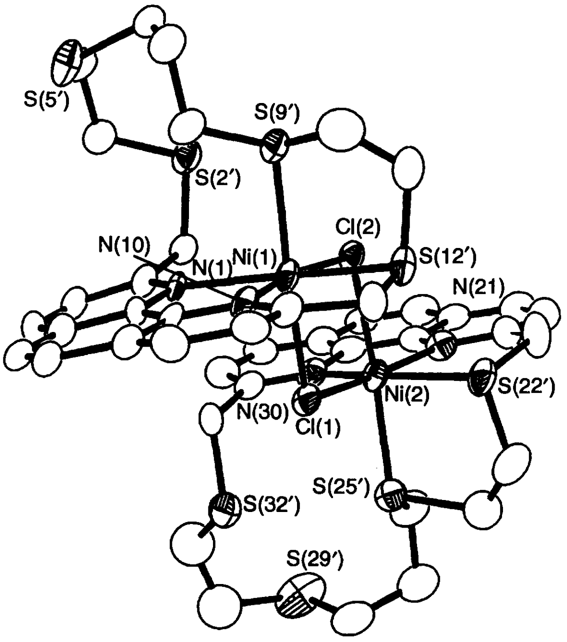

Fig. 4 View of $[Ni_2Cl_2\{[19]ane(phen\ N_2)S_4\}_2]^{2+}$ with the numbering scheme adopted. Thermal ellipsoids are drawn at 30% probability

Table 4 Selected bond lengths (Å) and angles (°) for $[NiCl_2\{[19]ane(phen\ N_2)S_4\}_2][BF_4]_2\cdot 3MeNO_2$

Ni(1)–Cl(1)	2.441(5)	Ni(2)–Cl(1)	2.388(4)
Ni(1)–Cl(2)	2.394(4)	Ni(2)–Cl(2)	2.456(5)
Ni(1)–N(1)	2.150(11)	Ni(2)–N(21)	2.023(12)
Ni(1)–N(10)	2.024(12)	Ni(2)–N(30)	2.14(2)
Ni(1)–S(9')	2.414(5)	Ni(2)–S(22')	2.446(6)
Ni(1)–S(12')	2.431(5)	Ni(2)–S(25')	2.415(5)
Cl(1)–Ni(1)–Cl(2)	84.37(14)	Cl(1)–Ni(2)–N(21)	168.0(5)
Cl(1)–Ni(1)–N(1)	89.9(3)	Cl(1)–Ni(2)–N(30)	109.3(4)
Cl(1)–Ni(1)–N(10)	90.2(4)	Cl(1)–Ni(2)–S(22')	88.9(2)
Cl(1)–Ni(1)–S(9')	175.5(2)	Cl(1)–Ni(2)–S(25')	88.5(2)
Cl(1)–Ni(1)–S(12')	93.0(2)	Cl(2)–Ni(2)–N(21)	89.2(4)
Cl(2)–Ni(1)–N(1)	108.2(3)	Cl(2)–Ni(2)–N(30)	92.5(4)
Cl(2)–Ni(1)–N(10)	169.8(4)	Cl(2)–Ni(2)–S(22')	92.2(2)
Cl(2)–Ni(1)–S(9')	91.2(2)	Cl(2)–Ni(2)–S(25')	172.69(14)
Cl(2)–Ni(1)–S(12')	88.7(2)	N(21)–Ni(2)–N(30)	80.9(6)
N(1)–Ni(1)–N(10)	80.3(5)	N(21)–Ni(2)–S(22')	81.3(5)
N(1)–Ni(1)–S(9')	92.1(3)	N(21)–Ni(2)–S(25')	97.9(4)
N(1)–Ni(1)–S(12')	163.0(3)	N(30)–Ni(2)–S(22')	161.5(4)
N(10)–Ni(1)–S(9')	94.1(4)	N(30)–Ni(2)–S(25')	90.3(4)
N(10)–Ni(1)–S(12')	83.0(4)	S(25')–Ni(2)–S(22')	87.2(2)
S(9')–Ni(1)–S(12')	86.2(2)	Ni(2)–Cl(1)–Ni(1)	95.9(2)
Cl(1)–Ni(2)–Cl(2)	84.17(14)	Ni(1)–Cl(2)–Ni(2)	95.3(2)

