Correlation of the Redox Properties and Stereochemical Features of Copper Complexes of $[18]aneN_2S_4$ (1,4,10,13-tetrathia-7,16-diazacyclooctadecane) and its *N,N'*-Dimethyl Derivative $Me_2[18]aneN_2S_4$. Crystal Structures of $[Cu^{II}([18]aneN_2S_4)][ClO_4]_2 \cdot H_2O$, $[Cu^{II}(Me_2[18]aneN_2S_4)][PF_6]_2$, $[Cu^{I2}([18]aneN_2S_4)]BPh_4$, $[Cu^{I}(Me_2[18]aneN_2S_4)]PF_6$ and $[Cu^{I}_2(Me_2[18]aneN_2S_4)(NCMe)_2][PF_6]_2$†

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Reaction of copper(II) salts with L = $[18]aneN_2S_4$ (1,4,10,13-tetrathia-7,16-diazacyclooctadecane) or its 7,16-dimethyl derivative $Me_2[18]aneN_2S_4$ affords the cations $[CuL]^{2+}$ in high yields. The complex $[Cu([18]aneN_2S_4)][ClO_4]_2 \cdot H_2O$ crystallises in the orthorhombic space group *Pcab* with *a* = 12.020(8), *b* = 17.733(17), *c* = 21.999(23) Å and *Z* = 8. A single-crystal structure determination has shown the Cu^{II} to be bound *via* all six macrocyclic donors atoms to give a tetragonally compressed octahedral stereochemistry, Cu–S(1) 2.577(5), Cu–S(4) 2.487(5), Cu–S(10) 2.528(5), Cu–S(13) 2.578(5), Cu–N(7) 2.007(13) and Cu–N(16) 2.036(12) Å, with the macrocycle in a *rac* configuration. The complex $[Cu(Me_2[18]aneN_2S_4)][PF_6]_2$ crystallises in the trigonal space group $P\bar{3}m1$, *a* = 10.5140(4), *c* = 6.6604(5) Å and *Z* = 1. The Cu^{II} occupies a site of D_{3d} symmetry, bound to the six macrocyclic donor atoms to give a tetragonally elongated octahedral stereochemistry in a *meso* configuration, Cu–S 2.496(5) and Cu–N 2.191(17) Å. The ion $[Cu([18]aneN_2S_4)]^{2+}$ shows a reversible Cu^{II}–Cu^{I} redox couple at $E_{\frac{1}{2}} = -0.31$ V *vs.* ferrocene–ferrocenium, while that for $[Cu(Me_2[18]aneN_2S_4)]^{2+}$ occurs at a more anodic potential, $E_{\frac{1}{2}} = +0.06$ V. The diamagnetic copper(I) species $[CuL]^{+}$ can be generated electochemically from the copper(II) precursors by controlled-potential electrolysis, although the direct route *via* reaction of $[Cu(NCMe)_4]^{+}$ with 1 molar equivalent of L in refluxing MeOH under N_2 is better. The complex $[Cu(Me_2[18]aneN_2S_4)]PF_6$ crystallises in the triclinic space group $P\bar{1}$, *a* = 10.3386(23), *b* = 10.7643(25), *c* = 12.054(3) Å, α = 102.450(9), β = 113.951(11), γ = 102.692(10)° and *Z* = 2. The Cu^{I} is bound *via* three macrocyclic S- and one macrocyclic N-donor atom, Cu–S 2.2516(16), 2.2612(16), 2.3342(17), Cu–N 2.175(5) Å, giving a distorted-tetrahedral stereochemistry. The complex $[Cu([18]aneN_2S_4)]BPh_4$ crystallises in the orthorhombic space group $P2_12_12_1$, with *a* = 12.270(4), *b* = 14.314(8), *c* = 19.914(5) Å and *Z* = 4. The structure is very similar to that of $[Cu(Me_2[18]aneN_2S_4)]^{+}$ with the Cu^{I} bound *via* three S- and one N-donor atom, Cu–S 2.250(3), 2.245(3), 2.357(4), Cu–N 2.121(9) Å, giving a distorted-tetrahedral stereochemistry. The differences in potentials for the Cu^{II}–Cu^{I} couples in $[Cu([18]aneN_2S_4)]^{2+/+}$ and $[Cu(Me_2[18]aneN_2S_4)]^{2+/+}$ are therefore due to the different configurations, *meso* and *rac*, in the parent copper(II) species rather than to differences in the copper(I) structure. Reaction of $Me_2[18]aneN_2S_4$ with 2 molar equivalents of $[Cu(NCMe)_4]^{+}$ affords the binuclear copper(I) species $[Cu_2(Me_2[18]aneN_2S_4)(NCMe)_2]^{2+}$ the PF_6^{-} salt of which crystallises in the triclinic space group $P\bar{1}$, *a* = 7.3435(18), *b* = 11.0562(3), *c* = 11.824(3) Å, α = 62.298(10), β = 81.904(15), γ = 82.764(16)° and *Z* = 1. The cation lies across an inversion centre, with each Cu^{I} bound *via* two macrocyclic S- and one macrocyclic N-donor atom, Cu–S 2.317(4), 2.286(4), Cu–N 2.165(7) Å, with an NCMe solvent molecule completing the distorted-tetrahedral stereochemistry, Cu–N 1.924(9) Å.

Macrocyclic copper complexes incorporating conformationally restricted thioether/aza ligands are of interest as potential models for the blue copper proteins.[1,2] The ability to control the Cu^{II}–Cu^{I} redox couple as a function of stereochemistry is an important feature in these systems,[2–4] and is linked to the ability of such metalloenzymes to alter the co-ordination geometry of the metal ion at the active site. Thioether crowns have been shown to show similar co-ordinative flexibility, and this has led to the stabilisation of a wide range of unusual metal oxidation states.[5,6]

In their original work on hexadentate macrocyclic complexation, Black and McLean[7] proposed two geometric isomers for $[18]aneN_2S_4$ (1,4,10,13-tetrathia-7,16-diazacyclooctadecane) and its derivatives upon co-ordination to a transition-metal

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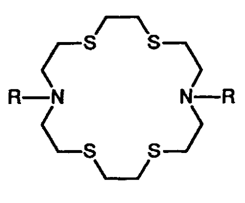
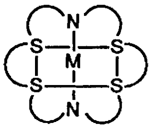
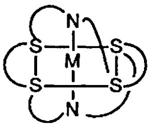
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



R = H : $[18]aneN_2S_4$
R = Me : $Me_2[18]aneN_2S_4$



meso



rac

centre in an octahedral field: *rac* involving meridional binding of the $SCH_2CH_2NCH_2CH_2S$ linkages, and *meso* involving facial binding of these linkages.

In the course of our studies we have noted that $[18]aneN_2S_4$ and $Me_2[18]aneN_2S_4$ (7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclooctadecane) bind readily to a range of transition-metal centres in various co-ordination geometries, and that the resultant complexes can exhibit highly unusual and unexpected redox characteristics.[6] For example, stabilisation of mononuclear Pd^I has been achieved using $Me_2[18]aneN_2S_4$, while palladium(III) species have been stabilised by $[18]aneN_2S_4$.[8] The vastly different redox properties for these two complexes are attributed to the different stereochemistries observed for the parent palladium(II) complexes. We were, therefore, interested to determine whether co-ordination of $[18]aneN_2S_4$ and $Me_2[18]aneN_2S_4$ to Cu^{II} and Cu^I would lead to similar structural and redox correlations.[9] We report herein the synthesis and single-crystal X-ray structures of the copper(II) complexes $[Cu([18]aneN_2S_4)][ClO_4]_2{\cdot}H_2O$ and $[Cu(Me_2[18]aneN_2S_4)][PF_6]_2$, as well as their copper(I) analogues $[Cu([18]aneN_2S_4)]BPh_4$, $[Cu(Me_2[18]aneN_2S_4)]PF_6$ and of the binuclear copper(I) species $[Cu_2(Me_2[18]aneN_2S_4)(NCMe)_2][PF_6]_2$. The electrochemistry of these species is also described and an attempt is made to rationalise the behaviour observed in terms of the different geometries of the parent species. A preliminary communication on this work has already appeared.[10]

Results and Discussion

Treatment of $Cu(NO_3)_2{\cdot}6H_2O$ with 1 molar equivalent of $[18]aneN_2S_4$ in refluxing EtOH–water affords a bright green solution. Addition of excess of NH_4PF_6 gave a green precipitate which was recrystallised from water to give the product as green crystals. The IR spectrum shows peaks at 3270 and 3160 cm^{-1} corresponding to N–H stretching vibrations, ν(N–H), as well as other peaks confirming the presence of co-ordinated $[18]aneN_2S_4$. Strong absorptions at 840 and 555 cm^{-1} are characteristic of the PF_6^- counter ion. The fast atom bombardment (FAB) mass spectrum exhibits molecular ion peaks with the correct isotopic distributions at $m/z = 535$ and 389 assigned to $[^{63}Cu([18]aneN_2S_4 + H)(PF_6)]^+$ and $[^{63}Cu([18]aneN_2S_4)]^+$ respectively. This, together with microanalytical data confirms the formulation $[Cu([18]aneN_2S_4)][PF_6]_2$. The electronic spectrum of the complex exhibits two charge-transfer transitions at $\lambda_{max} = 395$ ($\varepsilon_{max} = 2460$) and 302 nm (1970 $dm^3\ mol^{-1}\ cm^{-1}$). A weaker absorption at 612 nm (202 $dm^3\ mol^{-1}\ cm^{-1}$) is also identifiable and is assigned as a d–d transition. The corresponding perchlorate salt $[Cu([18]aneN_2S_4)][ClO_4]_2$ can be prepared by using $NaClO_4$ in place of NH_4PF_6 in the above synthesis.

