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Synthesis and complexation of nickel(II) and copper(II) by pendant-arm alcohol derivatives of [9]aneNS$_2$ (7-aza-1,4-dithiacyclononane)

Alexander J. Blake,[a] Jonathan P. Danks,[a] Ian A. Fallis,[b] Andrew Harrison,[b] Wan-Sheung Li,[a] Simon Parsons,[b] Steven A. Ross,[b] Gavin Whittaker[b] and Martin Schröder *[a]

[a] *School of Chemistry, The University of Nottingham, University Park, Nottingham, UK NG7 2RD*
[b] *Department of Chemistry, The University of Edinburgh, Edinburgh, UK EH9 3JJ*

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A simplified procedure for the preparation of [9]aneNS$_2$ (7-aza-1,4-dithiacyclononane) is described. The structure of the complex [Cu([9]aneNS$_2$)$_2$]$^{2+}$ confirms that the Cu(II) centre is in a distorted octahedral environment, Cu–S(1) 2.5469(14), Cu–S(4) 2.5386(13), Cu–N(7) 2.016(4) Å. Reaction of [9]aneNS$_2$ with isobutylene oxide or 2,2-diphenyloxirane gives the alcohol derivatives, HL^1 and HL^2, respectively. The 1 : 1 metal : ligand complex [Cu$_2$(L^1)$_2$]$^{2+}$ was found to be binuclear with the alcohol functions deprotonated to form alkoxide bridges between two Cu(II) centres, Cu–N(1) 2.042(4), Cu–S(4) 2.452(2), Cu–S(7) 2.430(2), Cu–O(14) 1.927(4), Cu–O(14′) 1.922(4), Cu–Cu′ 3.0063(9) Å, Cu–O–Cu′ 102.7(2)°. Magnetochemical data for this complex confirm antiferromagnetic coupling between the two Cu(II) centres with $2J = -417 \pm 2$ cm^{-1}. With Ni(II) the complex [Ni(HL^1)(CH$_3$CO$_2$)]$^+$ can be isolated, the structure of which shows it to be a monomer with the ligand HL^1 acting as a tetradentate ligand to the metal centre, Ni–N(1) 2.064(3), Ni–S(4) 2.3658(12), Ni–S(7) 2.3875(13), Ni–O(14) 2.061(3) Å. A chelating acetate ligand completes the distorted octahedral geometry, Ni–O(16) 2.098(3), Ni–O(17) 2.102(3) Å.

Introduction

The co-ordination chemistry of [9]aneN$_3$[1] and [9]aneS$_3$[2] has been thoroughly investigated over recent years. The mixed-donor analogue [9]aneN$_2$S has also been the subject of extended study,[3–5] particularly by Mattes and co-workers.[6] In contrast however, the co-ordination chemistry and functionalisation of [9]aneNS$_2$, which completes the homologous group of nine-membered N/S-donor macrocycles, is by far the least studied.[3] This is due to the synthetic difficulties and costs encountered in the synthesis of the ligand itself. Derivatives of [9]aneNS$_2$ incorporating monodentate donors would be expected to form potentially four-co-ordinate, unsaturated complexes in the absence of additional ligands.

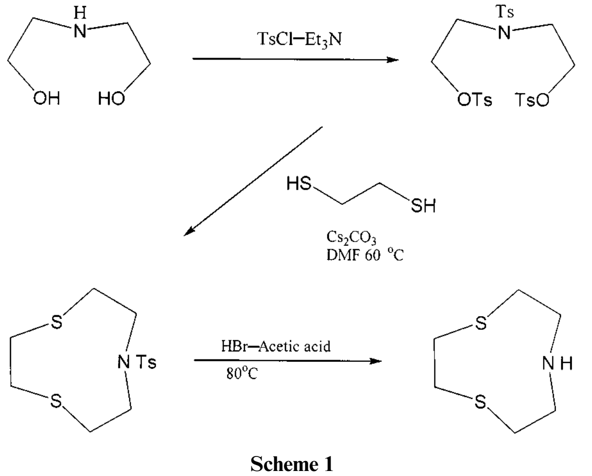
We report herein a simplified synthesis of [9]aneNS$_2$ (7-aza-1,4-dithiacyclononane) and its bis-sandwich Cu(II) complex [Cu([9]aneNS$_2$)$_2$]$^{2+}$. The reaction of [9]aneNS$_2$ with isobutylene oxide or 2,2-diphenyloxirane to give pendant arm alcohol derivatives HL^1 and HL^2 and complexes with Cu(II) and Ni(II) are also reported.

Results and discussion

The synthesis of 7-aza-1,4-dithiacyclononane, [9]aneNS$_2$, was first reported by both Parker[7] and McAuley[8] independently in 1990. Whilst the ring-closure step for both [9]aneN$_3$ and [9]aneN$_2$S does not require high-dilution techniques to avoid appreciable polymerisation, this is not the case for [9]aneNS$_2$ and [9]aneS$_3$, which both involve the addition of the reactants over several hours into a large volume of solvent. Both routes employed by these workers were essentially the same differing only in the final detosylation step. McAuley reported difficulty in this step and finally used phosphoric acid to afford the product macrocycle in 50% yield.[8] Parker and co-workers opted for deprotection using HBr–acetic acid and reported a yield of 73% for the deprotection step. McAuley has since reported the synthesis of [10]aneNS$_2$ *via* an alternative route requiring fewer steps.[9] We have modified the procedure for the synthesis of [10]aneNS$_2$ and used it for the synthesis of [9]aneNS$_2$ thereby simplifying the overall synthesis of this macrocyclic system.

Ligand synthesis

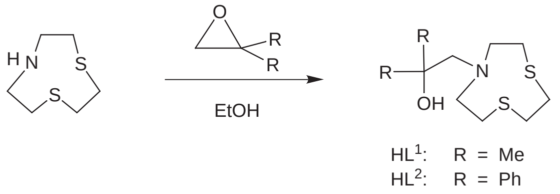
The synthesis of [9]aneNS$_2$ was accomplished *via* a modification of the three-step route reported for [10]aneNS$_2$ (Scheme 1).[9] Reaction of diethanolamine with *p*-toluenesulfonyl chloride in triethylamine at 0 °C gives the corresponding tritosylate in 81% yield. A solution of the tritosylate and ethane-1,2-dithiol in DMF was added over a period of 12 h to a suspension of Cs$_2$CO$_3$ in DMF under high-dilution conditions. This is followed by a further addition of Cs$_2$CO$_3$ to the reaction mixture, followed by another slow addition of a solution of the tritosylate and ethane-1,2-dithiol in DMF over 12 h. The ring-closure step proceeds typically in 32% yield in our hands.



