Gold Thioether Chemistry: Synthesis, Structure, and Redox Interconversion of $[Au([9]aneS_3)_2]^{+/2+/3+}$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane)

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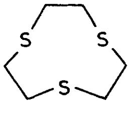
The crystal structure of $[Au([9]aneS_3)_2]PF_6$ shows distorted tetrahedral S_4 co-ordination at Au^I with one $[9]aneS_3$ bound in a unidentate manner [Au(1)–S(11) 2.302(6) Å], and the other bound asymmetrically through three S-donors [Au(1)–S(21) 2.350(7), Au(1)–S(24) 2.733(8), Au(1)–S(27) 2.825(8) Å]; oxidation of this complex affords the Au^{III} analogue $[Au([9]aneS_3)_2]^{3+}$ which has a distorted octahedral stereochemistry [Au(1) · · · S(1) 2.926(4), Au(1)–S(4) 2.348(4), Au(1)–S(7) 2.354(4) Å]; the intermediate paramagnetic Au^{II} species has been identified by e.s.r. spectroscopy.

The trithia macrocyclic ligand $[9]aneS_3$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane) has been shown to bind facially to a range of transition metal ions.[1] We have been investigating the binding of this ligand to heavy metal ions, *e.g.* Rh^{II},[2,3] Pd^{II},[2,4] and Pt^{II},[5] whose co-ordinative properties are not fully compatible with facial binding of $[9]aneS_3$. This has led to the synthesis of a range of complexes showing unusual stereochemical and redox properties.[2–6] The chemistry of Au^I is dominated by linear and oligomeric complexes,[7] and a study of the binding of $[9]aneS_3$ to Au^I was therefore undertaken. Wieghardt and co-workers have reported recently a very interesting trimeric Ag^I complex $[Ag_3([9]aneS_3)_3]^{3+}$ incorporating bridging thioether ligands.[8] The binding of thioether macrocycles to Au has not been reported previously, and we report herein the synthesis, structure and redox interconversion of $[Au([9]aneS_3)_2]^{+/2+/3+}$.

Reaction of $KAuCl_4$ with $[9]aneS_3$ affords a yellow complex



$[9]aneS_3$

of stoicheiometry $AuCl_3([9]aneS_3)$. Reaction with a second equivalent of $[9]aneS_3$ under reducing conditions (water/MeOH) gives the corresponding Au^I species $[Au([9]aneS_3)_2]^+$ which can be isolated as a PF_6^- salt in low yield. The single crystal *X*-ray structure† of $[Au([9]aneS_3)_2]PF_6$ (Figure 1) has two independent Au^I ions per asymmetric unit. The structural determination shows the Au^I centre bound asymmetrically to three S-donors of one ligand [Au(1)–S(21) 2.350(7), Au(1)–S(24) 2.733(8), Au(1)–S(27) 2.825(8) Å for one cation, and Au(2)–S(41) 2.341(8), Au(2)–S(44) 2.801(8), Au(2)–S(47) 2.807(8) Å for the other cation] and to one S-donor of the second $[9]aneS_3$ [Au(1)–S(11) 2.302(6) and Au(2)–S(31) 2.289(7) Å]. There are, therefore, two short and two long Au–S distances with the angles around the Au^I centre highly distorted from tetrahedral, ∠S(11)–Au(1)–S(21) 153.98(23), S(11)–Au(1)–S(24) 113.06(23), S(11)–Au(1)–S(27) 118.35(21), S(31)–Au(2)–S(41) 156.4(3), S(31)–Au(2)–S(44) 115.53(23), S(31)–Au(2)–S(47) 110.78(24)°. Importantly, $[Au([9]aneS_3)_2]^+$ is *not* isostructural with the Ag^I congener $[Ag([9]aneS_3)_2]^+$; the latter shows a centrosymmetric octahedral structure with the metal ion bound to six S-donors [Ag–S(1) 2.6665(12), Ag–S(4) 2.7813(10) Å].[8,9] The structure of $[Au([9]aneS_3)_2]^+$ can therefore be regarded as a compromise between the preferred facial co-ordination of $[9]aneS_3$,[1] and the tendency of mononuclear Au^I to form linear complexes.[7] No example of terminally bound monodentate $[9]aneS_3$ has been reported previously.