Crystals of suitable quality for a single-crystal X-ray analysis were obtained by slow evaporation from an aqueous solution of $[Cu([18]aneN_2S_4)][ClO_4]_2$. The structure shows (Fig. 1, Tables 1–3) the Cu^{II} bound *via* all six macrocyclic donor atoms with the complex adopting a *rac* configuration. The restricted bite angle of the meridional $SCH_2CH_2NCH_2CH_2S$ linkages leads to a small but significant tetrahedral distortion of the S-donor atoms out of the least-squares S_4 co-ordination plane with S(1) and S(13) lying 0.230 and 0.232 Å respectively above this plane, and S(4) and S(10) lying 0.228 and 0.231 Å respectively below this plane. The cation adopts a tetragonally compressed stereochemistry, the compression occurring along the N–Cu–N axis, Cu–N(7) 2.007(13) and Cu–N(16) 2.036(12) Å. The effect of the shorter Cu–N bond lengths compared to Cu–S and the conformational rigidity of the macrocycle is to push the S-donors away from the metal centre, leading to unusually long Cu–S bond lengths, Cu–S(1) 2.577(5), Cu–S(4) 2.487(5), Cu–S(10) 2.528(5) and Cu–S(13) 2.578(5) Å. These are considerably longer than in related copper(II) thioether macrocyclic complexes, *e.g.* $[Cu([18]aneS_6)]^{2+}$ ($[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane) [$Cu–S_{eq}$ 2.323(1), 2.402(1), $Cu–S_{ap}$ 2.635(1) Å],[11] $[Cu([9]aneS_3)_2]^{2+}$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane), [Cu–S 2.419(3), 2.426(3) and 2.459(3) Å],[12] $[Cu([14]aneS_4)]^{2+}$ ($[14]aneS_4$ = 1,4,8,11-tetrathiacyclotetradecane), [Cu–S 2.297(1) and 2.308(1) Å],[13] and $[Cu([15]aneS_5)]^{2+}$ ($[15]aneS_5$ = 1,4,7,10,13-pentathiacyclopentadecane), [$Cu–S_{eq}$ 2.289(2), 2.315(2), 2.331(2), $Cu–S_{ap}$ 2.398(2) Å].[4] The stereochemistry observed for $[Cu([18]aneN_2S_4)]^{2+}$ contrasts with that of $[Cu([18]aneS_6)]^{2+}$ which exhibits a tetragonally elongated stereochemistry in a *meso* configuration,[11] while the structure of $[Cu([9]aneS_3)_2]^{2+}$ shows the Cu^{II} in an almost perfect octahedral geometry with each tridentate macrocycle binding facially.[12]

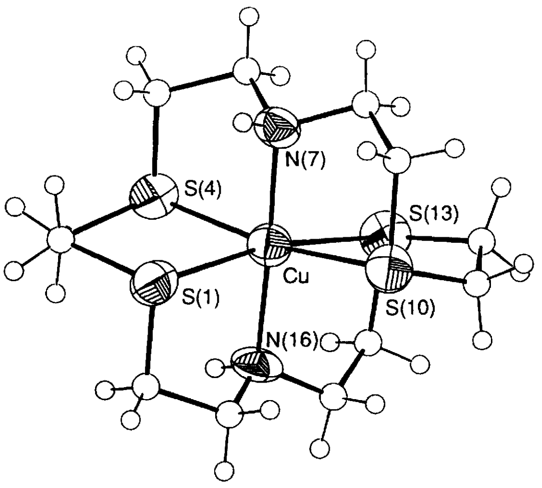


Fig. 1 Structure of the cation in *rac*-$[Cu([18]aneN_2S_4)][ClO_4]_2{\cdot}H_2O$ with numbering scheme adopted

The di-*N*-methylated analogue $[Cu(Me_2[18]aneN_2S_4)][PF_6]_2$ was prepared by a similar route to that used for $[Cu([18]aneN_2S_4)][PF_6]_2$, and characterised by microanalytical, IR and electronic spectroscopic data. The FAB mass spectrum shows molecular ion peaks at m/z = 563, 433 and 417 corresponding to $[^{63}Cu(Me_2[18]aneN_2S_4 + H)(PF_6)]^+$, $[^{63}Cu(Me_2[18]aneN_2S_4)(H_2O) - 2H]^+$ and $[^{63}Cu(Me_2[18]aneN_2S_4)]^+$ respectively, confirming the product to be $[Cu(Me_2[18]aneN_2S_4)][PF_6]_2$. The X-band ESR spectra of $[Cu([18]aneN_2S_4)]^{2+}$ and $[Cu(Me_2[18]aneN_2S_4)]^{2+}$ in solution and as frozen glasses in MeCN at 77 K are rather uninformative showing broad resonances centred near $g = 2.10$ with no hyperfine coupling to N or Cu nuclei being discernible.

Cyclic voltammetry of $[Cu([18]aneN_2S_4)]^{2+}$ at platinum electrodes at 298 K in MeCN with 0.1 mol dm^{-3} $NBu^n_4PF_6$ as supporting electrolyte shows a chemically reversible reduction at $E_{\frac{1}{2}} = -0.31$ V *vs.* ferrocene–ferrocenium. In contrast,

Table 1 Summary of torsion angle distribution in copper(II) macrocyclic complexes

Linkage	$[Cu([18]aneS_6)]^{2+}$ [11]	$[Cu(Me_2[18]aneN_2S_4)]^{2+}$	$[Cu([18]aneN_2S_4)]^{2+}$
C-S-C-C	12 synclinal	8 synclinal	6 synclinal 2 anticlinal
S-C-C-S	6 synclinal	2 synclinal	2 synclinal
C-N-C-C		4 anticlinal	4 antiperiplanar
N-C-C-S		4 synclinal	4 synclinal

Table 2 Bond lengths (Å), angles and torsion angles (°) for $[Cu([18]aneN_2S_4)][ClO_4]_2{\cdot}H_2O$

Cu–S(1)	2.577(5)	C(6)–N(7)	1.484(20)
Cu–S(4)	2.487(5)	N(7)–C(8)	1.502(20)
Cu–N(7)	2.007(13)	C(8)–C(9)	1.466(22)
Cu–S(10)	2.528(5)	C(9)–S(10)	1.819(18)
Cu–S(13)	2.578(5)	S(10)–C(11)	1.771(19)
Cu–N(16)	2.036(12)	C(11)–C(12)	1.580(27)
S(1)–C(2)	1.818(19)	C(12)–S(13)	1.792(19)
S(1)–C(18)	1.797(15)	S(13)–C(14)	1.822(15)
C(2)–C(3)	1.588(24)	C(14)–C(15)	1.485(26)
C(3)–S(4)	1.808(18)	C(15)–N(16)	1.482(22)
S(4)–C(5)	1.822(19)	N(16)–C(17)	1.500(20)
C(5)–C(6)	1.480(23)	C(17)–C(18)	1.513(24)
S(1)–Cu–S(4)	86.11(16)	S(4)–C(5)–C(6)	109.0(12)
S(1)–Cu–N(7)	95.4(4)	C(5)–C(6)–N(7)	111.2(12)
S(4)–Cu–N(7)	84.9(4)	Cu–N(7)–C(6)	111.8(10)
S(1)–Cu–S(10)	95.23(16)	Cu–N(7)–C(8)	112.6(9)
S(4)–Cu–S(10)	169.68(17)	C(6)–N(7)–C(8)	110.9(11)
N(7)–Cu–S(10)	84.8(4)	N(7)–C(8)–C(9)	110.2(13)
S(1)–Cu–S(13)	169.46(17)	C(8)–C(9)–S(10)	115.5(12)
S(4)–Cu–S(13)	96.30(16)	Cu–S(10)–C(9)	92.5(5)
N(7)–Cu–S(13)	95.1(4)	Cu–S(10)–C(11)	104.8(5)
S(10)–Cu–S(13)	84.23(17)	C(9)–S(10)–C(11)	101.9(9)
S(1)–Cu–N(16)	83.6(4)	S(10)–C(11)–C(12)	119.6(13)
S(4)–Cu–N(16)	94.55(45)	C(11)–C(12)–S(13)	117.0(12)
N(7)–Cu–N(16)	178.8(6)	Cu–S(13)–C(12)	104.9(6)
S(10)–Cu–N(16)	95.8(5)	Cu–S(13)–C(14)	91.1(6)
S(13)–Cu–N(16)	86.0(4)	C(12)–S(13)–C(14)	103.8(9)
Cu–S(1)–C(2)	101.7(5)	C(14)–C(15)–N(16)	113.5(15)
Cu–S(1)–C(18)	94.3(6)	S(13)–C(14)–C(15)	115.4(13)
C(2)–S(1)–C(18)	101.6(8)	Cu–N(16)–C(15)	112.8(10)
S(1)–C(2)–C(3)	114.6(13)	Cu–N(16)–C(17)	109.9(10)
C(2)–C(3)–S(4)	115.9(13)	C(15)–N(16)–C(17)	113.6(13)
Cu–S(4)–C(3)	102.6(6)	N(16)–C(17)–C(18)	111.9(13)
Cu–S(4)–C(5)	93.9(5)	S(1)–C(18)–C(17)	109.5(11)
C(3)–S(4)–C(5)	103.2(8)		

C(18)–S(1)–C(2)–C(3)	−65.8
C(2)–S(1)–C(18)–C(17)	132.0
S(1)–C(2)–C(3)–S(4)	−49.5
C(2)–C(3)–S(4)–C(5)	−59.2
C(3)–S(4)–C(5)–C(6)	139.0
S(4)–C(5)–C(6)–N(7)	−62.2
C(5)–C(6)–N(7)–C(8)	−177.6
C(6)–N(7)–C(8)–C(9)	−179.0
N(7)–C(8)–C(9)–S(10)	52.1
C(8)–C(9)–S(10)–C(11)	81.5
C(9)–S(10)–C(11)–C(12)	−67.2
S(10)–C(11)–C(12)–S(13)	−36.7
C(11)–C(12)–S(13)–C(14)	−73.1
C(12)–S(13)–C(14)–C(15)	78.8
N(16)–C(15)–C(14)–S(13)	52.2
C(14)–C(15)–N(16)–C(17)	−172.9
C(15)–N(16)–C(17)–C(18)	−172.9
N(16)–C(17)–C(18)–S(1)	−60.7

Table 3 Atomic coordinates (× 10^4) with e.s.d.s in parentheses for $[Cu([18]aneN_2S_4)][ClO_4]_2{\cdot}H_2O$