Scheme 1

Detosylation was carried out according to Parker and co-workers[7] using HBr–acetic acid[2] and subsequent base extraction affords the free cyclic amine as a white solid in 78% yield.

Functionalisation of [9]aneNS$_2$ was achieved *via* reaction of [9]aneNS$_2$ in EtOH with 3 equivalents of isobutylene oxide sealed in a sample vial for 10 days. Removal of the solvent led to the isolation of the pendant-arm alcohol derivative HL^1 in quantitative yield (Scheme 2).



Scheme 2

The potential co-ordination properties of functionalised pendant-arm macrocycles can be altered by changing the steric bulk of the substituents on the pendant arm. Peacock and co-workers have reported[10] that by changing the substituent on the pendant-arm from methyl to isopropyl, a marked difference in complex formation can be observed. In general, mononuclear complexes of divalent metal ions incorporating pendant-alcohol donors are often found to be protonated, the retention of the alcohol proton in divalent metal–ion complexes being attributed to the poorer Lewis acidity of M(II) ions in comparison with M(III) ions. Also, the higher the oxidation state of the metal centre co-ordinated to an alcohol, the more acidic is the alcohol proton.[10] Interestingly, mononuclear M(II) complexes with alkoxide ligands can be prepared if electron-withdrawing groups are present, thereby increasing the acidity of the alcohol proton. An example of such a complex is Na$_2$-Cu[OCH(CF$_3$)$_2$]$_4$.[11]

We were interested in the preparation of pendant-arm derivatives of [9]aneNS$_2$ containing bulky substituents on the pendant-arm in order to compare the co-ordination behaviour with that of HL^1. The macrocycle HL^2 was prepared from the reaction between [9]aneNS$_2$ and 2,2-diphenyloxirane. The oxirane was prepared according to the method reported by Corey,[12] and reaction of 2,2-diphenyloxirane with [9]aneNS$_2$ in refluxing EtOH for 2 days, followed by flash column chromatography on alumina affords HL^2 in 52% yield.

Complexation studies

[Cu([9]aneNS$_2$)$_2$][PF$_6$]$_2$. Addition of Cu(NO$_3$)$_2$·3H$_2$O in EtOH to [9]aneNS$_2$ in EtOH immediately affords a deep green solution. Counter-anion exchange can be achieved by the addition of excess NH$_4$PF$_6$ in H$_2$O to give the complex [Cu([9]aneNS$_2$)$_2$][PF$_6$]$_2$ as a deep green solid. The stoichiometry of the complex was confirmed by mass spectrometry and elemental analysis. Slow diffusion of Et$_2$O into a solution of the complex in MeCN led to the isolation of green columnar crystals suitable for X-ray analysis. The crystal structure of [Cu([9]aneNS$_2$)$_2$][PF$_6$]$_2$ confirms (Fig. 1, Table 1) facial co-ordination of the two tridentate ligands to Cu(II). The Cu(II) centre, which occupies a crystallographic inversion centre, is co-ordinated by one N- and two S-donors from each ligand to give an overall distorted octahedral geometry. Two geometrical isomers are possible for [Cu([9]aneNS$_2$)$_2$]$^{2+}$, with the N-donors of the rings positioned either mutually *syn* or *anti* to one another. In this case the *anti* isomer is observed with four S-atoms bound equatorially and two N-atoms occupying the axial positions, Cu–S 2.5469(14), 2.5386(13), Cu–N 2.016(4) Å. Interestingly, in the case of [Cu([9]aneN$_2$S)$_2$]$^{2+}$, Cu–N 2.09(1), 2.01(1), Cu–S 2.707(1) Å,[5] the Jahn–Teller distortion manifests itself by elongation of the two axial S-atoms, which are *anti* to one another. In [Cu([9]aneNS$_2$)$_2$]$^{2+}$ the Jahn–Teller distortion manifests itself in the Cu–N distances, with relatively elongated Cu–S distances. The structure of [Cu([9]aneNS$_2$)$_2$]$^{2+}$ is therefore similar to [Cu([18]aneN$_2$S$_4$)]$^{2+}$, Cu–N 2.007(13), 2.036(12), Cu–S 2.577(5), 2.487(5), 2.528(5), 2.578(5) Å,[13] the larger ligand offering the same co-ordination donor set and geometry to the metal centre as two [9]aneNS$_2$ ligands. The average Cu–S and Cu–N bond distances of [Cu([9]aneNS$_2$)$_2$]$^{2+}$ and [Cu([18]aneN$_2$S$_4$)]$^{2+}$ are very similar, indicating that the metal centre is dominating the co-ordination environment in both cases. The X-band EPR spectrum of [Cu([9]aneNS$_2$)$_2$][PF$_6$]$_2$ recorded as a frozen glass at 77 K in MeCN shows a strong broad spectrum with $g_1 = 2.122$, $g_2 = 2.056$, $g_3 = 2.009$.

Table 1 Selected bond lengths (Å) and angles (°) for [Cu([9]aneNS$_2$)$_2$][PF$_6$]$_2$

Cu–S1	2.5469(14)	C3–S4	1.812(5)
Cu–S4	2.5386(13)	S4–C5	1.819(6)
Cu–N7	2.016(4)	C5–C6	1.512(7)
S1–C2	1.814(5)	C6–N7	1.494(7)
S1–C9	1.816(6)	N7–C8	1.496(7)
C2–C3	1.502(8)	C8–C9	1.496(9)
S1–Cu–S4	84.41(4)	C3–S4–C5	103.4(3)
S1–Cu–N7	85.79(13)	C6–C5–S4	112.0(4)
S4–Cu–N7	83.74(13)	N7–C6–C5	114.0(4)
C2–S1–C9	102.7(3)	C6–N7–C8	111.7(4)
C3–C2–S1	115.0(4)	C9–C8–N7	114.0(4)
C2–C3–S4	118.1(4)	C8–C9–S1	114.4(4)

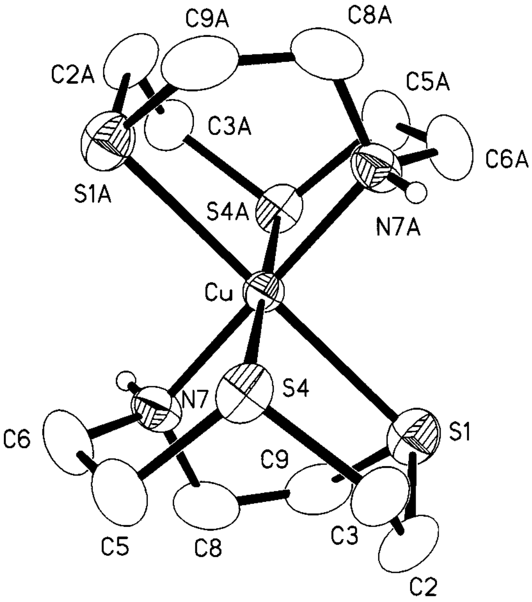


Fig. 1 View of structure of [Cu([9]aneNS$_2$)$_2$][PF$_6$]$_2$ with numbering scheme adopted.