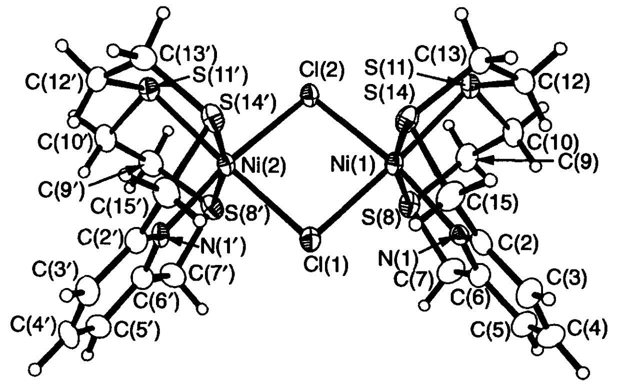

Fig. 5 View of $[Ni_2Cl_2\{[12]ane(py\ N)S_3\}_2]^{2+}$ with the numbering scheme adopted. Thermal ellipsoids are drawn at 30% probability

Table 5 Selected bond lengths (Å) and angles (°) for $[Ni_2Cl_2\{[12]ane(py\ N)S_3\}_2][BF_4]_2\cdot 1.5MeNO_2$

Ni(1)–Cl(1)	2.4010(11)	Cl(1)–Ni(2)	2.3954(11)
Ni(1)–Cl(2)	2.4091(11)	Cl(2)–Ni(2)	2.3981(11)
Ni(1)–N(1)	2.057(3)	Ni(2)–N(1')	2.059(3)
Ni(1)–S(8)	2.3998(12)	Ni(2)–S(8')	2.3983(12)
Ni(1)–S(11)	2.3874(11)	Ni(2)–S(11')	2.3950(12)
Ni(1)–S(14)	2.3978(12)	Ni(2)–S(14')	2.3972(12)
N(1)–Ni(1)–S(11)	97.23(8)	Ni(2)–Cl(1)–Ni(1)	93.74(4)
N(1)–Ni(1)–S(14)	85.13(8)	Ni(2)–Cl(2)–Ni(1)	93.47(4)
S(11)–Ni(1)–S(14)	85.41(4)	N(1')–Ni(2)–S(11')	96.26(8)
N(1)–Ni(1)–S(8)	84.74(8)	N(1')–Ni(2)–Cl(1)	86.39(8)
S(11)–Ni(1)–S(8)	86.44(4)	S(11')–Ni(2)–Cl(1)	177.35(3)
S(14)–Ni(1)–S(8)	166.10(3)	N(1')–Ni(2)–S(14')	85.57(8)
N(1)–Ni(1)–Cl(1)	85.83(8)	S(11')–Ni(2)–S(14')	85.73(4)
S(11)–Ni(1)–Cl(1)	176.71(3)	Cl(1)–Ni(2)–S(14')	94.33(4)
S(14)–Ni(1)–Cl(1)	93.65(4)	N(1')–Ni(2)–Cl(2)	172.75(7)
S(8)–Ni(1)–Cl(1)	95.08(4)	S(11')–Ni(2)–Cl(2)	90.96(4)
N(1)–Ni(1)–Cl(2)	171.85(7)	Cl(1)–Ni(2)–Cl(2)	86.39(4)
S(11)–Ni(1)–Cl(2)	90.92(4)	S(14')–Ni(2)–Cl(2)	94.29(4)
S(14)–Ni(1)–Cl(2)	95.29(4)	N(1')–Ni(2)–S(8')	84.35(8)
S(8)–Ni(1)–Cl(2)	96.08(4)	S(11')–Ni(2)–S(8')	85.91(4)
Cl(1)–Ni(1)–Cl(2)	86.02(4)	Cl(1)–Ni(2)–S(8')	94.52(4)
Cl(2)–Ni(2)–S(8')	96.92(4)	S(14')–Ni(2)–S(8')	166.12(3)

of the crown, Ni–S (*trans* to N) 2.446(6), 2.431(5), Ni–S (*trans* to Cl^-) 2.414(5), 2.415(5) Å. The co-ordination at Ni^{II} is completed by two bridging chloro ligands, Ni–Cl (*trans* to N) 2.388(4), 2.394(4) Å, Ni–Cl (*trans* to S) 2.441(5), 2.456(5) Å. These bond lengths reflect the strong π-acceptor and π-donor abilities of phen and Cl^- respectively, and the weaker π effects of the thioether S-donor. The structure is reminiscent of those of the dichloro-bridged complexes $[Ni_2Cl_2L_2]^{2+}$ (L = [12]aneS$_4$, [14]aneS$_4$ or [16]aneS$_4$).[22]