Atom	*x*	*y*	*z*
Cu	3061(2)	942(1)	6470(1)
S(1)	1670(3)	1336(3)	5637(2)
C(2)	2563(14)	1389(10)	4972(9)
C(3)	3549(15)	793(11)	4962(9)
S(4)	4424(3)	774(3)	5630(2)
C(5)	4940(12)	1738(11)	5679(8)
C(6)	4903(14)	1986(11)	6321(8)
N(7)	3750(9)	1967(7)	6561(6)
C(8)	3712(13)	2249(9)	7205(8)
C(9)	2566(16)	2235(10)	7433(9)
S(10)	1841(4)	1341(3)	7349(2)
C(11)	2349(17)	824(10)	7980(8)
C(12)	3617(15)	593(10)	8004(8)
S(13)	4255(4)	317(3)	7303(2)
C(14)	3639(16)	−601(10)	7141(10)
C(15)	2485(17)	−582(10)	6901(9)
N(16)	2353(11)	−92(7)	6360(7)
C(17)	1169(12)	−6(10)	6157(9)
C(18)	1083(13)	409(9)	5558(8)
Cl(1)	5188(4)	−2628(3)	6148(3)
O(1)	5494(24)	−1936(15)	6105(15)
O(2)	4024(15)	−2631(15)	6148(12)
O(3)	5489(29)	−3005(15)	5619(10)
O(4)	5549(11)	−3046(9)	6655(7)
Cl(2)	3022(4)	3848(2)	6059(2)
O(5)	3063(15)	4436(9)	5653(8)
O(6)	2782(13)	3184(8)	5746(7)
O(7)	2217(11)	3965(10)	6526(8)
O(8)	4074(10)	3806(8)	6350(6)
O(100)	3218(14)	−1202(9)	5527(7)

$[Cu(Me_2[18]aneN_2S_4)]^{2+}$ exhibits a reversible reduction at $E_{\frac{1}{2}} = +0.06$ V. Coulometric measurements on both complexes in MeCN in the presence of 0.1 mol dm^{-3} $NBu^n{}_4PF_6$ as supporting electrolyte at a platinum-basket electrode confirm that these processes each correspond to a one-electron reduction, generating a colourless, ESR-silent solution consistent with the formation of d^{10} copper(I) species, The cyclic voltammograms of the reduced copper(I) solutions are identical to those of the precursor copper(II) complexes confirming the reversibility of the systems. The large difference in Cu^{II}–Cu^{I} couples for $[Cu([18]aneN_2S_4)]^{2+}$ and $[Cu(Me_2[18]aneN_2S_4)]^{2+}$ is rather surprising considering that the ligands differ only in the degree of alkylation of the macrocyclic aza functions, with NH being replaced by NMe. Furthermore, methylation of N-donors would be expected to stabilise the higher copper(II) oxidation state rather than Cu^{I} due to the higher basicity of the tertiary N-donors in $Me_2[18]aneN_2S_4$ compared to the secondary N-donors in $[18]aneN_2S_4$; the opposite is observed in these complexes with $Me_2[18]aneN_2S_4$ apparently stabilising Cu^{I}. These electrochemical results urged us to investigate the stereochemistry at the copper(II) centre in $[Cu(Me_2[18]aneN_2S_4)]^{2+}$ in order that these redox properties might be explained.

Dark green crystals of $[Cu(Me_2[18]aneN_2S_4)][PF_6]_2$ were obtained by slow evaporation from a solution of the complex in MeCN–EtOH (1 : 1 v/v). The structure shows (Fig. 2, Tables 4 and 5) the cation disordered on a site of D_{3d} symmetry, the 1/3 occupied NMe function being superimposed on the 2/3 occupied S. Thus, the Cu^{II} is co-ordinated to all six macrocyclic donor atoms in a distorted-octahedral environment, Cu–S 2.496(5) and Cu–N 2.191(17) Å. Notwithstanding the disorder identified, the single-crystal X-ray structure unambiguously confirms the cation as a *meso* isomer. As a result, the Cu–N

Table 4 Bond lengths (Å), angles and torsion angles (°) for $[Cu(Me_2[18]aneN_2S_4)][PF_6]_2$. Note that all ring atoms of the same type are symmetry equivalent. Values in { } are from $[Cu([18]aneS_6)]^{2+}$ with the axial S atom in place of N.[11] Values in [ ] are symmetry related to other values in the Table

Cu–S	2.496(5)	{2.323, 2.402}
Cu–N	2.191(17)	{2.635}
S–C	1.759(10)	{1.812, 1.811}
N–C	1.564(19)	{1.802}
C–C	1.427(11)	{1.510, 1.525, 1.523}
N–Me	1.42(4)	
S–Cu–S	89.79(2)	{89.5}
S–Cu–N	78.4(5)	{87.6, 85.8}
S–C–C	124.7(6)	{116.6, 118.4, 118.2, 115.3}
C–S–C	99.8(4)	{106.6, 105.5}
N–C–C	102.4(8)	{118.0, 118.2}
C–N–C	118.8(11)	{105.6}
C–N–Me	94.7(17)	
C–S–C–C	−78.1(8)	{−83.9}
S–C–C–S	−32.5(11)	{−44.2}
C–C–S–C	[−78.1]	{−73.8}
C–S–C–C	[+78.1]	{+82.7}
S–C–C–N	+43.2(11)	{+42.9}
C–C–N–C	+106.6(12)	{+67.0}
C–N–C–C	[−106.6]	{−78.6}
N–C–C–S	[−43.2]	{−42.8}
C–C–S–C	[−78.1]	{−73.1}
C–S–C–C	[+78.1]	{+83.9}
S–C–C–S	[+32.5]	{+44.2}
C–C–S–C	[+78.1]	{+73.8}
C–S–C–C	[−78.1]	{−82.7}
S–C–C–N	[−43.2]	{−42.9}
C–C–N–C	[−106.6]	{−67.0}
C–N–C–C	[+106.6]	{+78.6}
N–C–C–S	[+43.2]	{+42.8}
C–C–S–C	[+78.1]	{+73.1}

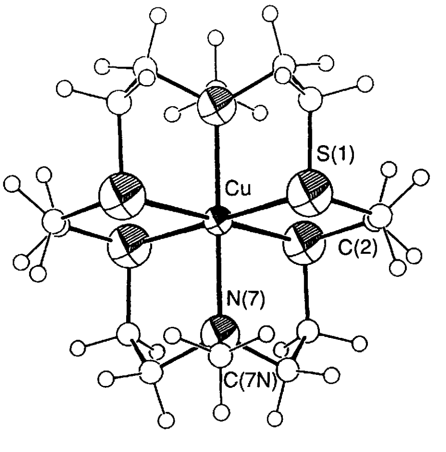


Fig. 2 Structure of the cation in *meso*-$[Cu(Me_2[18]aneN_2S_4)][PF_6]_2$ with numbering scheme adopted

Table 5 Atomic coordinates for $[Cu(Me_2[18]aneN_2S_4)][PF_6]_2$. Parameters in square brackets are related to others by symmetry

Atom	*x*	*y*	*z*	K^a	M^b
Cu	0	0	0	1	1/12
S(1)	0.1121(3)	[0.2243(6)]	0.2156(8)	2/3	1/2
C(2)	0.2855(8)	0.3150(8)	0.0992(11)	1	1
N(7)	0.1139(11)	[−0.1139(11)]	0.107(4)	1/3	1/2
C(7N)	0.1062(24)	[−0.1062(24)]	0.318(7)	1/3	1/2
P	1/3	2/3	0.5609(4)	1	1/6
F(1)	1/3	2/3	0.3252(11)	1	1/6
F(2)	1/3	2/3	0.7974(14)	1	1/6
F(3)	0.188(3)	0.5262(20)	0.575(3)	1/3	1
F(4)	0.2432(17)	[0.486(3)]	0.530(4)	1/3	1/2
F(5)	0.4108(15)	[0.822(3)]	0.569(8)	1/3	1/2

[a] *K* = Site occupancy. [b] Symmetry multiplicity.

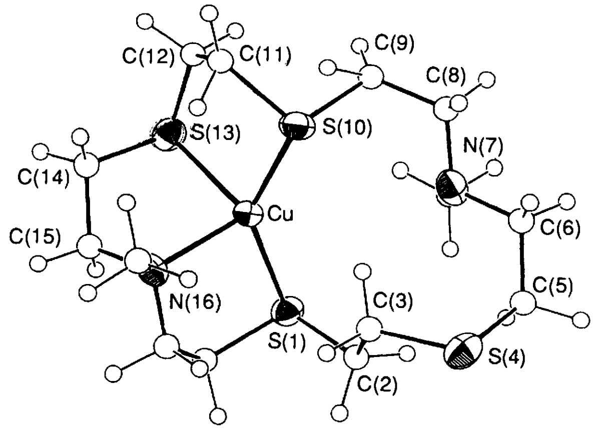


Fig. 3 Structure of the cation in $[Cu(Me_2[18]aneN_2S_4)]PF_6$ with numbering scheme adopted

distances are longer, and the Cu–S distances shorter in *meso*-$[Cu(Me_2[18]aneN_2S_4)]^{2+}$ compared to *rac*-$[Cu([18]aneN_2S_4)]^{2+}$. This is fully consistent with the observed redox properties, since closer interaction between the Cu^{II} and the four soft S-donor atoms is allowed in the *meso* configuration compared to the *rac* analogue, thus providing greater stability of the copper(I) species. Comment should be made regarding the preference of $[18]aneN_2S_4$ for co-ordination in a *rac* manner and $Me_2[18]aneN_2S_4$ in the *meso* form. The *rac* configuration adopted by $[Cu([18]aneN_2S_4)]^{2+}$ probably reflects the preference for torsion angles at secondary amine functions C–N–C–C to adopt *anti*periplanar (*anti*) placements, while those involving thioether donors C–S–C–C prefer to adopt *syn*clinal (*gauche*) placements, thereby minimising unfavourable 1,4 interactions.[14] A summary of the in-ring torsion angles for *meso*-$[Cu([18]aneS_6)]^{2+}$,[11] *meso*-$[Cu(Me_2[18]aneN_2S_4)]^{2+}$ and *rac*-$[Cu([18]aneN_2S_4)]^{2+}$ are summarised in Table 1. Both *meso*-$[Cu([18]aneS_6)]^{2+}$ and *meso*-$[Cu(Me_2[18]aneN_2S_4)]^{2+}$ show synclinal (*gauche*) torsion angles for all the C–S–C–C linkages, while *rac*-$[Cu([18]aneN_2S_4)]^{2+}$ shows six synclinal and two anticlinal. The strain introduced by the two anticlinal torsions in *rac*-$[Cu([18]aneN_2S_4)]^{2+}$ is counterbalanced by the favoured antiperiplanar torsion angles observed for all the C–N–C–C linkages, these linkages being anticlinal (106°) for *meso*-$[Cu(Me_2[18]aneN_2S_4)]^{2+}$. Interestingly, *meso*-$[Cu(Me_2[18]aneN_2S_4)]^{2+}$ shows synclinal S–C–C–S torsions (32.5°) which are significantly more acute than for *meso*-$[Cu([18]aneS_6)]^{2+}$ (44.2–42.9°); this counterbalances the relatively unfavourable anticlinal C–N–C–C torsions for *meso*-$[Cu(Me_2[18]aneN_2S_4)]^{2+}$. The role of the methyl group on the N-donors should also be considered. Molecular mechanics calculations were carried out by computer-simulated replacement of the NH protons in *rac*-$[Cu([18]aneN_2S_4)]^{2+}$ by methyl groups. A number of unfavourable steric interactions were apparent at the co-ordinated N-donors suggesting that methylation causes elongation of the Cu–N distance, as observed experimentally. Thus, a complex balance of relatively favoured and unfavoured torsion angles and steric interactions is established for these ring conformations.