There are few sandwich complexes of type [M([9]aneNS$_2$)$_2$]$^{n+}$ reported in the literature. The structure of [Ni([9]aneNS$_2$)$_2$]$^{2+}$ shows[8] octahedral co-ordination at the metal centre with the two nitrogen atoms *anti* to one another and the four S-donors and the Ni(II) centre lying in the equatorial plane, Ni–N 2.104(4), Ni–S 2.408(1), 2.415(1) Å. The structure of [Zn([9]aneNS$_2$)$_2$]$^{2+}$, Zn–N 2.121(4), Zn–S 2.540(1), 2.546(1) Å, shows[14] a similar structural motif to [Cu([9]aneNS$_2$)$_2$]$^{2+}$ and [Ni([9]aneNS$_2$)$_2$]$^{2+}$. In [Pd([9]aneNS$_2$)$_2$]$^{2+}$,[15] the Pd(II) centre is co-ordinated to two N- and two S-donors in a square-planar configuration with Pd–N 2.081(9), Pd–S 2.322(3) Å. Two long-range apical interactions are provided by the two remaining sulfur atoms at 3.011(3) Å.

[Cu([9]aneNS$_2$)$_2$]$^{2+}$ exhibits an irreversible Cu$^{II/I}$ reduction at $E_{pc} = -0.92$ V *vs.* Fc/Fc$^+$. Significantly, this is 600 mV more cathodic than the reversible couple observed for [Cu([18]aneN$_2$S$_4$)]$^{2+}$,[13] indicating that the larger [18]aneN$_2$S$_4$ is able to stabilise the Cu(I) oxidation state more effectively than

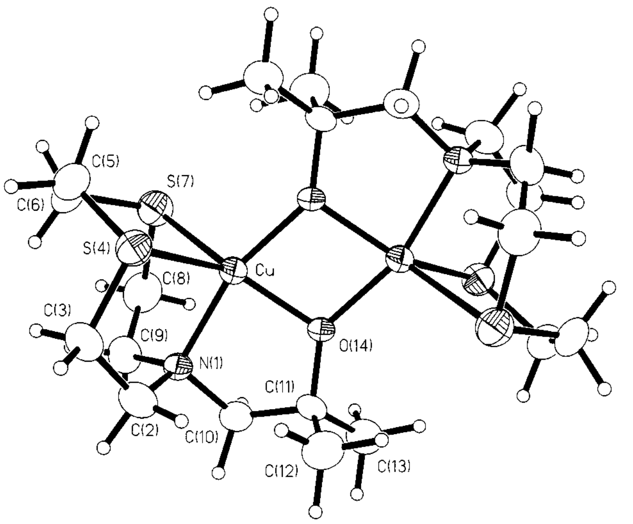


Fig. 2 View of structure of $[Cu(L^1)]_2[BPh_4]_2$ with numbering scheme adopted.

[9]aneNS$_2$. The irreversibility of the $\mathrm{Cu^{II/I}}$ couple in $[Cu([9]aneNS_2)_2]^{2+}$ probably reflects the breaking up of the bis-sandwich structure leading to the formation of Cu(I) oligomers.[16] In general, changing the donor atoms from nitrogen to sulfur has a dramatic effect upon the electrochemistry of Cu(II) complexes. For example, $[Cu([9]aneN_3)_2]^{2+}$ has an irreversible reduction at a potential of −1.41 V *vs.* Fc/Fc$^+$.[17] On replacing the N-donors with S-donors the potential at which the $\mathrm{Cu^{II/I}}$ reduction occurs becomes more anodic, −0.92 V *vs.* Fc/Fc$^+$ for $[Cu([9]aneNS_2)_2]^{2+}$ and +0.12 V *vs.* Fc/Fc$^+$ for $[Cu([9]aneS_3)_2]^{2+}$[18] reflecting the ability of thioether S-donors to stabilise low oxidation states.

$[Cu(L^1)]_2[BPh_4]_2$. Reaction of $Cu(CH_3CO_2)_2$ with 1 equivalent of HL^1 affords, after counter-anion metathesis and recrystallisation from MeCN, a green product, analysis of which indicates the empirical formula $[Cu(L^1)]BPh_4$. The presence of only one counter anion per Cu(II) centre suggested that the ligand was deprotonated to form an alkoxide linkage. The deprotonation of an alcohol to form an alkoxide on complexation is unusual for a single 2+ cation, a 3+ charge being usually required to render the alcohol proton suitably acidic.[1,10,19] We therefore argued that a binuclear structure for this complex was likely. In principle a tetrameric cubane structure in which the alkoxide donor bridges between three Cu(II) centres was also possible, as reported for $[\{CuBr(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$[20] and for related phenoxy-bridged Schiff-base Cu(II) complexes.[21]

Slow evaporation of a solution of the complex in MeCN yielded green crystals suitable for X-ray structure determination. The structure shows (Fig. 2, Table 2) that the complex is indeed dimeric with the formula $[Cu(L^1)]_2[BPh_4]_2$. Each Cu(II) cation is five-co-ordinate being bound facially by the macrocycle, Cu–N 2.042(4), Cu–S 2.452(2), 2.430(2) Å. The alcohol group is deprotonated and two $[Cu(L^1)]^+$ fragments are linked by two alkoxide bridges, Cu–O 1.927(4), 1.922(4) Å, typical for bridging alkoxide linkages to Cu(II).[22–24] The overall co-ordination geometry at the metal is distorted trigonal bipyramidal, with S(4), S(7) and O(14) lying in the equatorial plane and N(1) and O(14′) occupying the axial positions.

Two Cu(II) centres bridged by alkoxide ligands can show interesting magnetic properties.[24,25] Exchange processes can occur between the metal centres and the unpaired electrons can couple either antiferromagnetically or ferromagnetically. Antiferromagnetic coupling leads to the observation of lower than the predicted spin-only magnetic moment of 1.72 μ_B per metal centre. Conversely, ferromagnetic coupling leads to a value greater than that predicted.