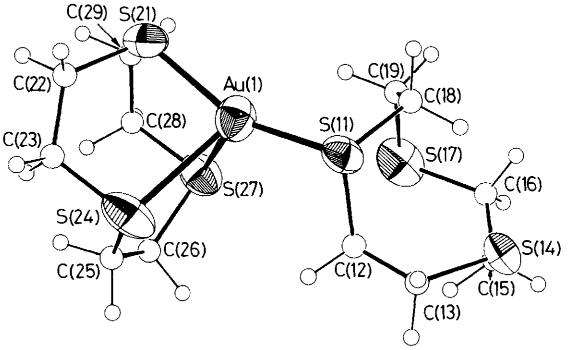


Figure 1. View of one $[Au([9]aneS_3)_2]^+$ cation with numbering scheme.

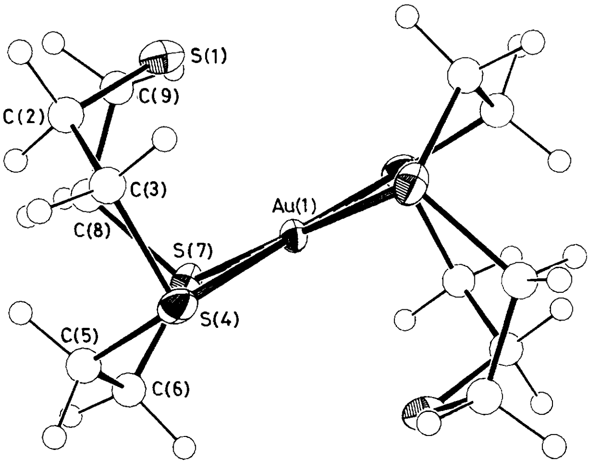


Figure 2. View of the centrosymmetric $[Au([9]aneS_3)_2]^{3+}$ cation with numbering scheme.

$[Au([9]aneS_3)_2]^+$ is air-sensitive in solution, and can be readily oxidised chemically or aerially to a yellow intermediate species ($\lambda_{max.}$ = 403 nm), the e.s.r. spectrum of which shows g_{av} = 2.019 with hyperfine coupling to ^{197}Au (I = 3/2, 100%), A = 59 G (G = 10^{-4} T). These spectral data, and the relative inertness of $[9]aneS_3$ under these reaction conditions, indicate the formation of a genuine paramagnetic d^9 Au^{II} species in

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† *X*-Ray structure determination of $[Au([9]aneS_3)_2]^+$ PF_6^-. A colourless plate (0.39 × 0.19 × 0.038 mm) was obtained by recrystallisation from MeCN/diethyl ether (vapour diffusion). *Crystal Data:* $C_{12}H_{24}S_6Au^+$ PF_6^-, M = 702.56, monoclinic, space group $P2_1$, a = 7.4119(5), b = 19.1391(18), c = 16.1197(13) Å, β = 102.362(7)°, V = 2233.7 Å^3 [from 2θ values of 50 reflections measured at ±ω (2θ = 22 → 25°, $\bar{\lambda}$ = 0.71073 Å)], T = 298 K, D_c = 2.089 g cm^{-3}, Z = 4; $F(000)$ = 1360, μ = 72.29 cm^{-1}. Stoë STADI-4 four-circle diffractometer, Mo-K_α *X*-radiation, ω–2θ scans using the learnt-profile method,[11] 3024 unique reflections measured ($2\theta_{max}$ = 45°, h −7 → 7, k 0 → 20, l 0 → 17), initial correction for absorption by means of 180 ψ scans, giving 2548 data with $F \geq 6\sigma(F)$. Linear isotropic decay (*ca.* 12%) corrected for. The Au atoms were located from a Patterson synthesis. Least-squares refinement and difference Fourier synthesis[12] located all non-H atoms. At isotropic convergence, final corrections for absorption were made using DIFABS[13] (max 1.707, min 0.510). Anisotropic thermal parameters were refined for Au, S, P, and fully occupied F atoms. H atoms were included in fixed, calculated positions.[12] The structure contained elements of disorder which required to be modelled: for the one disordered PF_6^- anion, this was achieved using partially occupied F atoms. The more significant disorder, however, affected the two $-CH_2-CH_2-$ moieties bonded to S(24): restrained refinement[12] (S–C 1.83, C–C 1.52 Å; ∠SCC 108.5°) converged satisfactorily, giving occupancies of 0.72(5) for C(22), C(23) and 0.62(5) for C(25), C(26). No enantiomorph discrimination was detectable despite the application of a methodology, based on consideration of those reflections calculated to be most enantiomorph-sensitive, which had been successful previously.[14] We were, therefore, unable to determine the absolute structure in this case. The data quoted in the text refers to one of the two possible enantiomorphs. The weighting scheme $w^{-1} = \sigma^2(F) + 0.002103F^2$ gave satisfactory agreement analyses. At final convergence R, R_w = 0.0608, 0.0839 respectively for 344 parameters, S = 1.124. The maximum and minimum residues in the final ΔF syntheses were +1.01 and −1.47 e Å^{-3} respectively.