We have chemically synthesised the copper(I) complexes $[Cu([18]aneN_2S_4)]BPh_4$ and $[Cu(Me_2[18]aneN_2S_4)]PF_6$ by reaction of $[Cu(NCMe)_4]PF_6$ with 1 molar equivalent of macrocycle in refluxing dry, degassed MeOH. The FAB mass spectrum of $[Cu(Me_2[18]aneN_2S_4)]PF_6$ shows a molecular

Table 6 Bond lengths (Å), angles and torsion angles (°) for $[Cu(Me_2[18]aneN_2S_4)]PF_6$

Cu–S(1)	2.2516(16)	N(7)–C(8)	1.472(8)
Cu–S(10)	2.2612(16)	C(8)–C(9)	1.510(9)
Cu–S(13)	2.3342(17)	C(9)–S(10)	1.837(7)
Cu–N(16)	2.175(5)	S(10)–C(11)	1.821(7)
S(1)–C(2)	1.829(6)	C(11)–C(12)	1.509(9)
S(1)–C(18)	1.822(7)	C(12)–S(13)	1.819(7)
C(2)–C(3)	1.517(9)	S(13)–C(14)	1.817(8)
C(3)–S(4)	1.801(6)	C(14)–C(15)	1.527(10)
S(4)–C(5)	1.796(7)	C(15)–N(16)	1.467(9)
C(5)–C(6)	1.523(10)	N(16)–C(16N)	1.460(9)
C(6)–N(7)	1.467(8)	N(16)–C(17)	1.488(9)
N(7)–C(7N)	1.461(8)	C(17)–C(18)	1.472(10)

S(1)–Cu–S(10)	136.58(6)	Cu–S(10)–C(9)	111.05(21)
S(1)–Cu–S(13)	122.12(6)	Cu–S(10)–C(11)	97.27(21)
S(1)–Cu–N(16)	90.76(13)	C(9)–S(10)–C(11)	99.6(3)
S(10)–Cu–S(13)	94.82(6)	S(10)–C(11)–C(12)	114.6(5)
S(10)–Cu–N(16)	114.12(13)	C(11)–C(12)–S(13)	115.8(5)
S(13)–Cu–N(16)	88.42(13)	Cu–S(13)–C(12)	97.75(22)
Cu–S(1)–C(2)	109.97(20)	Cu–S(13)–C(14)	95.18(24)
Cu–S(1)–C(18)	95.24(23)	C(12)–S(13)–C(14)	103.2(3)
C(2)–S(1)–C(18)	103.7(3)	S(13)–C(14)–C(15)	110.2(5)
S(1)–C(2)–C(3)	115.3(4)	C(14)–C(15)–N(16)	122.8(6)
C(2)–C(3)–S(4)	113.3(4)	Cu–N(16)–C(15)	106.7(4)
C(3)–S(4)–C(5)	103.7(3)	Cu–N(16)–C(16N)	113.8(4)
S(4)–C(5)–C(6)	117.0(5)	Cu–N(16)–C(17)	106.4(4)
C(5)–C(6)–N(7)	114.9(5)	C(15)–N(16)–C(16N)	112.6(5)
C(6)–N(7)–C(7N)	111.1(5)	C(15)–N(16)–C(17)	109.4(5)
C(6)–N(7)–C(8)	110.7(5)	C(16N)–N(16)–C(17)	107.9(5)
C(7N)–N(7)–C(8)	110.9(5)	N(16)–C(17)–C(18)	115.3(6)
N(7)–C(8)–C(9)	114.2(5)	S(1)–C(18)–C(17)	114.1(5)
C(8)–C(9)–S(10)	109.4(4)		

C(18)–S(1)–C(2)–C(3)	−92.9(5)
C(2)–S(1)–C(18)–C(17)	77.9(6)
S(1)–C(2)–C(3)–S(4)	−156.3(3)
C(2)–C(3)–S(4)–C(5)	64.4(5)
C(3)–S(4)–C(5)–C(6)	68.6(6)
S(4)–C(5)–C(6)–N(7)	−70.8(7)
C(5)–C(6)–N(7)–C(7N)	−73.5(7)
C(5)–C(6)–N(7)–C(8)	162.8(5)
C(6)–N(7)–C(8)–C(9)	−167.5(5)
C(7N)–N(7)–C(8)–C(9)	68.7(7)
N(7)–C(8)–C(9)–S(10)	59.7(6)
C(8)–C(9)–S(10)–C(11)	163.1(4)
C(9)–S(10)–C(11)–C(12)	69.7(5)
S(10)–C(11)–C(12)–S(13)	52.1(6)
C(11)–C(12)–S(13)–C(14)	68.6(5)
C(12)–S(13)–C(14)–C(15)	−137.1(5)
S(13)–C(14)–C(15)–N(16)	60.8(7)
C(14)–C(15)–N(16)–C(16N)	78.6(7)
C(14)–C(15)–N(16)–C(17)	−161.5(6)
C(15)–N(16)–C(17)–C(18)	77.9(7)
C(16N)–N(16)–C(17)–C(18)	−1 59.3(6)
N(16)–C(17)–C(18)–S(1)	51.4(7)

Table 7 Atomic coordinates for $[Cu(Me_2[18]aneN_2S_4)]PF_6$

Atom	*x*	*y*	*z*
Cu	0.094 81(7)	0.568 02(6)	0.828 08(6)
S(1)	0.346 88(14)	0.629 07(14)	0.943 79(12)
C(2)	0.424 5(6)	0.571 8(6)	0.838 4(5)
C(3)	0.313 5(6)	0.513 4(6)	0.695 1(5)
S(4)	0.367 11(16)	0.399 72(16)	0.603 17(14)
C(5)	0.359 7(7)	0.261 5(6)	0.664 0(6)
C(6)	0.204 7(7)	0.171 9(6)	0.633 0(6)
N(7)	0.133 8(5)	0.235 9(4)	0.701 2(4)
C(7N)	0.205 9(7)	0.247 8(6)	0.837 2(5)
C(8)	−0.029 1(6)	0.160 4(5)	0.638 1(5)
C(9)	−0.116 5(6)	0.234 3(5)	0.683 5(5)
S(10)	−0.093 27(14)	0.395 07(13)	0.651 71(13)
C(11)	−0.249 9(6)	0.433 7(6)	0.666 0(5)
C(12)	−0.230 0(6)	0.471 7(6)	0.801 4(6)
S(13)	−0.054 90(15)	0.605 78(15)	0.924 58(13)
C(14)	−0.075 4(7)	0.755 2(6)	0.882 6(6)
C(15)	0.071 8(8)	0.840 0(6)	0.894 2(7)
N(16)	0.117 5(5)	0.766 3(4)	0.807 5(4)
C(16N)	0.034 0(8)	0.760 9(7)	0.674 6(6)
C(17)	0.280 5(7)	0.834 9(6)	0.853 0(6)
C(18)	0.384 8(7)	0.808 3(6)	0.964 0(6)
P	0.598 97(18)	−0.087 73(16)	0.706 83(15)
F(1)	0.615 5(6)	0.066 4(4)	0.747 2(5)
F(2)	0.612 3(6)	−0.093 0(4)	0.841 2(4)
F(3)	0.423 9(5)	−0.137 3(7)	0.645 1(5)
F(4)	0.588 2(7)	−0.240 8(4)	0.669 7(5)
F(5)	0.776 4(5)	−0.041 3(5)	0.770 5(5)
F(6)	0.588 8(7)	−0.082 3(5)	0.575 6(4)