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu(L^1)]_2[BPh_4]_2$

Cu–N1	2.042(4)	C3–S4	1.812(6)
Cu–S4	2.452(2)	S4–C5	1.804(6)
Cu–S7	2.430(2)	C5–C6	1.515(8)
Cu–O14	1.927(4)	C6–S7	1.823(6)
Cu–Cu′	3.0063(9)	S7–C8	1.818(6)
Cu–O14′	1.922(4)	C8–C9	1.501(8)
N1–C2	1.482(7)	C10–C11	1.536(8)
N1–C9	1.499(7)	C11–C12	1.521(8)
N1–C10	1.499(7)	C11–C13	1.523(8)
C2–C3	1.512(8)	C11–O14	1.420(6)
N1–Cu–S4	86.53(12)	C3–S4–C5	101.6(3)
N1–Cu–S7	89.00(12)	S4–C5–C6	118.1(4)
N1–Cu–O14	85.6(2)	C5–C6–S7	115.9(4)
S4–Cu–S7	88.39(5)	Cu–S7–C6	102.4(2)
S4–Cu–O14	135.89(12)	Cu–S7–C8	88.6(2)
S7–Cu–O14	134.67(12)	C6–S7–C8	103.00(3)
O14–Cu–O14′	77.28(15)	S7–C8–C9	114.2(4)
Cu–N1–C2	109.6(3)	N1–C9–C8	113.1(5)
Cu–N1–C9	112.9(3)	N1–C10–C11	113.8(4)
Cu–N1–C10	104.6(3)	C10–C11–C12	114.7(5)
C2–N1–C9	109(4(4)	C10–C11–C13	107.1(5)
C2–N1–C10	111.9(4)	C10–C11–O14	105.0(4)
C9–N1–C10	108.4(4)	C12–C11–C13	109.1(5)
N1–C2–C3	113.6(5)	C12–C11–O14	110.8(4)
C2–C3–S4	112.6(4)	C13–C11–O14	110.0(4)
Cu–S4–C3	95.1(2)	Cu–O14–C11	116.7(3)
Cu–S4–C5	101.1(2)	Cu–O14–Cu′	102.7(2)

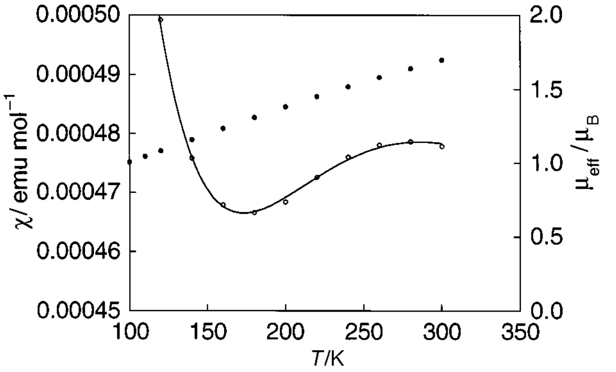


Fig. 3 Magnetic susceptibility of $[Cu(L^1)]_2[BPh_4]_2$ per mol of Cu(II) (○), emphasising the higher temperature measurements which reveal a characteristic cusp for an antiferromagnetically-coupled binuclear complex. The line through the data represents the best fit to a Bleaney–Bowers equation plus a paramagnetic term and a temperature independent term. The effective moment of the sample, once correction has been made for the temperature independent term (●).

Magnetic measurements were carried out on $[Cu(L^1)]_2[BPh_4]_2$ in the temperature range 4 to 300 K on a SQUID magnetometer (Quantum Design MPMS$_2$) in a field of 0.1 T, and corrected for the diamagnetism of the sample and holder (Fig. 3). It is apparent from this figure that two magnetic species are present: a cusp in the susceptibility centred in the region of 270 K may be fitted to the Bleaney–Bowers equation,[26] with an exchange coupling $2J$ of $-407 \pm 2\ \mathrm{cm^{-1}}$; the rise in susceptibility on further cooling indicates that the material is contaminated by a significant proportion of paramagnetic impurity, possibly arising from the presence of monomeric species in the sample. All attempts to purify the compound by recrystallisation and Sephadex column chromotography failed to remove this impurity. This may suggest that a dynamic equilibrium between monomeric and dimeric species is occurring in solution.

The form of the data, and the chemical character of the system indicate that the following expression (1) might represent

$$\chi_{\mathrm{mol}} = \mathbf{a}\frac{C}{T} + \mathbf{b}\frac{C'}{T}\left(\frac{2e^{2x}}{1 + 3e^{2x}}\right) + \chi_{\mathrm{TIP}} \qquad (1)$$

the susceptibility per mole of Cu(II) in the sample over the full experimental range of temperature, where **a** and **b** are the mole fractions of Cu(II) in the mononuclear and binuclear species respectively; the second term is the Curie Law for $S = \frac{1}{2}$ with $C = N(g_{\mathrm{monomer}}^2)\mu_B^2/4k$ (where N is the Avogadro constant, g_{monomer} is the Landé g factor for Cu(II) in the mononuclear species, μ_B is the Bohr magneton and k the Boltzmann constant); the third term is the Bleaney–Bowers equation where $C' = N(g_{\mathrm{binuclear}}^2)\mu_B^2/2k$ (where $g_{\mathrm{binuclear}}$ is the Landé g factor for Cu(II) in the binuclear complex), $x = J/kT$; and χ_{TIP} is the temperature independent susceptibility of Cu(II) (assumed to be the same in the two species). Expression (1) was fitted successfully to the data with all the parameters allowed to vary independently, yielding the optimised values $\mathbf{a} = 0.10 \pm 1$, $\mathbf{b} = 0.83 \pm 5$, $\chi_{\mathrm{TIP}} = 141 \pm 8 \times 10^{-6}$ emu mol^{-1} and $2J = 417 \pm 2$ cm^{-1}. The oberved value of the magnetic moment of 1.68 μ_B per Cu(II) at 300 K is unusually low for Cu(II), typical values lying in the range 1.9–2.3 μ_B, somewhat greater than the spin-only value of 1.732 μ_B[27] on account of spin–orbit coupling with excited orbital triplet states. χ_{TIP} is also anomalously high for Cu(II), and is more commonly about half this value. However, it should be noted that the data taken at higher temperatures correspond to a relatively weak signal for a dimer of small spins with strong antiferromagnetic coupling, and correction for the diamagnetism of the sample and container, combined with correlation between values in the fit, can lead to significant errors in fitted parameters. Thus, the value of 1.68 μ_B is smaller than that expected for a mononuclear centre but is consistent with the observed anti-ferromagnetic coupling for the complex.