We wished to compare the co-ordination characteristics of the mixed phen–thioether crowns with those of the nickel(II) complexes of the related crown [12]ane(py N)S$_3$. The synthesis of this compound has been described previously,[5,23] and its structure[24] and those of its mercury(II)[25] and silver(I)[26] complexes have been reported. Reaction of $NiCl_2\cdot 6H_2O$ with [12]ane(py N)S$_3$ affords a blue product, the single-crystal structure of which (Fig. 5, Table 5) confirms the formation of the dichloro-bridged binuclear complex $[Ni_2Cl_2\{[12]ane(py\ N)S_3\}_2]^{2+}$. Each nickel(II) centre is octahedral, co-ordinated to two chloro, three thioether S-donors and one pyridyl N-donor, Ni–Cl 2.3954(11)–2.4091(11), Ni–N 2.057(3), 2.059(3) and Ni–S 2.3874(11)–2.3998(12) Å. Thus, the formation of octahedral dichloro-bridged nickel(II) complexes reflects the relatively weak ligand fields of the aza-thioether ligands [19]ane(phen N$_2$)S$_4$ and [12]ane(py N)S$_3$ which do not allow the formation of square-planar Ni^{II} under the above conditions.

The redox properties of $[Ni\{[15]ane(phen\ N_2)S_3\}(NCMe)][BF_4]_2$ were monitored by cyclic voltammetry in MeCN solution (0.1 mol dm^{-3} $NBu^n{}_4BF_4$). The free macrocycle [15]ane(phen N$_2$)S$_3$ was found to be electrochemically inactive in the range +1.8 to −1.8 V *vs.* ferrocene–ferrocenium. No oxidation of the nickel(II) complex was observed in the solvent range (up to +1.8 V *vs.* Ag–AgCl). However, reductive cyclic voltammetry (scan rate 0.4 V s^{-1} at 298 K) showed a quasi-reversible reduction at $E_{\frac{1}{2}} = -0.98$ V and a second broad essentially irreversible process at $E_{pc} = -1.91$ V (*vs.* ferrocene–ferrocenium). Preliminary coulometric measurements upon the first reduction in MeCN suggest that this is a one-electron process to afford a grey-yellow solution and a brown precipitate. The insolubility of one of the redox product(s) led to problems in obtaining satisfactory and unambiguous characterisation by *in situ* ESR and electronic spectral measurements on the reduced species. However, on the basis of previously published data,[27] the one-electron reduction at $E_{\frac{1}{2}} = -0.982$ V can be assigned tentatively to a metal-based Ni^{II}–Ni^{I} couple. Free phenanthroline exhibits an irreversible reduction at −2.040 V and complexes of phenanthroline such as $[Fe(phen)_3]^{2+}$ have been reported as showing reversible one-electron reduction processes around −1.6 V (*vs.* ferrocene–ferrocenium).[27] These potentials are significantly more negative than the $E_{\frac{1}{2}}$ value of −0.982 V that we have measured for $[Ni\{[15]ane(phen\ N_2)S_3\}(NCMe)]^{2+}$.

A range of nickel(II) complexes incorporating mixed phen- and py–thioether crowns have been prepared and characterised. Complexes of Ni^{II} with mixed-donor N/S ligands have been implicated in modelling of nickel biosites particularly hydrogenase enzymes.[28] Current work is aimed at characterising the redox products of these macrocyclic complexes.

