Interconversion of Au$^{I/II/III}$ Centres in Thioether Macrocyclic Complexes: the Synthesis, Structures and Redox Properties of [Au([18]aneS$_6$)]PF$_6$ and [Au$_2$([15]aneS$_5$)$_2$][B(C$_6$F$_5$)$_4$]$_2$

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The interconversion of mononuclear Au$^{I/II/III}$ centres in thioether macrocyclic complexes is related to the stereochemical properties of the parent Au^I species; the structure of [Au([18]aneS$_6$)]$^+$ shows a distorted tetrahedral [2 + 2] coordination at Au^I, while the Au^I complex of [15]aneS$_5$ is binuclear with Au^I ions bridging [15]aneS$_5$ ligands in a macrobicyclic structure.

Au^I is well known to prefer linear coordination.[1] As part of a study of the coordination and redox properties of second and third row transition metal thioether macrocyclic complexes,[2] we have been interested in establishing the coordination geometries of Au^I complexes of ligands which do not necessarily conform to the linear stereochemical preferences of Au^I. The resultant complexes should, therefore, show interesting structural and redox properties.[3]

Reaction of [Au(tht)$_2$]PF$_6$ (tht = tetrahydrothiophene)[4] with [15]aneS$_5$, [18]aneS$_6$, Me$_2$[18]aneN$_2$S$_4$, [18]aneN$_2$S$_4$ and [16]aneS$_4$ (L) in 1:1 molar ratios in CH$_2$Cl$_2$ affords the complexes of stoichiometry [Au(L)]PF$_6$.† Similarly, reaction of [Au(tht)$_2$]PF$_6$ with [28]aneS$_8$ in a 2:1 molar ratio affords [Au$_2$([28]aneS$_8$)](PF$_6$)$_2$.†

The structure of [Au([18]aneS$_6$)]PF$_6$ (Fig. 1) shows‡ a distorted tetrahedral geometry with Au(I) coordinated to four S-donors of the macrocycle with two short and two long Au–S distances, Au–S(1) = 2.321(3), Au–S(10) = 2.320(4), Au–S(7) = 2.856(4), Au–S(4) = 2.870(4) Å. The two remaining thioether S-donors are non-interacting, with the complex incorporating an unusual chelate ring <S(1)–Au–S(10) spanning 155.93(12)°. Additionally, there is disorder represented by two conformations in a section of the macrocycle from C(12) to C(14) involving up and down orientations of the

dangling S(13) atom. The structure of [Au([18]aneS$_6$)]$^+$ differs markedly from that of [Ag([18]aneS$_6$)]$^+$, which shows[5] octahedral coordination at Ag^I, Ag–S = 2.6665(12), 2.7813(10) Å.

We have shown previously that complexes of [15]aneS$_5$ can show highly unusual structural features with Ag^I in the solid state.[6] We were interested in assessing the coordination and stereochemistry of Au^I complexes of [15]aneS$_5$ given the inherent strain that would be imposed on Au^I encapsulated by a 15-membered ring macrocycle. The single crystal X-ray determination of [Au([15]aneS$_5$)]B(C$_6$F$_5$)$_4$ shows§ the cation to be dimeric and lying across a crystallographic inversion centre with Au^I centres bridging [15]aneS$_5$ crowns in a macrobicyclic structure (Fig. 2), Au–S(1) = 2.3001(13), Au–S(10') = 2.2927(13), Au···S(4) = 3.2088(14), Au···S(13) = 3.1055(13), Au···Au' = 5.6943(3) Å, S(1)–Au–S(10') =