Magnetic data measured using a Faraday balance afforded a value of $2J = -440$ cm^{-1}, in close accord with data obtained from the SQUID magnetometer. The X-band EPR spectrum of $[Cu(L^1)]_2[BPh_4]_2$ recorded as a frozen glass at 77 K in MeCN shows a very weak signal at $g_{\parallel} = 2.434$ and $g_{\perp} = 2.082$, with a much stronger signal based at $g = 2.01$ for the mononuclear impurity.

The size and sign of $2J$ has been demonstrated to be directly dependent upon the Cu–O–Cu angle (φ) for hydroxy-bridged dimers, assuming planarity of the Cu_2O_2 fragment.[24] An angle below 97.6° results in ferromagnetic coupling and a positive value for $2J$, while for Cu–O–Cu angles above 97.6° antiferromagnetic coupling is observed. At angles approaching 97.6° there is little or no exchange between the Cu(II) centres. Binuclear Cu(II) centres with alkoxide bridges also exhibit a dependence of $2J$ upon φ but there appears to be no such clear linear relationship.[25] More recently, Thompson and co-workers have shown that the crossover between ferromagnetic and antiferromagentic exchange in phenoxy-bridged binuclear Cu(II) centres is significantly less than 90°.[28] Significantly, the value of φ in $[Cu(L^1)]_2[BPh_4]_2$ is 102.7(2)° consistent with the observed antiferromagnetic coupling.

The cyclic voltammogram of $[Cu(L^1)]_2[BPh_4]_2$ shows irreversible reductive behaviour with two irreversible reduction waves at $E_{pc} = -0.3$ and -1.0 V *vs.* Fc/Fc$^+$. There is also an additional oxidation observed at $E_{pa} = -0.2$ V *vs.* Fc/Fc$^+$. This oxidation wave does not appear when the cyclic voltammetry experiment is carried out between the potentials 0.0 and -0.25 V, suggesting that this oxidation wave results from the daughter product of reduction of the Cu(II) dimer.

$[Cu(L^2)]_2[BPh_4]_2$. Reaction of $Cu(CH_3CO_2)_2{\cdot}H_2O$ with 1 molar equivalent of HL^2 in EtOH gives a dark green solution. Addition of excess $NaBPh_4$ afforded a grey–green solid, which was recrystallised from MeCN yielding dark green columnar crystals. The IR spectrum of this material and the analytical data suggest an overall stoichiometry $[Cu(L^2)]BPh_4$. The FAB mass spectrum of the product showed peaks for $[HL^2]^+$ and $[Cu(L^2)]^+$ at m/z 360 and 422 respectively. The colour of this material was identical to that of $[Cu(L^1)]_2[BPh_4]_2$, and the evidence suggests an overall structure $[Cu(L^2)]_2[BPh_4]_2$. Unfortunately, attempts to characterise this material by single crystal X-ray studies were unsuccessful.

Table 3 Selected bond lengths (Å) and angles (°) for $[Ni(HL^1)(CH_3CO_2)]BPh_4{\cdot}CH_3CN$

Ni–N1	2.064(3)	C5–C6	1.511(6)
Ni–S4	2.3658(12)	C6–S7	1.822(4)
Ni–S7	2.3875(13)	S7–C8	1.837(4)
Ni–O14	2.061(3)	C8–C9	1.523(6)
Ni–O16	2.098(3)	C10–C11	1.538(6)
Ni–O17	2.102(3)	C11–C12	1.532(7)
N1–C2	1.499(5)	C11–C13	1.526(7)
N1–C9	1.493(5)	C11–O14	1.452(5)
N1–C10	1.499(5)	C15–O16	1.259(5)
C2–C3	1.528(6)	C15–O17	1.290(5)
C3–S4	1.820(4)	C15–C18	1.500(7)
S4–C5	1.826(4)		
N1–Ni–S4	89.16(10)	C2–C3–S4	113.9(3)
N1–Ni–S7	88.86(10)	Ni–S4–C3	92.57(14)
N1–Ni–O14	79.06(12)	Ni–S4–C5	102.65(14)
N1–Ni–C15	129.74(14)	C3–S4–C5	101.0(2)
N1–Ni–O16	99.43(12)	S4–C5–C6	113.00(3)
N1–Ni–O17	160.01(12)	Ni–S7–C6	100.8(2)
S4–Ni–S7	89.20(4)	C5–C6–S7	115.3(3)
S4–Ni–O14	90.13(8)	Ni–S7–C8	95.23(14)
S4–Ni–C15	140.62(11)	C6–S7–C8	101.9(2)
S4–Ni–O16	171.39(9)	S7–C8–C9	111.2(3)
S4–Ni–O17	108.77(8)	N1–C9–C8	113.8(3)
S7–Ni–O14	167.91(9)	N1–C10–C11	114.0(4)
S7–Ni–C15	96.48(11)	C10–C11–C12	108.8(4)
S7–Ni–O16	90.34(9)	C10–C11–C13	113.3(4)
S7–Ni–O17	99.86(8)	C10–C11–O14	106.3(3)
O14–Ni–C15	91.69(13)	C12–C11–C13	110.0(4)
O14–Ni–O16	92.11(11)	C12–C11–O14	108.5(4)
O14–Ni–O17	91.79(11)	C13–C11–O14	109.8(4)
O16–Ni–O17	62.86(11)	Ni–O14–C11	116.0(2)
Ni–N1–C2	113.4(2)	Ni–C15–C18	177.90(3)
Ni–N1–C9	106.9(2)	O16–C15–O17	118.5(4)
Ni–N1–C10	103.8(2)	O16–C15–C18	121.4(4)
C2–N1–C9	110.80(3)	O17–C15–C18	120.1(4)
C2–N1–C10	113.5(3)	Ni–O16–C15	89.8(3)
C9–N1–C10	108.0(3)	Ni–O17–C15	88.8(2)
N1–C2–C3	114.4(3)		

$[Ni(HL^1)(CH_3CO_2)]BPh_4{\cdot}CH_3CN$. Reaction of $Ni(CH_3CO_2)_2$ with 1 equivalent of HL^1 gives, after counter-anion exchange with $NaBPh_4$ and recrystallisation from MeCN, a blue product. Infrared spectroscopy indicates the presence of macrocycle, co-ordinated acetate and BPh_4^- counter anion. The positions of the acetate stretching vibrations (1546 and 1410 cm^{-1}) suggested that it was acting as a bidentate ligand.[29] The bands do not however determine whether the ligating mode of the acetate is bidentate bridging or bidentate chelating. A structural determination was therefore undertaken to establish the mode of acetate binding. Slow evaporation of a solution of the complex in MeCN led to the isolation of crystals suitable for X-ray analysis. The crystal structure confirms (Fig. 4, Table 3) a Ni(II) centre co-ordinated by the macrocycle in the expected facial manner, Ni–N(1) 2.064(3), Ni–S(4) 2.3658(12), Ni–S(7) 2.3875(13) Å. The pendant-arm alcohol is not deprotonated and co-ordinates to the metal centre at a distance of 2.061(3) Å. The co-ordination sphere is completed by a chelating bidentate acetate ligand. The Ni(II) centre is in a very distorted octahedral geometry, much of the distortion being due to the small bite angle of the acetate of only 62.86(11)°.