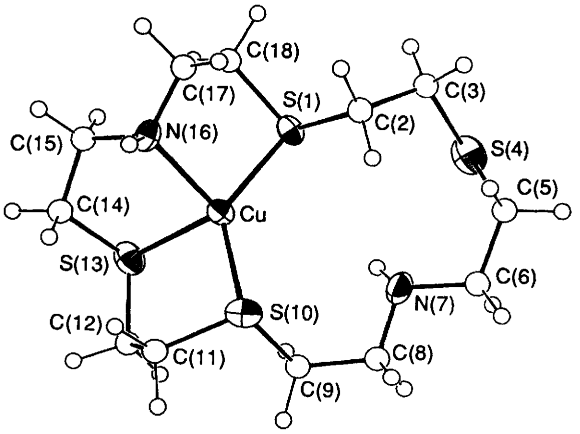


Fig. 4 Structure of the cation in $[Cu([18]aneN_2S_4)]BPh_4$ with numbering scheme adopted

ion peak at *m*/*z* = 417, corresponding to $[^{63}Cu(Me_2[18]aneN_2S_4)]^+$. In order to determine the stereochemistry of this species a single-crystal X-ray structure analysis was undertaken. The structure shows (Fig. 3, Tables 6 and 7) the Cu^I co-ordinated *via* an NS_3 donor set in a distorted-tetrahedral geometry, Cu–S(1) 2.2516(16), Cu–S(10) 2.2612(16), Cu–S(13) 2.3342(17) Å and Cu–N(16) 2.175(5) Å. Atoms S(4) and N(7) are directed away from and do not interact with the metal ion, Cu ··· S(4) 4.988(2) and Cu ··· N(7) 3.750(5) Å. The FAB mass spectrum of $[Cu([18]aneN_2S_4)]BPh_4$ shows a molecular ion peak at *m*/*z* 389 assigned to $[^{63}Cu([18]aneN_2S_4)]^+$. Interestingly, we could not isolate $[Cu([18]aneN_2S_4)]PF_6$ as an analytically pure solid; in solution, $[Cu([18]aneN_2S_4)]PF_6$ was stable at elevated temperatures, but on cooling the complex isolated was contaminated with the corresponding copper(II) salt. Addition of $NaBPh_4$, a more reducing anion than PF_6^-, afforded $[Cu([18]aneN_2S_4)]BPh_4$ in good yield. The single-crystal X-ray structure of $[Cu([18]aneN_2S_4)]^+$ shows (Fig. 4, Tables 8 and 9) a very similar stereochemistry to that of $[Cu(Me_2[18]aneN_2S_4)]^+$ with the tetrahedral Cu^I bound to three S-donors and one N-donor, Cu–S(1) 2.250(3), Cu–S(10) 2.245(3), Cu–S(13) 2.357(4) and Cu–N(16) 2.121(9) Å. Atoms S(4) and N(7) are directed away from and do not interact with the metal ion, Cu ··· S(4) 5.011(4) and Cu ··· N(7) 3.641(10) Å. Thus, reduction from Cu^{II} to Cu^I involves a significant stereochemical change from six-co-ordinate octahedral to four-co-ordinate tetrahedral, with S(4) and N(7) moving away from the metal centre. The reversibility of the Cu^{II}–Cu^I couple in the cyclic voltammetric experiment suggests that the process must involve rapid bond-breaking and -making. The pentathia and hexathia copper(II) analogues, $[Cu([15]aneS_5)]^{2+}$[4] and $[Cu([18]aneS_6)]^{2+}$,[11] each show a reversible one-electron reduction to give tetrahedral $[Cu([15]aneS_5)]^+$ and $[Cu([18]aneS_6)]^+$ involving co-ordination of the macrocycle *via* four thioether donors, Cu–S 2.243(5), 2.245(5), 2.317(5) and 2.338(5)

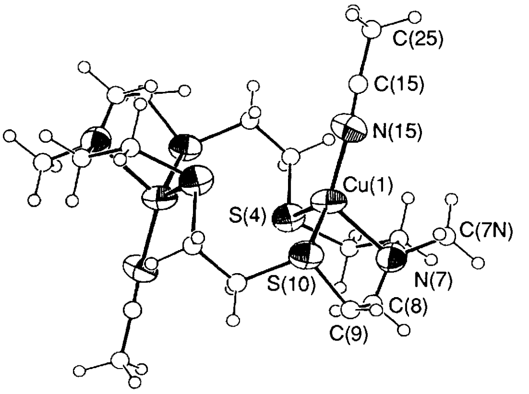


Fig. 5 Structure of the cation in $[Cu_2(Me_2[18]aneN_2S_4)(NCMe)_2][PF_6]_2$ with numbering scheme adopted

Å for $[Cu([15]aneS_5)]^+$,[4] 2.245(2), 2.253(2), 2.358(2) and 2.360(2) Å for $[Cu([18]aneS_6)]^+$. In both complexes the remaining S-donors do not interact with the tetrahedral copper(I) centres. The Cu^{II}–Cu^I couples occur at $E_{\frac{1}{2}} = +0.68$[15] and +0.96 V[11] *vs.* normal hydrogen electrode for $[Cu([15]aneS_5)]^{2+/+}$ and $[Cu([18]aneS_6)]^{2+/+}$ respectively. This reflects the net π acidity of the S-donors over N-donor atoms, the Cu^{II}–Cu^I couples becoming more cathodic on replacement of S- by N-donors.[15] The S_3N co-ordination of the N_2S_4 macrocycles to Cu^I in $[Cu(Me_2[18]aneN_2S_4)]^+$ and $[Cu([18]aneN_2S_4)]^+$ is preferred over the alternative tetrahedral S_4 co-ordination. Tetrahedral S_3N co-ordination affords three stable five-membered, and one relatively unstable eleven-membered chelate rings at the Cu^I compared to only two five-membered and two eight-membered chelate rings with tetrahedral S_4 co-ordination. These configurational considerations appear to override the additional stability that would be afforded by co-ordination of Cu^I by four soft thioether donors rather than by one aza and three thioether donors.

The affinity of $Me_2[18]aneN_2S_4$ for low-valent copper centres is further exemplified by the formation of the air-stable binuclear copper(I) species $[Cu_2(Me_2[18]aneN_2S_4)(NCMe)_2][PF_6]_2$. This complex cation can be prepared by reaction of $Me_2[18]aneN_2S_4$ with 2 molar equivalents of $[Cu(NCMe)_4]PF_6$ in refluxing MeCN, and has been characterised by FAB mass spectroscopy giving molecular ion peaks at $m/z = 481$ and 417 corresponding to $[^{63}Cu_2(Me_2[18]aneN_2S_4 + H)]^+$ and $[^{63}Cu(Me_2[18]aneN_2S_4)]^+$ respectively. Infrared spectroscopy and elemental analytical data confirm the assignment of the product as $[Cu_2(Me_2[18]aneN_2S_4)(NCMe)_2][PF_6]_2$. The complex is stable to aerial oxidation in MeCN at room temperature, again reflecting the net π-acceptor properties of the thioether donor atoms. Crystals of $[Cu_2(Me_2[18]aneN_2S_4)(NCMe)_2][PF_6]_2$ were obtained by slow evaporation from a solution of the complex in MeCN–EtOH. A single-crystal structure determination shows (Fig. 5, Tables 10 and 11) the cation lying across an inversion centre with each Cu^I bound tetrahedrally to two S-donors and one N-donor of the macrocycle, Cu–S(4) 2.317(4), Cu–S(10) 2.286(4) and Cu–N(7) 2.165(7) Å, and to one MeCN molecule, Cu–N(1S) 1.924(9) Å. The Cu ··· Cu separation is 4.283(2) Å with each Cu^I bound by an N_2S_2 donor set. Similar co-ordination has been reported for Type 1 copper proteins, although thiolate donation is involved in the biological systems.[1] We have observed a very similar stereochemistry previously for $[Cu_2([18]aneS_6)(NCMe)_2]^{2+}$, which shows NS_3 co-ordination to each Cu^I, Cu–S 2.300(15), 2.3250(15), 2.3415(16), Cu–N 1.939(5) Å.[3] The geometry at the Cu^I in the binuclear species $[Cu_2(Me_2[18]aneN_2S_4)(NCMe)_2]^{2+}$ is also rather similar to that in the mononuclear copper(I) species $[Cu(Me_2[18]aneN_2S_4)]^+$, the major difference being replacement of the NCMe ligand by another thioether donor of the macrocycle.

Table 8 Bond lengths (Å), angles and torsion angles (°) for $[Cu([18]aneN_2S_4)]BPh_4$

Cu–S(1)	2.250(3)	N(7)–C(8)	1.443(17)
Cu–S(10)	2.245(3)	C(8)–C(9)	1.503(19)
Cu–S(13)	2.357(4)	C(9)–S(10)	1.837(14)
Cu–N(16)	2.121(9)	S(10)–C(11)	1.816(14)
S(1)–C(2)	1.835(13)	C(11)–C(12)	1.522(20)
S(1)–C(18)	1.800(12)	C(12)–S(13)	1.808(14)
C(2)–C(3)	1.503(18)	S(13)–C(14)	1.837(14)
C(3)–S(4)	1.827(13)	C(14)–C(15)	1.493(19)
S(4)–C(5)	1.840(14)	C(15)–N(16)	1.502(16)
C(5)–C(6)	1.503(19)	N(16)–C(17)	1.449(15)
C(6)–N(7)	1.458(17)	C(17)–C(18)	1.535(16)
S(1)–Cu–S(10)	132.87(13)	C(8)–C(9)–S(10)	111.6(9)
S(1)–Cu–S(13)	121.31(12)	Cu–S(10)–C(9)	107.6(5)
S(1)–Cu–N(16)	90.8(3)	Cu–S(10)–C(11)	96.1(5)
S(10)–Cu–S(13)	95.01(12)	C(9)–S(10)–C(11)	100.1(6)
S(10)–Cu–N(16)	120.7(3)	S(10)–C(11)–C(12)	115.7(10)
S(13)–Cu–N(16)	89.6(3)	C(11)–C(12)–S(13)	115.3(10)
Cu–S(1)–C(2)	106.2(4)	Cu–S(13)–C(12)	97.7(5)
Cu–S(1)–C(18)	94.6(4)	Cu–S(13)–C(14)	91.7(4)
C(2)–S(1)–C(18)	100.7(5)	C(12)–S(13)–C(14)	103.5(6)
S(1)–C(2)–C(3)	110.7(9)	S(13)–C(14)–C(15)	110.3(9)
C(2)–C(3)–S(4)	112.9(9)	C(14)–C(15)–N(16)	110.8(10)
C(3)–S(4)–C(5)	100.7(6)	Cu–N(16)–C(15)	106.9(7)
S(4)–C(5)–C(6)	113.6(9)	Cu–N(16)–C(17)	108.6(7)
C(5)–C(6)–N(7)	112.5(11)	C(15)–N(16)–C(17)	113.6(9)
C(6)–N(7)–C(8)	110.7(10)	N(16)–C(17)–C(18)	111.5(9)
N(7)–C(8)–C(9)	112.5(11)	S(1)–C(18)–C(17)	113.8(8)

C(18)–S(1)–C(2)–C(3)	−110.2(9)
C(2)–S(1)–C(18)–C(17)	−73.0(9)
S(1)–C(2)–C(3)–S(4)	−70.2(10)
C(2)–C(3)–S(4)–C(5)	−68.8(10)
C(3)–S(4)–C(5)–C(6)	121.8(10)
S(4)–C(5)–C(6)–N(7)	−59.8(13)
C(5)–C(6)–N(7)–C(8)	−167.0(11)
C(6)–N(7)–C(8)–C(9)	−169.5(11)
N(7)–C(8)–C(9)–S(10)	−58.0(13)
C(8)–C(9)–S(10)–C(11)	−166.0(10)
C(9)–S(10)–C(11)–C(12)	−63.5(11)
S(10)–C(11)–C(12)–S(13)	−51.4(13)
C(11)–C(12)–S(13)–C(14)	−68.7(11)
C(12)–S(13)–C(14)–C(15)	141.8(9)
S(13)–C(14)–C(15)–N(16)	−65.1(12)
C(14)–C(15)–N(16)–C(17)	166.3(10)
C(15)–N(16)–C(17)–C(18)	−78.1(12)
N(16)–C(17)–C(18)–S(1)	−53.7(11)

The results described herein confirm the facile interconversion between octahedral copper(II) and tetrahedral copper(I) centres with N_2S_4 macrocyclic crowns. The Cu^{II}–Cu^I redox potentials are controlled by the donor power of these ligands and the configuration of the copper(II) species.