X-Ray structure determination of $[Au([9]aneS_3)_2]^{3+}$ (H_3O^+) $(4ClO_4^-)\cdot 3H_2O$. A red equant crystal (0.20 × 0.25 × 0.30 mm) was obtained by recrystallisation from $HClO_4$ solution. The crystal was sealed in a Lindemann capillary tube with a small amount of $HClO_4$ mother liquor and cooled on the diffractometer using an Oxford Cryosystems low temperature device;[15] a temperature of 223 ± 0.2 K was maintained during data collection. *Crystal Data:* $C_{12}H_{24}S_6Au^{3+}$ (H_3O^+) $(4ClO_4^-)\cdot 3H_2O$, M = 1029.4, monoclinic, space group $C2/c$, a = 20.398(10), b = 9.425(10), c = 20.051(11) Å, β = 124.93(3)°, V = 3160.2 Å^3 [from 2θ values of 26 reflections measured at ±ω (2θ = 24 → 25°, $\bar{\lambda}$ = 0.71073 Å)], T = 223 K, D_c = 2.163 g cm^{-3}, Z = 4, $F(000)$ = 2036, μ = 54.45 cm^{-1}. Stoë STADI-4 four-circle diffractometer, Mo-K_α *X*-radiation, ω–2θ scans using the learnt-profile method,[11] 2546 reflections measured ($2\theta_{max}$ = 45°, h −20 → 21, k 0 → 10, l 0 → 21), 2048 unique reflections (R_{int} = 0.057), giving 1561 data with $F \geq 6\sigma(F)$. The atomic co-ordinates for $[Pd([9]aneS_3)_2]^{3+}\cdot H_3O^+\cdot 4ClO_4^-$ (ref. 2) were taken as starting values for least-squares refinement and difference Fourier synthesis[12] located all remaining non-H atoms. At isotropic convergence, corrections for absorption were made using DIFABS[13] (max 1.190, min 0.800). Anisotropic thermal parameters were refined for Au, S, Cl, O, and C atoms. Methylene H atoms were included in calculated positions, while H_3O^+ and H_2O were refined as rigid groups.[12] The weighting scheme $w^{-1} = \sigma^2(F) + 0.005768F^2$ gave satisfactory agreement analyses. At final convergence R, R_w = 0.0584, 0.0808 respectively for 211 parameters, S = 1.035. The maximum and minimum residues in the final ΔF syntheses were +3.56 and −2.67 e Å^{-3} respectively.