Current work is aimed at the investigation of the co-ordination chemistry of these and related potential binucleating ligands as a function of steric bulk and of electronic properties of the pendant-arm system, and the study of the magnetochemical and redox properties of the resultant mono- and polynuclear complexes.

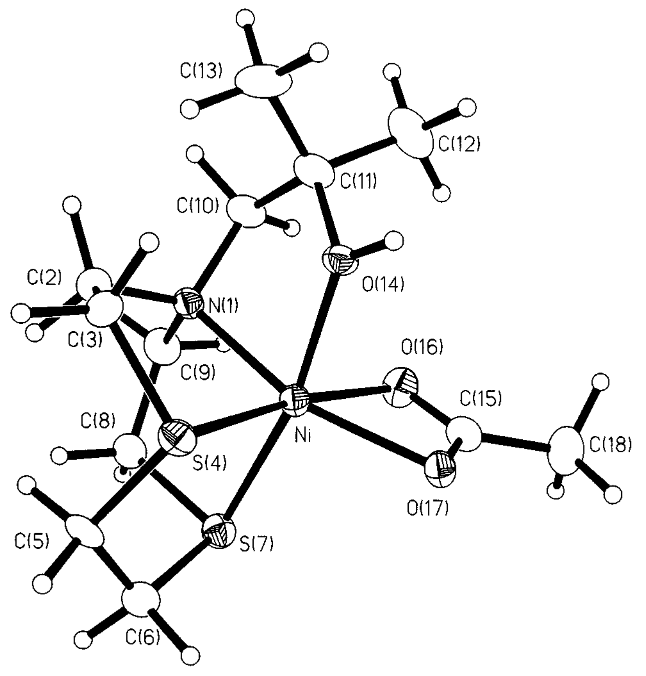


Fig. 4 View of structure of the cation [Ni(HL^1)(CH$_3$CO$_2$)]BPh$_4$·CH$_3$CN with numbering scheme adopted.

Experimental

Unless otherwise stated, commercial grade chemicals were used without further purification. Isobutylene oxide was purchased from the Lancaster Chemical Company.

Instrumental methods

Elemental analyses were carried out by the University of Nottingham Analytical Service within the School of Chemistry. Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. NMR spectra (^{1}H and ^{13}C) were recorded on a Bruker DPX300 instrument operating at 300 and 75.15 MHz respectively. Cyclic voltammetry was carried out with an Autolab PGStat20 potentiostat using a Ag–AgCl reference electrode and Bu$_4$NPF$_6$ as base electrolyte. UV/VIS spectra were recorded on a Unicam UV/VIS 2 spectrophotometer. Fast atom bombardment (FAB) and electron impact mass spectra were run on a Kratos MS50TC spectrometer. X-Band EPR spectra were recorded on a Bruker EMX EPR spectrometer employing 100 kHz modulation. Spectra were recorded as frozen glasses at 77 K under a nitrogen atmosphere. Magnetic measurements were carried out on a MPMS$_2$ SQUID magnetometer (Quantum Design), at the University of Edinburgh, operating with a magnetic field of 1000 G. Diamagnetic corrections were calculated using Pascal's constants. Single X-ray data were collected on a Stoë STADI-4 four-circle diffractometer, fitted with an Oxford Cryosystems low temperature device.[30]

Syntheses

N**,*****N*****-Bis[2-(*****p*****-tolylsulfonyloxy)ethyl]toluene-*****p*****-sulfonamide.** Diethanolamine (19.01 g, 0.181 mol) was dissolved in dry triethylamine (300 cm^3). The solution was cooled to 0 °C and *p*-toluenesulfonyl chloride (103.2 g, 0.543 mol) was added in small portions so as to keep the temperature below 5 °C. After the final addition the solution was stirred for 1 hour and the resulting white precipitate was filtered off and washed with copious amounts of water. The dried solid was recrystallised from chloroform–diethyl ether to give the product as a white solid, 82.8 g, 80.7%. δ_H(CDCl$_3$) 2.45 (3H, s, CH$_3$), 2.48 (3H, s, CH$_3$), 4.00 (4H, t, CH$_2$N), 4.13 (4H, t, CH$_2$O) and 7.30–8.0 (12H, s, aromatic H); δ_C(CDCl$_3$) 21.32, 21.46 (CH$_3$), 48.22 (CH$_2$N), 68.09 (CH$_2$O), 126.99, 127.72, 129.76, 129.82 (aromatic CH), 132.09, 134.95, 143.96 and 145.03 (aromatic quaternary).

7-(***p*****-Tolylsulfonyl)-7-aza-1,4-dithiacyclononane.** A 5 litre three necked round bottom flask equipped with a mechanical stirrer, a precision dropping funnel and a reflux condenser was purged with nitrogen. Freshly distilled DMF (2.2 litres) and dry caesium carbonate (13.04 g, 0.04 mol) were added and the mixture heated to 60 °C. A solution comprising ethane-1,2-dithiol (1.88 g, 0.02 mol) and *N*,*N*-bis[2-(*p*-tolylsulfonyloxy)ethyl]toluene-*p*-sulfonamide (11.35 g, 0.02 mol) in DMF (300 cm^3) was added *via* the dropping funnel over a period of 12 hours. After the addition was complete a second portion of caesium carbonate (13.04 g, 0.04 mol) was added to the flask followed by a further addition of ethane-1,2-dithiol (1.88 g, 0.02 mol) and *N*,*N*-bis[2-(*p*-tolylsulfonyloxy)ethyl]toluene-*p*-sulfonamide (11.35 g, 0.02 mol) in DMF (300 cm^3) over 12 hours. After the reactants had been added the yellow solution was heated at 60 °C for a further 6 hours. The DMF was removed *in vacuo* to yield a brown paste which was redissolved in CH$_2$Cl$_2$ and washed with a copious amount of water. The solvent was again removed and the residue redissolved in the minimum amount of CH$_2$Cl$_2$–MeOH and eluted through a pad of flash silica to remove the majority of the polymeric impurities. The solvent was removed to reveal an off-white sticky solid, which on repeated recrystallisation from hot ethanol gave the pure tosylated macrocycle as white crystals 4.1 g, 32%. δ_H(CDCl$_3$) 2.43 (3H, s, CH$_3$), 3.11 (4H, t, $\mathrm{NCH_2C}H_2\mathrm{S}$), 3.15 (4H, s, $\mathrm{SC}H_2\mathrm{C}H_2\mathrm{S}$), 3.40 (4H, t $\mathrm{NC}H_2\mathrm{CH_2S}$) and 7.31–7.70 (8H, m, aromatic H).