[9]aneS$_3$

[15]aneS$_5$　　　　　　　　[18]aneS$_6$

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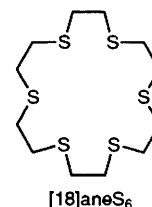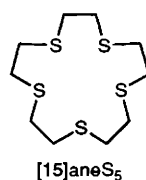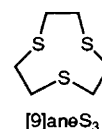
† All complexes have been fully characterised by elemental analysis, ^{1}H, ^{13}C NMR, FAB mass, IR and electronic spectroscopy. The single crystal X-ray structure of [Au(Me$_2$[18]aneN$_2$S$_4$)]$^+$ shows two short and one long Au–S distance: Au–S(1) = 2.304(2), Au–S(10) = 2.314(2), Au–S(4) = 2.888(2), Au···S(13) = 3.624(2), Au···N(7) = 3.795(5), Au···N(16) = 3.660(5) Å, <S(1)–Au–S(10) = 177.30(5)°. The single crystal X-ray structure of [Au$_2$([28]aneS$_8$)]$^{2+}$ shows two Au^I centres complexed tetrahedrally within the octadentate ring in a [2 + 2] manner, Au–S(1) = 2.3301(19), Au–S(11) = 2.3378(18), Au–S(4) = 2.7891(20), Au–S(8) = 2.7629(20), Au···Au = 5.6977(6) Å, <S(1)–Au–S(11) = 155.58(6)°.

‡ *Crystal data*: [C$_{12}$H$_{24}$S$_6$Au]$^+$[PF$_6$]$^-$, M = 702.56, triclinic, space group $P\bar{1}$, a = 9.7537(15), b = 11.0127(17), c = 11.2005(21) Å, α = 79.235(9), β = 75.344(8), γ = 75.582(9)°, V = 1117.4 Å^3 [from 2θ values of 36 reflections measured at ±ω (26 < 2θ < 30°), λ = 0.71073 Å], D_c = 2.088 g cm^{-3}, Z = 2, T = 298 K, μ = 7.226 mm^{-1}, F(000) = 680.

Data collection and processing: Stoë STADI-4 four circle diffractometer, graphite monochromated Mo-Kα radiation, ω-2θ scans with ω width (0.80 + 0.347 tan θ)°; 2845 data measured (2θ$_{max}$ 45°, h –9 → 10, k –11 → 11, l 0 → 12 giving 2536 with $F \geq$ 6σ(F) for use in all calculations. Initial absorption corrections (max 0.2490, min 0.0722) were made using Ψ scans.

Structure solution and refinement: A Patterson synthesis located the Au atom and iterative cycles of least-squares refinement and difference Fourier synthesis located the remaining non-H atoms. At isotropic convergence, final corrections (min 0.582, max 1.496) for absorption were applied using DIFABS.[10] Disorder in a part of the uncoordinated section of the macrocycle was modelled by half occupancy of two conformations with the C–C bond lengths fixed. Refinement by least-squares analysis on F with anisotropic thermal parameters for all ordered non-H atoms and with H-atoms in fixed, calculated positions converged at R, R_w = 0.0547, 0.0697, respectively, S = 0.991 for 243 refined parameters, and the final ΔF synthesis showed no feature above 1.39 eÅ^{-3}. The weighting scheme, w^{-1} = σ^2(F) + 0.000229F^2 gave satisfactory agreement analyses and in the final cycle (Δ/σ)$_{max}$ was 0.026.

§ *Crystal data*: [C$_{20}$H$_{40}$S$_{10}$Au$_2$]$^{2+}$·2[BC$_{24}$F$_{20}$], M = 2352.75, triclinic, space group $P\bar{1}$, a = 8.693(3), b = 14.819(5), c = 16.455(8) Å, α = 66.839(20), β = 89.45(3), γ = 76.72(3)°, V = 1889 Å^3 [from 2θ values of 22 reflections measured at ±ω (31 < 2θ < 32°), λ = 0.71073 Å], D_c = 2.068 g cm^{-3}, Z = 1, T = 150 K, μ = 4.276 mm^{-1}, F(000) = 1136.