Experimental

All melting points are uncorrected. The NMR spectra were recorded on a Varian VXR300 spectrometer (operating at 75.4 MHz). The spectrophotometric measurements were carried out at 25 °C by use of a Varian model Cary 5 UV/VIS/NIR spectrophotometer and EI mass spectra were obtained on a Fisons QMD 1000 mass spectrometer (70 eV, 200mA, ion-source temperature 200 °C). Microanalytical data were obtained by using a Fisons EA 1108 CHNS-O instrument (T = 1000 °C). Cyclic voltammetry was performed using a conventional three-electrode cell, with a platinum double-bead electrode and Ag–AgCl reference electrode. All measurements were taken in a 0.1 mol dm^{-3} solution of tetrabutylammonium tetrafluoroborate in acetonitrile, which was freshly distilled (from CaH_2) prior to use. All solvents were dried by conventional methods, freshly distilled and degassed. 2,9-Dimethyl-1,10-phenanthroline and 2-sulfanylethyl sulfide were commercially available. The following compounds were prepared according to the literature: 1,10-phenanthroline-2,9-dicarbaldehyde, 2,9-bis(hydroxymethyl)-1,10-phenanthroline, 2,9-bis(chloromethyl)-1,10-phenanthroline,[8,14] 3,7- dithianonane-1,9-dithiol.[29] The compounds [15]ane(phen N_2)S_3 and [19]ane(phen N_2)S_4 were synthesised by high-dilution addition of the appropriate dithiol to 2,9-bis(chloromethyl)-1,10-phenanthroline in the presence of Cs_2CO_3;[16] [12]ane(py N)S_3 was prepared according to the literature method.[5,23]

Preparations

2,5,8-Trithia[9],(2,9)-1,10-phenanthrolinophane, [15]ane(phen N_2)S_3. To a well stirred suspension of Cs_2CO_3 (1.375 g, 4.22 mmol) in dmf (50 cm^3) maintained at 55 °C was added under N_2 over 20 h a solution of 2,9-bis(chloromethyl)-1,10-phenanthroline (0.585 g, 2.11 mmol) and 2-sulfanylethyl sulfide (0.33 g, 2.11 mmol) in dmf (40 cm^3). The resultant mixture was stirred for 1 h at 55 °C and for 24 h at room temperature and subsequently concentrated *in vacuo*. The residue was extracted into CH_2Cl_2 (100 cm^3) and the organic extract filtered, washed with water, dried and concentrated *in vacuo*. The resulting deep yellow residue was purified by flash chromatography on silica gel using a mixture of CH_2Cl_2–$MeCO_2Et$–EtOH (5:1:0.25 v/v/v ratio) as eluent to give 0.52 g (69% yield) of the desired compound as a pale yellow product which was shown to be a single component by TLC analysis; m.p. 208 °C [Found (Calc. for $C_{18}H_{18}N_2S_3$): C, 60.0 (60.3); H, 5.4 (5.0); N, 7.5 (7.8); S, 27.0 (26.8)%]. NMR: ^{13}C (CH_2Cl_2), δ 159.46, 144.64, 137.13, 127.32, 125.81, 122.59, 37.06, 33.63 and 32.01; ^1H ($CDCl_3$), δ 8.21 (d, 2 H, J = 8.46), 7.75 (s, 2 H), 7.59 (d, 2 H, J = 8.45 Hz), 4.11 (s, 4 H), 3.06 (m, 4 H) and 2.7 (m, 4 H). Electronic spectrum (CH_2Cl_2): λ_{max} = 236 (ε_{max} = 42 290), 273 (20 470) and 289 nm (17 880 dm^3 mol^{-1} cm^{-1}). Mass spectrum (electron impact, EI): m/z = 358 {[15]ane(phen N_2)S_3}, 272 {[15]ane(phen N_2)S_3 − $(CH_2)_2S(CH_2)_2$} and 178 (phen) with the correct isotopic distribution.