Experimental

Infrared spectra were recorded as KBr and CsI discs using a Perkin Elmer 598 spectrometer over the range 200–4000 cm^{-1}, UV/VIS spectra in quartz cells using Perkin Elmer Lambda 9 and Philips Analytical SP8-400 spectrophotometers. Microanalyses were performed by the Edinburgh University Chemistry Department Microanalytical Service. Electrochemical measurements were performed on a Bruker E310 Universal Modular Polarograph. All readings were taken using a three-electrode potentiostatic system in acetonitrile containing 0.1 mol dm^{-3} $NBu^n{}_4PF_6$ or $NBu^n{}_4BF_4$ as supporting electrolyte. Cyclic voltammetric measurements were carried out using a double platinum electrode and an Ag–AgCl reference electrode. All potentials are quoted *vs.* ferrocene–ferrocenium. Mass spectra were run by electron impact (EI) on a Kratos MS 902 and by fast atom bombardment (3-nitrobenzyl alcohol matrix) on a Kratos MS 50TC spectrometer. Proton and ^{13}C NMR

Table 9 Atomic coordinates for $[Cu([18]aneN_2S_4)]BPh_4$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu	−0.310 96(10)	−0.183 43(9)	−0.312 19(7)	C(4R)	−0.319 2(6)	−0.297 9(4)	−0.647 9(3)
S(1)	−0.175 55(24)	−0.094 46(20)	−0.270 77(15)	C(5R)	−0.307 8(6)	−0.391 8(4)	−0.665 4(3)
C(2)	−0.108 4(10)	−0.040 8(9)	−0.343 6(6)	C(6R)	−0.317 7(6)	−0.460 9(4)	−0.616 4(3)
C(3)	−0.058 3(10)	0.051 4(8)	−0.324 7(7)	C(7R)	−0.465 6(4)	−0.500 5(5)	−0.445 2(4)
S(4)	−0.159 9(3)	0.141 78(23)	−0.307 88(19)	C(8R)	−0.479 0(4)	−0.529 8(5)	−0.378 9(4)
C(5)	−0.215 4(11)	0.160 1(9)	−0.392 7(7)	C(9R)	−0.580 3(4)	−0.521 2(5)	−0.347 8(4)
C(6)	−0.336 1(11)	0.143 6(9)	−0.397 4(8)	C(10R)	−0.668 2(4)	−0.483 3(5)	−0.382 9(4)
N(7)	−0.366 6(8)	0.048 6(7)	−0.378 8(5)	C(11R)	−0.654 8(4)	−0.454 0(5)	−0.449 2(4)
C(8)	−0.477 6(10)	0.029 2(9)	−0.398 3(7)	C(12R)	−0.553 4(4)	−0.462 7(5)	−0.480 4(4)
C(9)	−0.519 3(10)	−0.060 7(9)	−0.369 1(7)	C(13R)	−0.234 3(5)	−0.506 9(6)	−0.439 9(4)
S(10)	−0.434 23(24)	−0.160 51(23)	−0.393 86(16)	C(14R)	−0.220 1(5)	−0.575 0(6)	−0.390 6(4)
C(11)	−0.523 3(10)	−0.256 4(10)	−0.370 2(7)	C(15R)	−0.123 6(5)	−0.578 1(6)	−0.353 6(4)
C(12)	−0.548 7(10)	−0.264 5(9)	−0.295 6(7)	C(16R)	−0.041 3(5)	−0.513 2(6)	−0.366 0(4)
S(13)	−0.431 4(3)	−0.264 42(23)	−0.240 66(18)	C(17R)	−0.055 4(5)	−0.445 1(6)	−0.415 4(4)
C(14)	−0.364 7(10)	−0.376 5(8)	−0.259 1(8)	C(18R)	−0.151 9(5)	−0.442 0(6)	−0.452 3(4)
C(15)	−0.243 7(10)	−0.365 2(9)	−0.258 3(7)	C(19R)	−0.345 0(6)	−0.625 2(4)	−0.520 8(4)
N(16)	−0.207 0(7)	−0.301 8(6)	−0.313 9(5)	C(20R)	−0.441 2(6)	−0.676 3(4)	−0.527 9(4)
C(17)	−0.095 3(8)	−0.270 3(8)	−0.306 9(7)	C(21R)	−0.438 5(6)	−0.765 2(4)	−0.556 6(4)
C(18)	−0.085 7(9)	−0.191 4(8)	−0.255 1(6)	C(22R)	−0.339 8(6)	−0.803 0(4)	−0.578 2(4)
C(1R)	−0.339 1(6)	−0.436 2(4)	−0.549 9(3)	C(23R)	−0.243 6(6)	−0.751 9(4)	−0.571 1(4)
C(2R)	−0.350 5(6)	−0.342 4(4)	−0.532 4(3)	C(24R)	−0.246 2(6)	−0.663 1(4)	−0.542 4(4)
C(3R)	−0.340 6(6)	−0.273 2(4)	−0.581 4(3)	B	−0.347 4(10)	−0.517 3(9)	−0.487 2(7)

spectra were obtained on Bruker WP80 and WP200 instruments.

Methylation of $[18]aneN_2S_4$ was achieved by the literature method[16] (Found: C, 42.6; H, 8.70; N, 7.00. Calc. for $C_{14}H_{30}N_2S_4{\cdot}2H_2O$: C, 43.0; H, 8.75; N, 7.15%). FAB mass spectrum: *m/z* = 355; calc. for $[C_{14}H_{30}N_2O_2S_4]$ *m/z* = 354. NMR ($CDCl_3$, 298 K): ^1H (80.13 MHz), δ 2.76 (s, NCH_2, 8 H), 2.63 (s, SCH_2, 16 H) and 2.25 (s, CH_3, 6 H); ^{13}C distortionless enhancement of polarisation transfer (DEPT) (50.32 MHz), δ 57.20 (NCH_2), 42.30 (CH_3), 32.27 and 29.73 (2 × SCH_2).

Synthesis of $[Cu([18]aneN_2S_4)][PF_6]_2$.—The salt $Cu(NO_3)_2{\cdot}6H_2O$ (36 mg, 0.123 mmol) was added to a refluxing solution of $[18]aneN_2S_4$ (40 mg, 0.123 mmol) in EtOH–water (1:1 v/v, 40 cm^3). The resulting mixture was refluxed for 1 h under N_2 yielding a bright green solution. Addition of excess of NH_4PF_6 gave a green precipitate which was recrystallised from aqueous solution to give green crystals (yield: 70 mg, 84%) (Found: C, 20.5; H, 3.85; N, 4.05; S, 19.1. Calc. for $C_{12}H_{26}CuF_{12}N_2P_2S_4$: C, 21.2; H, 3.85; N, 4.10; S, 18.9%). FAB mass spectrum: *m/z* 535 and 389; calc. for $[^{63}Cu([18]aneN_2S_4(PF_6)]^+$ *m/z* = 534, $[^{63}Cu([18]aneN_2S_4)]^+$ *m/z* = 389. Electronic spectrum (in MeCN): λ_{max} = 612 (ε_{max} = 202), 395 (2460) and 302 nm (1970 dm^3 mol^{-1} cm^{-1}). IR (KBr disc): 3270m, 3160w, 2920w, 2840w, 1465m, 1425m, 1410m, 1320w, 1300w, 1280w, 1260w, 1090w, 1070m, 1020w, 1000w, 970m, 840vs, 780w, 740w, 640w, 555vs and 445w cm^{-1}.

Single-crystal Structure Determination of $[Cu([18]aneN_2S_4)][ClO_4]_2{\cdot}H_2O$.—A green crystal (0.30 × 0.30 × 0.30 mm) suitable for single-crystal X-ray analysis was obtained by slow evaporation from an aqueous solution of the complex. The crystal was set up to rotate about the *a* axis on a Stoë STADI2 diffractometer.

Crystal data. $C_{12}H_{28}Cl_2CuN_2O_9S_4$, *M* = 609.02, orthorhombic, space group *Pcab*, *a* = 12.020(8), *b* = 17.733(17), *c* = 21.999(23) Å, *U* = 4689.1 $Å^3$, *Z* = 8, D_m = 1.68 g cm^{-3}, D_c = 1.72 g cm^{-3}, *F*(000) = 2504, μ(Mo-Kα) = 1.581 mm^{-1}.

Data collection. Data were collected using Mo-Kα radiation (λ = 0.71073 Å) and variable-width ω scans. 4390 Independent reflections were measured ($2\theta_{max}$ = 50°, *h* 0–14, *k* 0–21, *l* 0–26) of which 1710 with $F > 5\sigma(F)$ were used in subsequent refinement.

Structure analysis and refinement. The structure was determined by the heavy-atom method. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to carbon and nitrogen were included in calculated positions and their thermal parameters refined, with those of atoms bonded to the same carbon atom constrained to be equivalent. The hydrogen atoms of the water molecule could not be located. The weighting scheme $w^{-1} = \sigma^2(F) + 0.003F^2$ gave satisfactory agreement analyses. At convergence *R*, *R′* = 0.085 and 0.091 respectively and *S* = 1.45 for 275 independent parameters. The maximum and minimum residues in the final Δ*F* synthesis were +0.92 and −0.95 e $Å^{-3}$ respectively. Bond lengths, angles and torsion angles are given in Table 2, fractional atomic coordinates in Table 3.