Data collection and processing: Stoë STADI-4 four circle diffractometer fitted with an Oxford Cryosystems low-temperature device,[11] graphite monochromated Mo-Kα radiation, ω-2θ scans using the learnt-profile method,[12] 5142 data measured (2θ$_{max}$ 45°, h –9 → 9, k –14 → 15, l 0 → 17) 4742 unique (R_{int} = 0.0007) giving 4638 with $F \geq$ 6σ(F) for use in all calculations. Linear isotropic crystal decay ($\simeq$ 2%) corrected for during data reduction, no absorption correction.

Structure solution and refinement: A Patterson synthesis located the Au atom and iterative cycles of least-squares refinement and difference Fourier synthesis located the remaining non-H atoms. At isotropic convergence, corrections (min 0.912, max 1.103) for absorption were applied using DIFABS.[10] Refinement by least-squares analysis on F, with anisotropic thermal parameters for all non-H atoms, with H-atoms in fixed, calculated positions and with the pentafluorophenyl groups of the [B(C$_6$F$_5$)$_4$]$^-$ counter-anion refined as rigid groups, converged at R, R_w = 0.0274, 0.0343 respectively, S = 1.126 for 503 refined parameters, and the final ΔF synthesis showed no feature above 0.88 e Å^{-3}. The weighting scheme w^{-1} = σ^2(F) + 0.000045F^2 gave satisfactory agreement analyses and in the final cycle (Δ/σ)$_{max}$ was 0.065. The single crystal X-ray structure of [Au([15]aneS$_5$)]PF$_6$ has also been determined and the cation has been found to be isostructural.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.
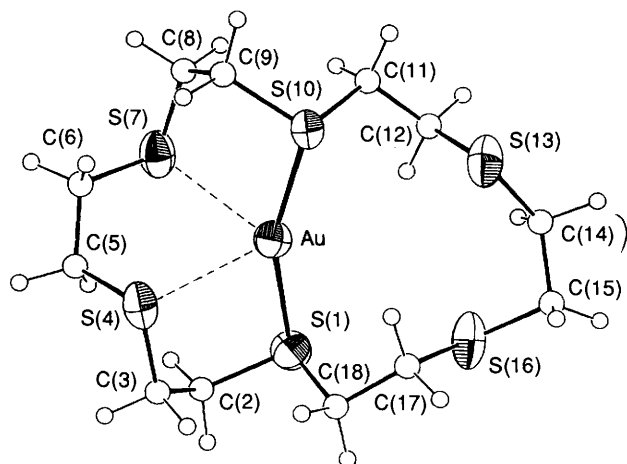
Fig. 1 View of the structure of [Au([18]aneS₆)]⁺ with numbering scheme adopted

Table 1 Cyclic voltammetric[a] and coulometric data for Au[I] thioether complexes

Complex	$^1E_{\frac{1}{2}}$/V	n[b]	$^2E_{\frac{1}{2}}$/V	n[b]
[Au([9]aneS₃)₂]⁺	+0.12[i,c]	1	+0.46	1
[Au([15]aneS₅)]⁺	+0.36	1	+0.54	1
[Au([18]aneS₆)]⁺	+0.36	1	+0.56	1
[Au(Me₂[18]aneN₂S₄)]⁺	+0.14	1	+0.43	1
[Au([18]aneN₂S₄)]⁺	+0.85[i]	2		
[Au₂([28]aneS₈)]²⁺	+0.55[br]	4		
[Au([16]aneS₄)]⁺ [d]	+0.14[br]	2		

i: Irreversible. [a] Measured in MeCN (0.1 mol dm⁻³ Buⁿ₄NPF₆) at 293 K at platinum electrodes at a scan rate of 100 mV s⁻¹ vs. ferrocene/ferrocinium, Fc/Fc⁺. [b] Number of electrons per cation obtained coulometrically at a Pt basket at 243 K. br: Broad wave with peak-to-peak separation of 200 mV s⁻¹. [c] Irreversible wave (E_{pc}) due to slow Au[I] → Au[II] electron transfer. The cyclic voltammogram of [Au([9]aneS₃)₂]⁺ at 298 K, 100 mV s⁻¹, shows a Au[I] → Au[III] couple in the oxidative scan, with two separated Au[III] → Au[II] and Au[II] → Au[I] couples observed on the return scan. [d] The structure of [Au([16]aneS₄)]⁺ is unknown, although we suspect a polynuclear or polymeric structure in the solid state.