$[Ni\{[15]ane(phen\ N_2)S_3\}(NCMe)][BF_4]_2$. A mixture of [15]ane(phen N_2)S_3 (100 mg, 0.28 mmol) and $NiCl_2{\cdot}6H_2O$ (66 mg, 0.28 mmol) were refluxed together in MeCN–water (80 cm^3, 1:1 v/v ratio) under N_2 for 2 h. Addition of a large excess of NH_4BF_4 and concentration *in vacuo* afforded the purple species $[Ni\{[15]ane(phen\ N_2)S_3\}(H_2O)][BF_4]_2$ (100 mg, 59% yield) [Found (Calc. for $C_{18}H_{20}B_2F_8N_2NiOS_3$): C, 35.2 (35.5); H, 3.60 (3.25); N, 4.65 (4.60); S, 15.4 (15.8)%]. Recrystallisation of the product by slow diffusion of Et_2O in an MeCN solution of the complex gave $[Ni\{[15]ane(phen\ N_2)S_3\}(NCMe)][BF_4]_2$ (85 mg, 48% yield) as well shaped blocks of purple crystals (m.p. 200 °C with decomposition) [Found (Calc. for $C_{20}H_{21}B_2F_8N_3NiS_3$): C, 37.7 (38.0); H, 3.5 (3.3); N, 7.0 (6.7); S, 15.3 (15.2)%]. Electronic spectrum: (MeCN), λ_{max} = 206 (ε_{max} = 23 130), 228 (30 830), 274 (25 700), 298 (10 390), 542 (36), 588 (27), 858 (61) and 970 nm (31 dm^3 mol^{-1} cm^{-1}); $10Dq$ = 11 655 cm^{-1}, B = 876;[2] (dmf), λ_{max} = 564 (ε_{max} = 40), 891 (68) and 979 nm (55 dm^3 mol^{-1} cm^{-1}); $10Dq$ = 11 220 cm^{-1}.

$[NiCl\{[15]ane(phen\ N_2)S_3\}]BF_4{\cdot}dmf$. This complex was obtained using the same synthetic procedure as for $[Ni\{[15]ane(phen\ N_2)S_3\}(NCMe)][BF_4]_2$ above except that 1 equivalent of NH_4BF_4 was added to the reaction mixture after reflux for 2 h. A deep green power was obtained on concentration *in vacuo*. Recrystallisation was achieved by slow diffusion of Et_2O vapour into a solution of the complex in dmf and afforded $[NiCl\{[15]ane(phen\ N_2)S_3\}]BF_4{\cdot}dmf$ (100 mg, 59% yield) as well shaped blocks of deep green crystals (m.p. 230 °C with decomposition) [Found (Calc. for $C_{21}H_{25}BClF_4N_3NiOS_3$): C, 41.2 (41.2); H, 4.20 (4.10); N, 6.75 (6.85); S, 15.75 (15.7)%]. Electronic spectrum: (MeCN), λ_{max} = 227 (ε_{max} = 24 360), 274 (20 840) and 297 nm (7760 dm^3 mol^{-1} cm^{-1}); (dmf), λ_{max} = 563 (ε_{max} = 54), 579 (52), 916 (55) and 1011 nm (45 dm^3 mol^{-1} cm^{-1}); $10Dq$ = 10 920 cm^{-1}.

$[NiI\{[15]ane(phen\ N_2)S_3\}][I_3]$. This complex was obtained by addition of $NBu^n{}_4I$ (23.4 mg, 0.063 mmol) and I_2 (16.1 mg, 0.063 mmol) to a solution of $[Ni\{[15]ane(phen\ N_2)S_3\}(NCMe)][BF_4]_2$ (20 mg, 0.032 mmol) in MeCN. Over several days black crystals were formed (15 mg, 51.7% yield), m.p. 230 °C with decomposition [Found (Calc. for $C_{18}H_{18}I_4N_2NiS_3$): C, 23.35 (23.35); H, 1.95 (1.95); N, 3.00 (3.00); S, 10.4 (10.4)%]. Electronic spectrum: (MeCN), λ_{max} = 228 (ε_{max} = 33 500), 275 (24 530) and 298 nm (10 740 dm^3 mol^{-1} cm^{-1}); (dmf), λ_{max} = 555 (ε_{max} = 67), 912 (60) and 1057 nm (32 dm^3 mol^{-1} cm^{-1}); $10Dq$ = 10 970 cm^{-1}.