7-Aza-1,4-dithiacyclononane ([9]aneNS$_2$). 7-(*p*-Tolylsulfonyl)-7-aza-1,4-dithiacyclononane (1.75 g, 5.5 mmol) was added to a solution of hydrogen bromide in acetic acid (45%, 30 cm^3) (Fluka) and phenol (3 g, 0.043 mol). The solution was stirred at 80 °C for 48 hours, after which a further quantity of hydrogen bromide in acetic acid (45%, 10 cm^3) was added and the reaction mixture was stirred for a further 30 hours at 80 °C. The resulting black solution was allowed to cool and toluene (100 cm^3) added and the solvent removed *in vacuo*. The black residue was taken up in water (40 cm^3) and was washed with CH$_2$Cl$_2$ until the organic layer became colourless. The pH of the solution was adjusted to 14 with NaOH solution and the aqueous layer was extracted with CHCl$_3$ (5 × 50 cm^3). The combined organic layer was dried over MgSO$_4$ and reduced *in vacuo* to yield the product as a white crystalline solid. Further purification was deemed unnecessary, 700 mg, 78%. δ_H(CDCl$_3$) 2.76 (4H, m, $\mathrm{NCH_2C}H_2\mathrm{S}$), 2.88 (1H, br s, NH) and 2.94 (8H, m, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{S}$ and $\mathrm{SC}H_2\mathrm{C}H_2\mathrm{S}$); δ_C(CDCl$_3$) 39.06 ($\mathrm{NCH_2}C\mathrm{H_2S}$ and $\mathrm{S}C\mathrm{H_2}C\mathrm{H_2S}$) and 47.96 ($\mathrm{N}C\mathrm{H_2CH_2S}$); *m*/*z* 163 [M$^+$].

7-(2-Hydroxy-2-methylpropyl)-7-aza-1,4-dithiacyclononane (HL^1). 7-Aza-1,4-dithiacyclononane (0.4 g, 25 mmol) and isobutylene oxide (0.53 g, 74 mmol) were dissolved in ethanol (15 cm^3) and left in a sealed flask for 10 days. The solvent and excess isobutylene oxide were removed *in vacuo* to yield the ligand as a pale yellow oil, 0.575 g, quantitative. δ_H(CDCl$_3$) 1.08 (6H, s, CH$_3$), 2.62–2.94 (8H, m, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{S}$), 2.89 (4H, s, $\mathrm{SC}H_2\mathrm{C}H_2\mathrm{S}$) and 3.58 (1H, br s, OH); δ_C(CDCl$_3$) 28.08 (CH$_3$), 34.09, 34.89 ($\mathrm{NCH_2}C\mathrm{H_2S}$ and $\mathrm{S}C\mathrm{H_2}C\mathrm{H_2S}$), 58.68 ($\mathrm{N}C\mathrm{H_2CH_2S}$), 69.27 ($\mathrm{N}C\mathrm{H_2C(CH_3)_2OH}$) and 69.27 ($\mathrm{NCH_2}C\mathrm{(CH_3)_2OH}$).

7-[2-Hydroxy-2,2-diphenyl)ethyl]-7-aza-1,4-dithiacyclononane (HL^2). *(a) 2,2-Diphenyloxirane.* This compound was prepared according to the method of Corey and Chaykovsky.[12] Sodium hydride (2.4 g of 60% dispersion in mineral oil, 0.06 mol) was weighed into a dry Schlenk tube. This was then washed carefully three times with light petroleum (bp 40–60 °C), and the sample pumped dry on a schlenk line. Trimethyl

Table 4 Crystallographic data[a]

	$[Cu([9]aneNS_2)_2][PF_6]_2$	$[Cu(L^1)]_2[BPh_4]_2$	$[Ni(HL^1)(CH_3CO_2)]BPh_4{\cdot}CH_3CN$
Chemical formula	$C_{12}H_{26}F_{12}N_2P_2S_4Cu$	$C_{68}H_{80}B_2N_2O_2S_4Cu_2$	$C_{36}H_{44}BNO_3S_2Ni{\cdot}CH_3CN$
M	680.07	1234.34	713.4
Crystal system	Monoclinic	Triclinic	Monoclinic
a/Å	7.5184(11)	9.723(2)	16.921(13)
b/Å	9.1630(14)	10.628(2)	12.139(9)
c/Å	16.925(3)	15.165(4)	19.319(11)
α/°		95.77(2)	
β/°	94.298(13)	92.120(2)	113.66(5)
γ/°		104.498(13)	
U/Å^3	1162.7	1506	3634.6
T/K	298	298	150[b]
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
Z	2	1	4
μ/mm^{-1}	1.538	0.886	0.682
Reflections collected	2036	3775	5123
Observed reflections [$F \geqslant 4\sigma(F)$]	1595	2759	4098
Parameters refined	147	313	386
R, R'[31]	—	0.0431, 0.0444	0.0482, 0.0482
$R1$, $wR2$[32]	0.0481, 0.1199	—	—

[a] Stoë STADI-4 four-circle diffractometer, graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). [b] Oxford Cryosystems low-temperature device.[30]

sulfoxonium iodide [$Me_3S(O)I$] (13.2 g, 0.06 mol) in DMSO (60 cm^3) was added and the reaction mixture stirred at room temperature until the effervescence had ceased (20 min) to generate dimethylsulfoxonium methylide. A solution of benzophenone (8.90 g, 0.050 mol) in DMSO (20 cm^3) was then added and the solution stirred at 50 °C for 1 hour. The flask was allowed to cool, water (120 cm^3) was added and the mixture was extracted with ether (4 × 50 cm^3). The combined extracts were washed with water (2 × 20 cm^3), dried over $MgSO_4$ and concentrated *in vacuo* to yield a white paste. Recrystallisation of this paste from ethanol yielded the product as a white solid which was stored at −20 °C (6.10 g, 51.8%). $R_f = 0.9$ (1 : 1 CH_2Cl_2–hexane on alumina); ^1H NMR (250.13 MHz, $CDCl_3$) δ 3.35 (2H, s, CH_2) and 7.43 (10H, m, aromatic H); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 56.57 (CH_2), 61.54 [$C(Ph)_2$], 127.24, 127.70, 128.04 (aromatic CH) and 139.35 (aromatic quaternary); IR (KBr disc) 3053m (CH), 2986m (CH), 1491s, 1446s, 1345s, 1302s, 900s, 757s and 696s cm^{-1}.