169.90(5)°. The remaining non-bonded S-donors point inward towards the cavity formed by the two metal-bridged [15]aneS₅ ligands. This is an unusual and unexpected structure which reflects the predisposition for a highly distorted tetrahedral Au[I] geometry in a homoleptic thioether environment, and the kinetically preferred exo coordination of the pentathioether crown.[7]

In solution, the complexes [Au([16]aneS₄)]⁺ and [Au₂([28]aneS₈)]²⁺ each show a two-electron oxidation process per Au; this corresponds to oxidation of d¹⁰ Au[I] directly to square-planar d⁸ Au[III]. [Au([18]aneN₂S₄)]⁺ readily undergoes demetallation reactions in solution under ambient conditions, and shows an apparent two-electron oxidation. We have found previously that complexes of [18]aneN₂S₄ and Me₂[18]aneN₂S₄ differ markedly in terms of structure and, therefore, redox properties.[8]

In solution, [Au([18]aneS₆)]⁺, [Au(Me₂[18]aneN₂S₄)]⁺ and [Au([15]aneS₅)]⁺ show reversible Au[I/II] and Au[II/III] redox couples. Cyclic voltammetric and coulometric data for Au[I] thioether macrocyclic complexes are summarized in Table 1. The formation of Au[II] and Au[III] species has been monitored spectroelectrochemically using in situ electronic spectroscopy, the interconversion of Au[I/II/III] centres occurring reversibly and isosbestically. The one-electron oxidation products are EPR-active and show four-line spectra in solution owing to
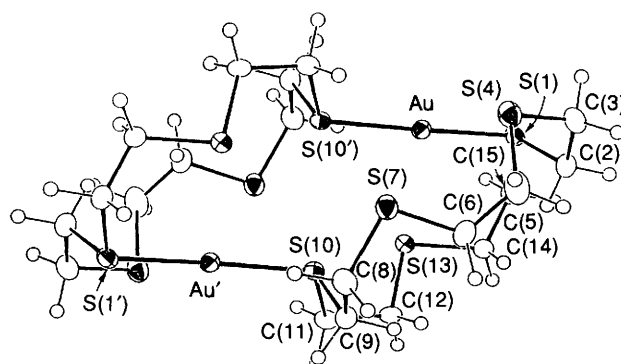

Fig. 2 View of the structure of [Au₂([15]aneS₅)₂]²⁺ with numbering scheme adopted. Primed atoms are related to their unprimed equivalents by operation of the inversion centre at (½, 0, 0)

hyperfine coupling to ¹⁹⁷Au ($I = 3/2$, 100%). Interestingly, the complexes of homoleptic thioether crowns that incorporate non-interacting S-donors in the precursor Au[I] species afford the most stable Au[II] species. This reflects the requirement of increasing coordination number on going from Au[I] [2 + 2] coordination to Au[II] (Jahn–Teller distorted octahedral coordination) to Au[III] [4 + 2] coordination.[3] Thus, these precursor Au[I] complexes may be regarded as stereochemically strained in the sense that the extra S-donors destabilise the d¹⁰ Au[I] configuration and provide a driving force for the formation of mononuclear Au[II] species. Facile metal-based electron transfer in these systems, therefore, necessitates rapid M–S bond making and breaking.[9] Significantly, the redox behaviour (two reversible, one-electron waves) of [Au([18]aneS₆)]⁺ differs from that of the bis-sandwich analogue [Au([9]aneS₃)₂]⁺ and reflects the importance of facile electron transfer between Au[I/II/III] centres within one encapsulating ligand.

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