$[Ag_2([15]aneS_5)_2]^{2+}$: a Binuclear Silver(I) Complex incorporating Asymmetrically Bridging Thioether Donors. ($[15]aneS_5$ = 1,4,7,10,13-Pentathiacyclopentadecane)

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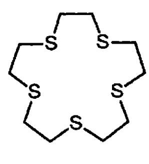
Reaction of $AgNO_3$ with $[15]aneS_5$ affords the homoleptic, binuclear complex $[Ag_2([15]aneS_5)_2]^{2+}$ which shows [3 + 1] thioether co-ordination to one silver(I) centre and [4 + 1] thioether donation to the other, with one S-donor of each macrocycle bridging asymmetrically between the two metal centres.

We have been investigating the co-ordination chemistry of thioether macrocyclic ligands,[1] and have found that an inherent mis-match between the co-ordinative preferences of the metal and crown thioether can lead to unusual stereochemical and/or redox properties in the resultant complexes. The co-ordinative flexibility of $[9]aneS_3$ and $[18]aneS_6$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane; $[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclo-octadecane) has been utilised in this way to stabilise mononuclear Pd^{III},[2] Pt^{III},[1,3] Rh^{II},[2,4] and Au^{II}[5] centres. The octahedral Ag^{I} complexes



[15]aneS_5

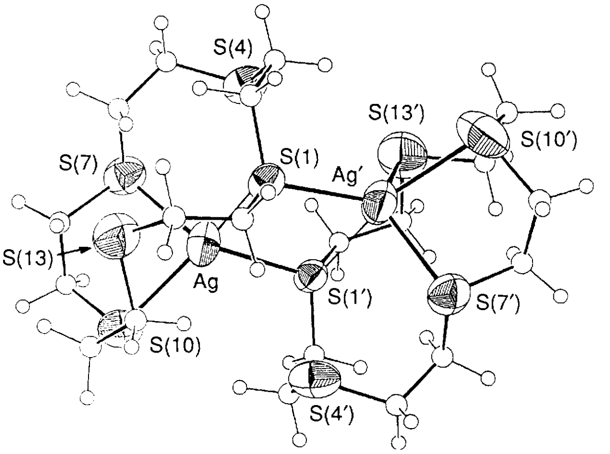


Figure 1. Single crystal X-ray structure of $[Ag_2([15]aneS_5)_2]^{2+}$ with numbering scheme adopted. Significant bond lengths are Ag · · · Ag′ 4.2225(15), Ag–S(7) 2.529(3), Ag–S(10) 2.608(4), Ag–S(1′) 2.537(3), Ag′–S(1) 2.486(3), Ag′–S(7′) 2.558(4), Ag′–S(10′) 2.623(5), Ag′–S(13′) 2.716(5), Ag · · · S(1) 2.907(3), Ag · · · S(1′) 3.131(3) Å.

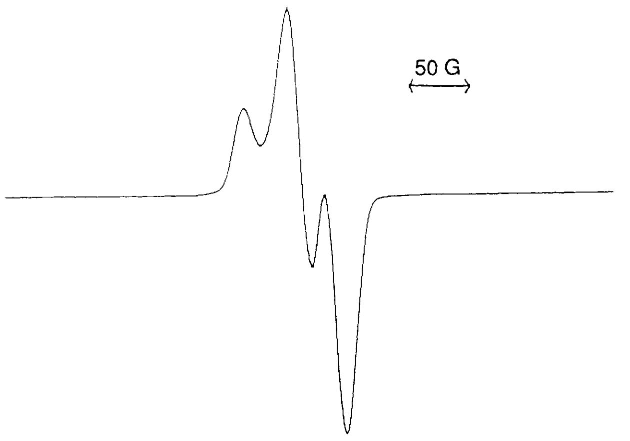


Figure 2. X-Band ESR spectrum (77 K) of the oxidation product of $[Ag_2([15]aneS_5)_2]^{2+}$ in H_2SO_4 glass.

$[Ag([9]aneS_3)_2]^+$[6,8] and $[Ag([18]aneS_6)]^+$[9] have been reported previously; however, we argued that a greater mismatch between metal and ligand might be generated by studying the co-ordination of Ag^I with the pentathia crown [15]aneS_5 (1,4,7,10,13-pentathiacyclopentadecane). In addition, there are very few reports on the co-ordination chemistry of [15]aneS_5 in the literature, most of these being concerned with $Cu^{II/I}$ complexes.[1,10]

Reaction of $AgNO_3$ with one molar equivalent of [15]aneS_5 in refluxing $MeOH/H_2O$ (1 : 1 v/v) followed by the addition of excess of $NaBPh_4$ affords a white, light-sensitive product in 72% yield. The FAB mass spectrum of this species shows molecular ion peaks at M^+ = 409 and 407 corresponding to $[^{109}Ag([15]aneS_5)]^+$ and $[^{107}Ag([15]aneS_5)]^+$ respectively. This, together with IR spectroscopic and microanalytical data, confirms the empirical formulation $[Ag([15]aneS_5)]BPh_4$ for the product.