Synthesis of $[Cu(Me_2[18]aneN_2S_4)][PF_6]_2$.—This was prepared as above using $Cu(NO_3)_2{\cdot}6H_2O$ (34 mg, 0.113 mmol) and $Me_2[18]aneN_2S_4$ (40 mg, 0.113 mmol) and isolated as deep green crystals (yield: 70 mg, 84%) (Found: C, 24.0; H, 4.30; N, 3.95; S, 16.9. Calc. for $C_{14}H_{30}CuF_{12}N_2P_2S_4$: C, 23.8; H, 4.25; N, 3.95; S, 18.1%). FAB mass spectrum: *m/z* = 563, 433 and 417; calc. for $[^{63}Cu(Me_2[18]aneN_2S_4)PF_6]^+$ *m/z* = 562, $[^{63}Cu(Me_2[18]aneN_2S_4)(H_2O)]^+$ *m/z* = 435 and $[^{63}Cu(Me_2[18]aneN_2S_4)]^+$ *m/z* = 417. Electronic spectrum (MeCN): λ_{max} = 667 (ε_{max} = 503) and 414 nm (9060 dm^3 mol^{-1} cm^{-1}). IR (KBr disc): 2980w, 2920w, 2860w, 1465m, 1435m, 1320w, 1290w, 1280w, 1260w, 1225w, 1210w, 1160w, 1135w, 1090w, 1070w, 1050w, 1015m, 1000w, 980m, 840vs, 740w, 720w, 640w, 620w, 555vs and 460w cm^{-1}.

Single-crystal Structure Determination of $[Cu(Me_2[18]aneN_2S_4)][PF_6]_2$.—A dark green needle (0.72 × 0.12 × 0.12 mm) suitable for X-ray analysis was obtained by slow evaporation from a solution of the complex in MeCN.

Crystal data. $C_{14}H_{30}CuF_{12}N_2P_2S_4$, *M* = 708.0, trigonal, space group $P\bar{3}m1$, *a* = 10.5140(4), *c* = 6.6604(5) Å, *U* = 637.6 $Å^3$ [from 2θ values of 35 reflections measured at ±ω (26 < 2θ < 30°, λ = 0.710 73 Å, *T* = 278 K], D_c = 1.84 g cm^{-3}, *Z* = 1, *F*(000) = 359, μ(Mo-Kα) = 1.39 mm^{-1}.

Data collection and processing. Stoë STADI-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device,[17] graphite-monochromated Mo-Kα X-radiation, ω–2θ scans, 1261 reflections measured ($2\theta_{max}$ = 60°, *h* −12 to 12, *k* 0–14, *l* 0–9), 728 unique, giving 447 with $F > 6\sigma(F)$. No significant crystal decay, no absorption correction.

Structure analysis and refinement. The Cu atom was fixed at

Table 10 Bond lengths (Å) and angles (°) for $[Cu_2(Me_2[18]aneN_2S_4)(NCMe)_2][PF_6]_2$

Cu(1)–S(4)	2.317(4)	S(10)–C(9)	1.807(8)
Cu(1)–S(10)	2.286(4)	S(10)–C(11)	1.804(11)
Cu(1)–N(7)	2.165(7)	C(3D)–C(11)	1.487(15)
Cu(1)–N(1S)	1.924(9)	N(7)–C(7N)	1.437(14)
S(4)–C(3)	1.846(11)	N(1S)–C(1S)	1.127(13)
S(4)–C(5)	1.860(8)	C(1S)–C(2S)	1.424(14)
S(4)–Cu(1)–S(10)	118.90(13)	Cu(1)–N(7)–C(8)	106.4(5)
S(4)–Cu(1)–N(7)	89.10(21)	Cu(1)–N(7)–C(6′)	110.4(5)
S(4)–Cu(1)–N(1S)	115.8(3)	Cu(1)–N(7)–C(8′)	108.9(5)
S(10)–Cu(1)–N(7)	88.30(21)	Cu(1)–N(7)–C(7N)	113.2(6)
S(10)–Cu(1)–N(1S)	118.5(3)	C(6)–N(7)–C(8)	123.7(6)
N(7)–Cu(1)–N(1S)	118.7(3)	C(6)–N(7)–C(7N)	80.7(6)
Cu(1)–S(4)–C(3)	106.4(4)	C(8)–N(7)–C(7N)	130.1(8)
Cu(1)–S(4)–C(5)	92.5(3)	C(6′)–N(7)–C(8′)	117.5(6)
C(3)–S(4)–C(5)	99.5(4)	C(6′)–N(7)–C(7N)	116.5(7)
Cu(1)–S(10)–C(9)	95.7(3)	C(8′)–N(7)–C(7N)	88.9(7)
Cu(1)–S(10)–C(11)	109.4(4)	S(10)–C(9)–C(8)	114.3(5)
C(9)–S(10)–C(11)	101.2(4)	S(10)–C(9)–C(8′)	113.7(5)
C(11)–C(3D)–S(4D)	111.1(7)	S(10)–C(11)–C(3D)	110.1(7)
S(4)–C(5)–C(6)	114.4(5)	Cu(1)–N(1S)–C(1S)	174.9(9)
S(4)–C(5)–C(6′)	112.9(5)	N(1S)–C(1S)–C(2S)	177.4(11)
Cu(1)–N(7)–C(6)	97.2(4)		

Table 11 Atomic coordinates for $[Cu_2(Me_2[18]aneN_2S_4)(NCMe)_2][PF_6]_2$

Atom	*x*	*y*	*z*
Cu(1)	0.484 25(19)	0.481 73(14)	0.189 50(14)
S(4)	0.243 5(4)	0.521 8(3)	0.066 5(3)
S(10)	0.669 6(4)	0.284 3(3)	0.242 9(3)
C(3)	0.193 9(12)	0.709 2(10)	−0.015 7(10)
C(5)	0.068 8(8)	0.477 3(7)	0.207 4(6)
C(6)	0.138 1(8)	0.471 5(7)	0.322 4(6)
C(6′)	0.134 6(8)	0.359 6(7)	0.327 0(6)
N(7)	0.303 5(8)	0.371 5(7)	0.360 2(6)
C(8)	0.307 7(8)	0.245 0(7)	0.374 8(6)
C(8′)	0.405 7(8)	0.242 2(7)	0.447 6(6)
C(9)	0.510 8(8)	0.175 3(7)	0.370 9(6)
C(11)	0.665 7(12)	0.224 3(9)	0.125 2(10)
C(7N)	0.297 3(13)	0.419 9(12)	0.454 4(10)
N(1S)	0.588 9(10)	0.642 0(8)	0.170 3(8)
C(1S)	0.647 3(11)	0.740 4(9)	0.150 0(9)
C(2S)	0.720 6(13)	0.862 6(10)	0.130 3(10)
P(1)	0.166 1(5)	0.918 6(4)	0.285 1(4)
F(1)	0.202 1(12)	0.872 0(10)	0.177 8(8)
F(2)	0.153 1(13)	0.957 1(11)	0.392 5(10)
F(3)	−0.050 7(13)	0.925 5(13)	0.308 0(12)
F(4)	0.141 4(14)	1.081 0(11)	0.203 6(13)
F(5)	0.367 6(13)	0.926 6(12)	0.281 9(13)
F(6)	0.018 7(14)	1.003 3(13)	0.189 0(14)
F(7)	0.339 4(14)	0.816 6(13)	0.340 9(12)
F(8)	0.298 2(14)	1.034 1(13)	0.203 1(13)
F(9)	0.167 6(15)	0.771 4(12)	0.403 7(12)
F(10)	0.051 9(15)	0.790 6(13)	0.329 4(13)

the origin, and a Patterson function located the P and partial S atom. Other non-H atoms were located by successive iterative cycles of least squares refinement and Fourier difference synthesis.[18] The cation was found to be disordered on a site of D_{3d} symmetry, the 1/3 occupied NMe function being superimposed on the 2/3 occupied S, with N–S 0.73 and S–Me 0.68 Å. A single carbon atom in a general position, representing all 12 methylene C atoms, refined well. The PF_6^- anion also exhibited disorder, with a four-fold axis coincident with a crystallographic three-fold axis. Anisotropic thermal parameters were refined for all non-H atoms except for the methyl carbon. Hydrogen atoms were placed in fixed, calculated positions. The high thermal parameters indicate that the estimated standard deviations (e.s.d.s) of the derived parameters are somewhat underestimated, but it is clear that the cation adopts a *meso* configuration. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,34F^2$ gave satisfactory agreement analyses. At final convergence $R = 0.052$, $R' = 0.058$, $S = 1.25$ for 57 independent parameters, and the final Fourier difference synthesis showed no feature above +0.37 or below −0.30 e Å^{-3}. Bond lengths, angles and torsion angles are given in Table 4, fractional atomic coordinates in Table 5.

Synthesis of $[Cu(Me_2[18]aneN_2S_4)]PF_6$.—To a solution of $Me_2[18]aneN_2S_4$ (30 mg, 0.085 mmol) in dry, degassed MeOH (30 cm^3) was added 1 molar equivalent of $[Cu(NCMe)_4]PF_6$ (30 mg, 0.085 mmol). The resulting mixture was refluxed under N_2 for 30 min to give a colourless solution from which a white precipitate was isolated upon addition of diethyl ether, recrystallised from MeCN and dried *in vacuo* (35 mg, 73%) (Found: C, 29.5; H, 5.30; N, 4.90; S, 23.4. Calc. for $C_{14}H_{30}CuF_6N_2PS_4$: C, 29.8; H, 5.35; N, 4.95; S, 22.8%). FAB mass spectrum: m/z = 417; calc. for $[^{63}Cu(Me_2[18]aneN_2S_4)]^+$ m/z = 417. ^{13}C NMR (50.32 MHz, CD_3NO_2, 298 K): δ 54.00 (NCH_2), 42.80 (CH_3) and 32.65 (SCH_2). IR (KBr disc): 2920m, 2855m, 1460m, 1430m, 1380w, 1310m, 1260m, 1230w, 1210w, 1125w, 1090w, 1050w, 1030w, 1000w, 955w, 930w, 840vs, 740m and 555vs cm^{-1}.