2,5,9,12-Tetrathia[13],(2,9)-1,10-phenanthrolinophane, [19]ane(phen N_2)S_4. To a well stirred suspension of Cs_2CO_3 (1.22 g, 3.76 mmol) in dmf (80 cm^3) maintained at 55 °C was added a solution of 2,9-bis(chloromethyl)-1,10-phenanthroline (0.50 g, 1.88 mmol) and 3,7-dithianonane-1,9-dithiol (0.41 g, 1.88 mmol) in dmf (50 cm^3) under N_2 over 24 h. The resultant mixture was stirred for 1 h at 55 °C and for 24 h at room temperature and subsequently concentrated *in vacuo*. The red oil obtained was dissolved in CH_2Cl_2 and the solution treated under reflux for 5 min with charcoal under N_2, filtered, and the solvent removed *in vacuo*. The orange oil obtained was dissolved in the minimum volume of CH_2Cl_2 and the solution poured slowly dropwise into hot EtOH with vigorous stirring (3 cm^3). The mixture was allowed to stand at −20 °C overnight. The reddish precipitate formed was discarded and the mother-liquor allowed to stand overnight again at −20 °C. A pale yellow powder of the desired compound was isolated and found to be pure by TLC analysis (199 mg, 20% yield), m.p. 129–130 °C [Found (Calc. for $C_{21}H_{24}N_2S_4$): C, 58.0 (58.3); H, 5.2 (5.6); N, 6.3 (6.5); S, 29.3 (29.6)%]. NMR: ^{13}C ($CDCl_3$), δ

Table 6 Summary of crystal data

Compound	$[Ni\{[15]ane(phen\ N_2)S_3\}(NCMe)][BF_4]_2$	$[NiCl\{[15]ane(phen\ N_2)S_3\}]BF_4\cdot dmf$	$[NiI\{[15]ane(phen\ N_2)S_3\}](I_3)$	$[Ni_2Cl_2\{[19]ane(phen\ N_2)S_4\}_2](BF_4)_2\cdot 3MeNO_2$	$[Ni_2Cl_2\{[12]ane(py\ N)S_3\}_2](BF_4)_2\cdot 1.5MeNO_2$
Formula	$C_{20}H_{21}B_2F_8N_3NiS_3$	$C_{21}H_{25}BClF_4N_3NiOS_3$	$C_{18}H_{18}I_4N_2NiS_3$	$C_{45}H_{57}B_2Cl_2F_8N_7Ni_2O_6S_8$	$C_{23.5}H_{34.5}B_2Cl_2F_8N_{3.5}Ni_2O_3S_6$
M	631.82	612.59	925.85	1410.4	968.34
Crystal appearance	Purple prism	Purple-green block	Deep blue plate	Green sphenoid	Blue column
Crystal size/mm	0.18 × 0.13 × 0.12	0.66 × 0.50 × 0.49	0.40 × 0.40 × 0.10	0.70 × 0.70 × 0.20	0.62 × 0.33 × 0.27
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2_12_12_1$ (no. 19)
a/Å	11.386(2)	10.857(3)	9.4369(9)	10.469(4)	9.484(4)
b/Å	19.700(3)	11.051(3)	9.5282(9)	25.357(12)	16.420(7)
c/Å	11.978(3)	11.101(3)	15.3147(11)	23.551(11)	24.970(12)
α/°		91.88(2)	74.160(6)		
β/°	107.65(2)	111.25(2)	83.760(6)	100.21(4)	
γ/°		99.77(2)	68.304(10)		
U/Å^3	2560.3	1216.9	1230.9	6153	3889
No. reflections for cell refinement	25	42	25	40	53
2θ Range/°	18–30	29–35	9–30	20–28	30–34
D_c/g cm^{-3}	1.639	1.672	2.498	1.523	1.654
Z	4	2	2	4	4
T/K	293	150	293	150	150
Diffractometer	Enraf-Nonius CAD4	Stoe Stadi-4	Siemens P4	Stoe Stadi-4	Stoe Stadi-4
μ(Mo-Kα)/mm^{-1}	1.07	1.217	6.071	1.044	1.499
F(000)	1280	628	856	2896	1968
$2\theta_{max}$/°	50	50	50	45	50
hkl Ranges	0–13, 0–23, −14 to 14	−12 to 11, −13 to 13, 0–13	−1 to 11, −10 to 10, −18 to 18	−11 to 11, 0–23, 0–25	−11 to 10, −1 to 19, −1 to 29
Reflections collected	4533	4210	5163	9804	6666
Unique reflections, R_{int}	4533, —	4210, —	4299, 0.026	7736, 0.045	5751, 0.020
Observed reflections	3468 [$I \geqslant 3\sigma(I)$]	3855 [$I \geqslant 2\sigma(I)$]	3108 [$I \geqslant 2\sigma(I)$]	3868 [$I \geqslant 2\sigma(I)$]	5121 [$I \geqslant 2\sigma(I)$]
Parameters refined	334	319	254	728	453
Refined on	*F*	F^2	F^2	F^2	F^2
Weighting schemes:					
$w^{-1} = [\sigma^2(I) + (pF_o^2)^2]^{\frac{1}{2}}$: p =	0.04	—	—	—	—
$w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$: x,y =	—	0.053, 1.13	0.150, 0.147	0.175, 52.4	0.052, 2.73
$P = \frac{1}{3}[\max(F_o^2, 0) + 2F_c^2]$					
R	0.042	0.0291	0.0626	0.1084	0.0360
R′/*wR*	0.057	0.0903	0.1797	0.3721	0.1067
S	2.06	0.999	1.033	1.010	1.067
Minimum, maximum in final Δ*F* synthesis/e Å^{-3}	+0.57, −0.36	+0.44, −0.48	+1.39, −1.78	+0.76, −0.58	+0.78, −0.28