Crystals of the complex were grown by slow evaporation from a solution of the compound in $MeNO_2$. The single crystal X-ray structure of the complex† shows (Figure 1) a highly unusual dimeric $[Ag_2([15]aneS_5)_2]^{2+}$ cation with one Ag^I ion bound to two S-donors of one crown and to one S-donor of another, Ag–S(7) 2.529(3), Ag–S(10) 2.608(4), Ag–S(1′) 2.537(3) Å. A long-range secondary interaction, Ag · · · S(1) 2.907(3) Å, gives an overall distorted tetrahedral geometry at Ag. The second metal ion, Ag′, adopts a different stereochemistry and is bound to three S-donors of one crown and to one of the other, Ag′–S(7′) 2.558(4), Ag′–S(10′) 2.623(5), Ag′–S(13′) 2.716(5), Ag′–S(1) 2.486(3) Å. S(1′) also interacts at long range, Ag′ · · · S(1′) 3.131(3) Å, while S(4), S(10), and S(4′) are bent well away from the two metal ions and do not interact with them, Ag(1) · · · S(4) 3.555(4), Ag(1) · · · S(13) 3.319(4), Ag′ · · · S(4′) 3.994(4) Å. Importantly, therefore, S(1) and S(1′) act as asymmetric bridges between Ag and Ag′. The Ag · · · Ag′ distance is 4.2225(15) Å. Thioether donors in non-macrocyclic configurations are poor donors to metal centres;[11] it is, therefore, remarkable that individual S-donor atoms in thioether crowns can act as bridges between metal ions. Although the complexes $[Ag_3([9]aneS_3)_3]^{3+}$[6] [Ag–S 2.595(4), 2.613(4), 2.724(23), Ag–S(bridge) 2.480(2) Å], and $[Mo_2(SH)_2([16]aneS_4)_2]^{2+}$[7] [Mo–S 2.320(1), 2.461(2), 2.483(2), 2.537(2), Mo–S(bridge) 2.380(1), Mo–S(hydrosulphide) 2.471(2) Å], incorporate bridging thioether donors, in both of these cases the bridges are symmetric and the products have been isolated only in low yield. The hexathia complexes $[Ag([9]aneS_3)_2]^+$ and $[Ag([18]aneS_6)]^+$ each adopt tetragonally compressed octahedral stereochemistries at Ag^I, Ag–S_{ax} 2.697(5), Ag–S_{eq} 2.753(4) Å for $[Ag([9]aneS_3)_2]^+$,[6,8] Ag–S_{ax} 2.6665(12), Ag–S_{eq} 2.7813(10) Å for $[Ag([18]aneS_6)]^+$.[9]

The ^1H and ^{13}C NMR spectra of $[Ag_2([15]aneS_5)_2]^{2+}$ in CD_3NO_2 at 298 K show single resonances at δ 3.07 and 31.59

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† *Crystal data* for $C_{20}H_{40}S_{10}Ag_2{}^{2+}\cdot 2BC_{24}H_{20}{}^-$. A colourless crystal (0.19 × 0.27 × 0.69 mm) was mounted on a Stoë STADI-4 four-circle diffractometer. Space group $P\bar{1}$, triclinic, a = 11.462(3), b = 11.895(3), c = 27.019(10) Å, α = 78.503(18), β = 84.729(13), γ = 67.118(18)°, V = 3325 Å^3 [from 2θ values of 18 reflections measured at ±ω (31 < 2θ < 32°, λ = 0.71073 Å)], D_c = 1.453 g cm^{-3}, Z = 2, μ = 0.89 mm^{-1}. Data collection used Mo-K_α radiation (λ = 0.71073 Å), ω/2θ scans and the learnt profile method,[12] 7925 unique reflections ($2\theta_{max.}$ = 45°, ±h, ±k, +l), initial corrections (min. 0.230, max. 0.323 respectively) for absorption by means of ψ scans, giving 5344 amplitudes with $F > 6\sigma(F)$ which were used in all calculations. A Patterson synthesis located the Ag atoms and the structure was developed by least-squares refinement and difference Fourier syntheses.[13] Disorder was identified in some of the macrocyclic methylene groups. Attempts to model this using partial C-atoms led to two equally likely sites for C(11′) and C(12′). These, and the other C-atoms [C(12) and C(14′)] exhibiting high thermal parameters were refined isotropically, and the C–C and C–S bond lengths in the regions S(7) to S(13) and S(7′) to S(13′) were constrained to be 1.50 and 1.83 Å respectively, with the angles around carbon tetrahedral.[13] At isotropic convergence final corrections (min. 0.691, max. 1.146) were made using DIFABS.[14] At final convergence, R = 0.0859, R_w = 0.1108, S = 1.117 for 634 parameters and the final difference map showed no feature above +2.15 or below −1.17 e Å^{-3}. Molecular geometry calculations utilised CALC[15] and Figure 1 was produced using ORTEPII;[16] scattering factors were inlaid or taken from ref. 17. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been desposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

respectively for co-ordinated [15]aneS_5 suggesting the formation of fluxional species, probably solvated monomers, in solution. Cyclic voltammetry of $[Ag_2([15]aneS_5)_2](PF_6)_2$ in MeCN (0.1 M $Bu^n{}_4NPF_6$) at platinum electrodes shows a reversible $Ag^{I/II}$ couple at $E_{1/2}$ +0.76 V and a quasi-reversible $Ag^{I/0}$ couple at $E_{1/2}$ −0.38 V *vs.* Fc/Fc$^+$. Controlled potential oxidation of the complex in MeCN affords a transient blue colouration at the electrode surface. Enhanced stabilisation of the oxidation product can be achieved by chemical oxidation under acidic conditions. The ESR spectrum of the resultant blue solution ($\lambda_{max.}$ 566 nm) shows a strong, rhombic signal with $g_1 = 2.061$, $g_2 = 2.038$, $g_3 = 2.011$ (Figure 2). Although the absence of hyperfine coupling to ^{107}Ag and ^{109}Ag (both I = 1/2) precludes conclusive identification of this species as a metal-based radical, the observation that metal-free[15]aneS_5 shows an irreversible oxidation at 1.38 V *vs.* Fc/Fc$^+$ strongly implies that the colouration is indeed due to a genuine mononuclear Ag^{II} species. These results show that Ag^0, Ag^I, and Ag^{II} centres can all be accommodated by the pentathia donor [15]aneS_5.

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