Single-crystal Structure Determination of $[Cu(Me_2[18]aneN_2S_4)]PF_6$.—An air-stable, colourless lath (0.12 × 0.21 × 0.43 mm) suitable for single-crystal X-ray analysis was obtained by vapour diffusion of diethyl ether into a solution of the complex in MeCN–MeOH (1:1).

Crystal data. $C_{14}H_{30}CuF_6N_2PS_4$, $M = 563.1$, triclinic, space group $P\bar{1}$, $a = 10.3386(23)$, $b = 10.7643(25)$, $c = 12.054(3)$ Å, $\alpha = 102.450(9)$, $\beta = 113.951(11)$, $\gamma = 102.692(10)°$, $U = 1124.0$ Å^3 [by least-squares refinement on 47 reflections measured at $\pm\omega$ ($26 < 2\theta < 30°$, $\lambda = 0.710\,73$ Å, $T = 278$ K)], $D_c = 1.664$ g cm^{-3}, $Z = 2$, $F(000)$, = 580, μ(Mo-Kα) = 1.453 mm^{-1}.

Data collection and processing. Stoë STADI-4 four-circle diffractometer, equipped with an Oxford Cryosystems low-temperature device,[17] graphite-monochromated Mo-Kα radiation, ω–2θ scans using the learnt-profile method,[19] 3039 reflections measured ($2\theta_{max} = 45°$, h −11 to 9, k −11 to 11, l 0–12) giving 2415 with $F > 6\sigma(F)$. No significant crystal decay, no absorption correction.

Structure analysis and refinement. The positions of the Cu, S and N atoms were deduced using direct methods. Iterative cycles of least-squares refinement and Fourier difference syntheses revealed the positions of all other non-hydrogen atoms giving a well ordered cation and PF_6^- anion. Anisotropic thermal parameters were refined for all non-hydrogen atoms. The H atoms were included in fixed, calculated positions. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,420F^2$ gave satisfactory agreement analyses. At final convergence $R = 0.0438$, $R' = 0.0589$, $S = 1.145$ for 253 independent parameters, and the final Fourier difference synthesis showed no feature above 0.69 or below −0.46 e Å^{-3}. Bond lengths, angles and torsion angles are given in Table 6, fractional coordinates in Table 7.

Synthesis of $[Cu([18]aneN_2S_4)]BPh_4$.—To a solution of $[18]aneN_2S_4$ (40 mg, 0.122 mmol) in dry, degassed MeOH–MeCN (1:1 v/v, 30 cm^3) was added 1 molar equivalent of $[Cu(NCMe)_4]PF_6$ (45 mg, 0.121 mmol). The resulting mixture was refluxed under N_2 for 1 h to give a colourless solution from which a white precipitate was isolated upon addition of an excess of $NaBPh_4$ and recrystallised from $MeNO_2$ (75 mg, 87%) (Found: C, 60.8; H, 6.45; N, 3.65. Calc. for $C_{36}H_{46}BCuN_2S_4$: C, 61.0; H, 6.55; N, 3.95%). FAB mass spectrum: m/z = 389; calc. for $[^{63}Cu([18]aneN_2S_4)]^+$ m/z = 389. IR (KBr disc): 3290w, 3260w, 3040m, 3020w, 2980w, 2910w, 1575m, 1470m, 1440m, 1420m, 1405w, 1290w, 1260m, 1125w, 1095m, 1060w, 1030m, 940w, 870w, 850m, 835vs, 810vs, 720w, 710m and 470w cm^{-1}.

Single-crystal Structure Determination of [Cu([18]aneN_2S_4)]BPh_4.—An air-stable, colourless lath (0.05 × 0.12 × 0.31 mm) suitable for single-crystal X-ray analysis was obtained by slow evaporation from a solution of the complex in $MeNO_2$.

Crystal data. $C_{36}H_{46}BCuN_2S_4$, $M = 709.4$, orthorhombic, space group $P2_12_12_1$, $a = 12.270(4)$, $b = 14.314(8)$, $c = 19.914(5)$ Å, $U = 3498$ Å^3 [by least-squares refinement on 30 reflections measured at $\pm\omega$ ($20 < 2\theta < 24°$, $\lambda = 0.710\,73$ Å, $T = 150$ K)], $D_c = 1.347$ g cm^{-3}, $Z = 4$, $F(000) = 1496$, μ(Mo-Kα) = 0.882 mm^{-1}.

Data collection and processing. Stoë STADI-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device,[17] graphite-monochromated Mo-Kα radiation, ω–2θ scans using the learnt-profile method,[19] 2626 reflections measured ($2\theta_{max} = 45°$, h 0–13, k 0–15, l 0–21) giving 1975 with $F > 2\sigma(F)$. No significant crystal decay, no absorption correction.

Structure analysis and refinement. The position of the Cu atom was deduced from a Patterson synthesis.[18] Iterative cycles of least-squares refinement and Fourier difference syntheses revealed the positions of all other non-hydrogen atoms giving a well ordered cation and BPh_4^- anion. Anisotropic thermal parameters were refined for all non-hydrogen atoms, and although this leads to a data:parameter ratio of only 6:1 the uncertainties and R values were considerably lower than with the C atoms isotropic. The H atoms were included in fixed, calculated positions, except for that on N(7). The alternative positions for this atom were refined competitively and this clearly indicated the correct location. The weighting scheme $w^{-1} = \sigma^2(F) + 0.001\,244F^2$ gave satisfactory agreement analyses. At final convergence $R = 0.0591$, $R' = 0.0720$, $S = 1.083$ for 344 independent parameters, and the final Fourier difference synthesis showed no feature above 0.48 or below −0.41 e Å^{-3}. Bond lengths, angles and torsion angles are given in Table 8, fractional coordinates in Table 9.

Synthesis of [Cu_2(Me_2[18]aneN_2S_4)(NCMe)$_2$][PF_6]$_2$.—Reaction of Me_2[18]aneN_2S_4 (30 mg, 0.085 mmol) with 2 molar equivalents of [Cu(NCMe)$_4$]PF_6 (66 mg, 0.178 mmol) in refluxing dry, degassed MeCN (30 cm^3) for 2 h gave a colourless solution. Addition of diethyl ether and recrystallisation from MeCN afforded a white precipitate (65 mg, 90%) (Found: C, 24.6; H, 4.15; N, 6.50; S, 15.6. Calc. for $C_{18}H_{36}Cu_2F_{12}N_4P_2S_4$: C, 25.3; H, 4.25; N, 6.55; S, 15.0%). FAB mass spectrum: m/z = 481 and 417; calc. for [$^{63}Cu_2$(Me_2[18]aneN_2S_4)]$^+$ m/z = 480, [^{63}Cu(Me_2[18]aneN_2S_4)]$^+$ m/z = 417. ^{13}C NMR (50.32 MHz, CD_3CN, 298 K): δ 54.41 (NCH_2), 48.27 (co-ordinated CH_3CN), 42.68 (CH_3) and 33.14 (SCH_2). IR (KBr disc): 2950m, 2920m, 2860m, 2820w, 2280m, 1460m, 1430m, 1420m, 1375m, 1310m, 1280m, 1255m, 1240w, 1230w, 1210w, 1140w, 1090m, 1050m, 1030w, 1005m, 960m, 940w, 840vs, 740m, 735m, 690w, 560vs and 515w cm^{-1}.

Single-crystal Structure Determination of [Cu_2(Me_2[18]aneN_2S_4)(NCMe)$_2$][PF_6]$_2$.—A pale green crystal (1.35 × 0.12 × 0.08 mm) suitable for single-crystal X-ray analysis was obtained by slow evaporation from a solution of the complex in MeCN–EtOH. The crystal was mounted in a glass capillary to prevent solvent loss.

Crystal data. $C_{18}H_{36}Cu_2F_{12}N_2P_2S_4$, $M = 853.8$, triclinic, space group $P\bar{1}$, $a = 7.3435(18)$, $b = 11.056(3)$, $c = 11.824(3)$ Å, $\alpha = 62.298(10)$, $\beta = 81.904(15)$, $\gamma = 82.764(16)°$, $U = 839.5$ Å^3 [by least-squares refinement on 22 reflections measured at $\pm\omega$ ($22 < 2\theta < 24°$, $\lambda = 0.710\,73$ Å, $T = 298$ K)], $D_c = 1.526$ g cm^{-3}, $Z = 1$, $F(000) = 359$, μ(Mo-Kα) = 1.017 mm^{-1}.

Data collection and processing. Stoë STADI-4 diffractometer, graphite-monochromated Mo-Kα radiation, ω–2θ scans, 2187 reflections measured ($2\theta_{max} = 45°$, h −7 to 7, k −10 to 11, l 0–12) giving 1208 with $F > 4\sigma(F)$. No significant crystal decay, no absorption correction.

Structure analysis and refinement. The copper position was deduced from a Patterson synthesis. Iterative cycles of least-squares refinement and Fourier difference syntheses revealed the positions of all other non-hydrogen atoms.[18] During refinement some disorder of the C atoms adjacent to the aza functions of the macrocycle became apparent. This was modelled successfully by refining the C–C–N units as rigid groups with idealised bond lengths (1.50 Å) and tetrahedral angles around each of these atoms; this identified two equally occupied sites for each C adjacent to N. The PF_6^- counter ions also showed some disorder. This was modelled using partially occupied F atoms, such that the total number of F atoms per P atom summed to six. Macrocyclic H atoms were included in fixed, calculated positions, while the methyl group in MeCN was refined as a rigid group. Anisotropic thermal parameters were refined for all non-hydrogen atoms, except for the disordered C atoms. The weighting scheme $w^{-1} = \sigma^2(F) + 0.009\,748F^2$ gave satisfactory agreement analyses. At final convergence $R = 0.0715$, $R' = 0.0839$, $S = 1.105$ for 218 independent parameters, and the final Fourier difference synthesis showed no feature above 0.88 or below −0.45 e Å^{-3}. Bond lengths, angles and torsion angles are given in Table 10, fractional coordinates in Table 11. For all structures illustrations were prepared using ORTEP,[20] molecular geometry calculations utilised CALC,[21] and scattering factor data were taken from ref. 22.

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

Acknowledgements

We thank the SERC for support and the Royal Society of Edinburgh and the Scottish Office Education Department for a Support Research Fellowship (to M. S.).

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Received 5th May 1992; *Paper* 2/02325C