(b) 7-[(2-Hydroxy-2,2-diphenyl)ethyl]-7-aza-1,4-dithiacyclononane (HL^2). 7-Aza-1,4-dithiacyclononane (0.20 g, 0.0012 mol) and 2,2-diphenyloxirane (0.72 g, 0.0037 mol) were heated at 60 °C in ethanol (10 cm^3) for 24 hours. The reaction was found to be incomplete by TLC. A second portion of oxirane (0.20 g, 0.0010 mol) was added and the mixture heated for a further 24 hours. The solvent was then removed *in vacuo* and the product was isolated by flash column chromatography on alumina (1 : 1 CH_2Cl_2–hexane). After removal of the solvent *in vacuo* and trituration with ethanol, the product was obtained as a white solid (0.230 g, 52.1%). $R_f = 0.35$ (1 : 1 CH_2Cl_2–hexane on alumina); ^1H NMR (250.13 MHz, $CDCl_3$) δ 2.5–2.85 (8H, m, NCH_2CH_2S), 2.83 (4H, s, SCH_2CH_2S), 3.48 (2H, s, NCH_2 arm), 7.15–7.59 (10H, m, aromatic H); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 33.99, 35.08 (SCH_2), 58.13 (NCH_2, ring), 68.95 (NCH_2, arm), 75.88 [$C(Ph)_2OH$], 125.54, 126.33, 127.81 (aromatic CH) and 146.62 (aromatic quaternary).

$[Cu([9]aneNS_2)_2][PF_6]_2$. 7-Aza-1,4-dithiacyclononane (0.1 g, 0.6 mmol) was dissolved in ethanol (3 cm^3). To this was added a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (74 mg, 0.3 mmol) in ethanol (3 cm^3). A green precipitate immediately formed which was collected by filtration. The complex was dissolved in a minimum of water and was added to an excess of NH_4PF_6. The resulting green precipitate was collected by filtration and recrystallised from acetonitrile–diethyl ether, 110 mg, 53% (Found: C, 21.5; H, 4.0; N, 4.1. $C_{12}H_{26}N_2S_4CuP_2F_{12}$ requires C, 21.2; H, 3.8; N, 4.1 %); m/z 389 (M − 2PF_6). Electronic spectrum: λ_{max}/nm (MeCN) 582 (ε/dm^3 mol^{-1} cm^{-1} 363).

$[Cu(L^1)]_2[BPh_4]_2$. $Cu(CH_3CO_2)_2{\cdot}H_2O$ (42 mg, 0.21 mmol) in MeOH (20 cm^3) was added to a solution of HL^1 (49 mg, 0.21 mmol) in MeOH (20 cm^3). The resulting green solution was added to a solution of $NaBPh_4$ (0.145 g, 0.42 mmol) in methanol (10 cm^3) and the fine precipitate was isolated by centrifugation and recrystallised from MeCN to yield the complex as green crystals, 81 mg, 62% (Found: C, 67.0; H, 6.9; N, 2.2. $C_{68}H_{80}N_2O_2S_4Cu_2B_2$ requires C, 66.2; H, 6.5; N, 2.3%). Electronic spectrum: λ_{max}/nm (MeCN) 618 (ε/dm^3 mol^{-1} cm^{-1} 555).

$[Cu(L^2)]_2[BPh_4]_2$. $Cu(CH_3CO_2)_2{\cdot}H_2O$ (0.028 g, 0.00014 mol) and HL^2 (0.050 g, 0.00014 mol) were each dissolved in MeOH (20 cm^3). Mixing of the two solutions gave a colour change to dark green. $NaBPh_4$ (0.096 g, 0.00028 mol) was added as a solution in MeOH (10 cm^3) to yield a fine grey–green precipitate. This was isolated by centrifugation and recrystallised from a large volume of warm MeCN, to afford the product as dark green columns (0.044 g, 42.0%) (Found: C, 71.0; H, 6.14; N, 1.82. $C_{88}H_{88}N_2O_2S_4B_2Cu_2$ requires C, 71.3; H, 5.94; N, 1.89%); IR (KBr disc) 3053w, 2982m, 1551s and 1420m cm^{-1}; FAB-MS (3-nitrobenzyl alcohol): m/z 360 [HL^2]$^+$, 422 [$Cu(L^2)$]$^+$.

$[Ni(HL^1)(CH_3CO_2)]BPh_4$. This complex was prepared in a similar manner to the Cu(II) complex of [9]aneNS$_2$, 84 mg, 39% (Found: C, 64.6; H, 7.2; N, 3.7. $C_{36}H_{44}NO_3S_2NiB{\cdot}CH_3CN$ requires C, 64.0; H, 6.6; N, 3.9%).

X-Ray crystallography

A summary of the crystal data, data collection and refinement parameters for the three compounds $[Cu([9]aneNS_2)_2][PF_6]_2$, $[Cu(L^1)]_2[BPh_4]_2$ and $[Ni(HL^1)(CH_3CO_2)]BPh_4$ is given in Table 4. The positions of the metal atom in all three structures were deduced from Patterson syntheses and the remaining atoms from subsequent difference-Fourier syntheses.

$[Cu([9]aneNS_2)_2][PF_6]_2$. Initial refinement showed high thermal parameters for four of the F atoms on the PF_6^- anion indicating the presence of some rotational disorder: each was resolved into two components with site occupancy factors of 0.5. All non-disordered H-atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in fixed calculated positions with $U_{iso}(H) = 1.2\ U_{eq}(C)$.

$[Cu(L^1)]_2[BPh_4]_2$. Phenyl rings in the anions were constrained as rigid, idealised hexagons and hydrogen atoms were included in calculated positions (C–H 1.08 Å) with fixed thermal parameters $U_{iso} = 0.04$ Å^2. In the final cycles of full-matrix least-squares refinement, all non H-atoms were refined with anisotropic thermal parameters.

$[Ni(HL^1)(CH_3CO_2)]BPh_4$. In the final cycles of refinement, all non H-atoms were refined with anisotropic thermal parameters and with the phenyl rings of the BPh_4 anion constrained to be rigid idealised hexagons. All H-atoms were placed at idealised positions (C–H 1.08 Å) with fixed thermal parameters $U_{iso} = 0.04$ Å^2, with the exception of the hydroxylic H(14) which was located in a difference-Fourier synthesis and restrained to lie 0.96(1) Å from O(14).

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