159.87, 144.68, 136.98, 127.62, 126.13, 122.93, 38.97, 31.70, 31.35, 29.82 and 28.65; ^1H ($CDCl_3$), δ 8.23 (d, 2 H, J = 8.37), 7.87 (d, 2 H, J = 8.36), 7.76 (s, 2 H), 4.31 (s, 4 H), 2.71 (m, 4 H), 2.61 (m, 4 H), 2.36 (t, 4 H, J = 5.96 Hz) and 1.57 (m, 2 H). Electronic spectrum (CH_2Cl_2): λ_{max} = 236 (ε_{max} = 54 330), 272 (32 180) and 286 nm (28 100 $dm^3\ mol^{-1}\ cm^{-1}$). Mass spectrum (EI): m/z = 432 {[19]ane(phen $N_2)S_4$}, 206 {[19]ane(phen $N_2)S_4 - (CH_2)_2S(CH_2)_3S(CH_2)_2$} and 178 (phen) with correct isotopic distribution.

$[Ni_2Cl_2\{[19]ane(phen\ N_2)S_4\}_2][BF_4]_2\cdot 3MeNO_2$. A mixture of [19]ane(phen $N_2)S_4$ (50 mg, 0.116 mmol), $NiCl_2\cdot 6H_2O$ (27.47 mg, 0.116 mmol) and MeCN–water (1 : 1 v/v ratio, 40 cm^3) was refluxed under N_2 for 2 h. Addition of a large excess of NH_4BF_4 to the resultant green solution and concentration *in vacuo* afforded a green powder (38% yield). Recrystallisation of the product by slow diffusion of Et_2O vapour into a solution of the complex in $MeNO_2$ gave green crystals of $[Ni_2Cl_2\{[19]ane(phen\ N_2)S_4\}_2][BF_4]_2\cdot 3MeNO_2$ (20 mg, 23.5% yield), m.p. 245 °C with decomposition [Found (Calc. for $C_{45}H_{57}B_2Cl_2F_8N_7Ni_2O_6S_8$): C, 38.5 (38.3); H, 4.25 (4.05); N, 6.5 (6.9); S, 18.7 (18.2)%]. Electronic spectrum: (MeCN), λ_{max} = 206 (ε_{max} = 34 740), 230 (35 110), 278 (28 270), 630 (20) and 1037 nm (38 $dm^3\ mol^{-1}\ cm^{-1}$); $10Dq$ = 9640 cm^{-1}; (dmf), λ_{max} = 642 (ε_{max} = 15) and 1070 nm (42 $dm^3\ mol^{-1}\ cm^{-1}$); $10Dq$ = 9350 cm^{-1}.

$[Ni_2Cl_2\{[12]ane(py\ N)S_3\}_2][BF_4]_2\cdot 1.5MeNO_2$. The compound [12]ane(py N)S_3 (prepared according to the literature method)[5,23] (100 mg, 3.88×10^{-4} mol), $NiCl_2\cdot 6H_2O$ (92.3 mg, 3.88×10^{-4} mol) and MeCN–water (1 : 1 v/v, 80 cm^3) were refluxed under N_2 for 2 h. An excess of NH_4BF_4 was added to the resultant blue solution and the solvent removed *in vacuo*. The residue was recrystallised twice from $MeNO_2$ and Et_2O to yield blue crystals of $[Ni_2Cl_2\{[12]ane(py\ N)S_3\}_2][BF_4]_2\cdot 1.5MeNO_2$ (50 mg, 16% yield) [Found (Calc. for $C_{23.5}H_{34.5}B_2Cl_2F_8N_{3.5}Ni_2O_3S_6$): C, 29.2 (29.2); H, 3.6 (3.6); N, 5.5 (5.1); S, 19.5 (19.9)%]. Electronic spectrum: ($MeNO_2$), λ_{max} = 995 (ε_{max} = 98), 896 (95) and 557 nm (30 $dm^3\ mol^{-1}\ cm^{-1}$).

Crystallography

Crystal data for all four structure determinations appear in Table 6. Only special features of the analyses are noted here.

$[Ni\{[15]ane(phen\ N_2)S_3\}(NCMe)][BF_4]_2$. This compound is polymorphic: its orthorhombic form [space group *Pbca* (no. 61), a = 18.232(6), b = 12.671(4), c = 21.866(7) Å] is stable under ordinary conditions but suffered rapid decay of the scattering power of the crystal on X-ray exposure. Therefore a limited set of data could be collected, sufficient only to ascertain the nature of the compound. However, crystals of the monoclinic form were stable to X-radiation and allowed a satisfactory structure determination. Data were acquired as ω–2θ scans and corrected for the effects of absorption by means of ψ scans, giving minimum and maximum corrections of 0.938 and 1.000 respectively. The structure was solved by a combination of heavy atom and Fourier methods.[30] All non-H atoms were refined anisotropically and H atoms were placed in calculated positions, thereafter to ride on their parent atoms.

$[NiCl\{[15]ane(phen\ N_2)S_3\}]BF_4\cdot dmf$. The crystal was cooled to 150 K using an Oxford Cryosystems open-flow nitrogen cryostat[31] and data were acquired as ω–θ scans using on-line profile fitting.[32] Absorption corrections (maximum and minimum transmission factors 0.447 and 0.641 respectively) were applied and the structure was solved by a combination of direct and Fourier methods.[33,34] All non-H atoms were refined anisotropically and H atoms were placed in calculated positions, except for those of solvate methyl groups which were located from a ΔF synthesis: thereafter all were allowed to ride on their parent atoms.[34]

$[NiI\{[15]ane(phen\ N_2)S_3\}][I_3]$. Data were acquired as ω–2θ scans and corrected for the effects of absorption by means of ψ scans, giving minimum and maximum corrections of 0.203 and 0.468 respectively. The structure was solved and refined as for $[Ni\{[15]ane(phen\ N_2)S_3\}(NCMe)][BF_4]_2$ above.[33,34] The largest features in the final ΔF synthesis lie within 1.3 Å of the iodine atoms.

$[Ni_2Cl_2\{[19]ane(phen\ N_2)S_4\}_2][BF_4]_2\cdot 3MeNO_2$. As the crystals were sensitive to solvent loss they were transferred from their mother-liquor to the cold stream[31] on the diffractometer under perfluoropolyether oil (Riedel de Häen type RS3000). Data were collected as ω scans with on-line profile fitting:[32] corrections were necessary for absorption (minimum and maximum transmission factors 0.204 and 0.254 respectively) and, despite cooling the crystal, for linear isotropic crystal decay (11%). The structure was solved as above[33,34] but disorder in one macrocycle, in the BF_4^- anions and in some solvent molecules required modelling with a total of 416 restraints to B–F, C–C and S–C distances and to solvate molecules. Two solvates were fully occupied and two had half occupancy. All ordered atoms heavier than B were refined anisotropically while B, disordered and partially occupied atoms were allowed only isotropic thermal parameters.[34] Apart from those in solvate methyl groups, where they were located from ΔF syntheses, H atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms. The extensive disorder is undoubtedly the main reason for the rather high agreement indices.

$[Ni_2Cl_2\{12ane(py\ N)S_3\}_2][BF_4]_2\cdot 1.5MeNO_2$. Data were collected at 150 K[31] as ω–θ scans and corrected for absorption by means of ψ scans, giving minimum and maximum corrections of 0.547 and 0.674 respectively. The structure was solved by direct methods[33] and refined[34] with anisotropic thermal motion for all fully occupied non-H atoms, disorder and partial occupancy of the solvates having been identified and modelled. Racemic twinning was detected and successfully included in the model.

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 186/164.

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