Illustrations were prepared using ORTEP[16], molecular geometry calculations utilised CALC,[17] and scattering factor data were taken from ref. 18.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

solution. The e.s.r. spectrum suggests a distorted octahedral stereochemistry for this intermediate. Very few examples of paramagnetic Au^{II} complexes have been reported,[10] the majority of such species being either mixed Au^{I}/Au^{III} complexes, or binuclear or cluster compounds.[7] Further oxidation of the Au^{II} species occurs readily in solution to afford the Au^{III} analogue $[Au([9]aneS_3)_2]^{3+}$ (λ_{max} 460, 340, 254 nm), the single crystal *X*-ray structure of which shows† the Au^{III} on a crystallographic inversion centre. The centrosymmetric complex cation has a distorted octahedral stereochemistry at the Au^{III} centre (Figure 2). Four Au–S bonds define a square plane [Au(1)–S(4) 2.348(4), Au(1)–S(7) 2.354(4) Å], while the two remaining thia donors participate in long-range apical interactions with the metal centre, [Au(1) · · · S(1) 2.926(4) Å]. Facial co-ordination of $[9]aneS_3$ to the metal centre is inhibited by the preferred square planar geometry of d^8 Au^{III}.

The facile interconversion of $Au^{I/II/III}$ species in the presence of $[9]aneS_3$ reflects the ability of this minicycle to act as a formal 2-, 4-, or 6-electron donor.

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References

1 R. S. Glass, W. N. Setzer, C. A. Ogle, and G. S. Wilson, *Inorg. Chem.*, 1983, **22**, 266; K. Wieghardt, H-J. Küppers, and J. Weiss, *ibid.*, 1985, **24**, 3067; D. Sellmann and P. Frank, *Angew. Chem.*, 1986, **98**, 1115; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1107; H-J. Küppers, A. Neves, C. Pomp, D. Ventur, K. Wieghardt, B. Nuber, and J. Weiss, *Inorg. Chem.*, 1986, **25**, 2400; G. S. Wilson, D. D. Swanson, and R. S. Glass, *ibid.*, 1986, **25**, 3827; E. W. Abel, P. D. Beer, I. Moss, K. G. Orrell, V. Sik, P. A. Bates, and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, 1987, 978; M. N. Bell, A. J. Blake, H-J. Küppers, M. Schröder, and K. Wieghardt, *Angew. Chem.*, 1987, **99**, 253; *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 250; S. C. Rawle and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, 1987, 308; H-J. Küppers, K. Wieghardt, B. Nuber, J. Weiss, E. Bill, and A. X. Trautwein, *Inorg. Chem.*, 1987, **26**, 3762; S. C. Rawle, T. J. Sewall, and S. R. Cooper, *Inorg. Chem.*, 1987, **26**, 3769; E. W. Abel, P. D. Beer, I. Moss, K. G. Orrell, V. Sik, P. A. Bates, and M. B. Hursthouse, *J. Organomet. Chem.*, 1988, **341**, 559; C. Pomp, S. Drüeke, H-J. Küppers, K. Wieghardt, C. Krüger, B. Nuber, and J. Weiss, *Z. Naturforsch., Teil B*, 1988, **43**, 299.

2 A. J. Blake, A. J. Holder, T. I. Hyde, and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1987, 987.

3 A. J. Holder, M. Schröder, and T. A. Stephenson, *Polyhedron*, 1987, **6**, 461; S. C. Rawle, R. Yagbasan, K. Prout, and S. R. Cooper, *J. Am. Chem. Soc.*., 1987, **109**, 6181; A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1988, 1861.

4 K. Wieghardt, H-J. Küppers, E. Raabe, and C. Krüger, *Angew. Chem.*, 1986, **98**, 1136; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1101; A. J. Blake, A. J. Holder, T. I. Hyde, Y. V. Roberts, A. J. Lavery, and M. Schröder, *J. Organomet. Chem.*, 1987, **323**, 261; A. J. Blake, A. J. Holder, Y. V. Roberts, and M. Schröder, *Acta Crystallogr., Sect. C*, 1988, **44**, 360.

5 A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, M. O. Odulate, A. J. Lavery, and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1987, 118.

6 M. Schröder, *Pure Appl. Chem.*, 1988, **60**, 517 and references therein; M. N. Bell, A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, A. J. Lavery, G. Reid, and M. Schröder, *J. Inclusion Phenom.*, 1987, **5**, 169; A. J. Blake, R. O. Gould, A. J. Lavery, and M. Schröder, *Angew. Chem.*, 1986, **98**, 282; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 274.

7 R. J. Puddephatt, in 'Comprehensive Coordination Chemistry,' eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 5, Ch. 54, p. 861.

8 H-J. Küppers, K. Wieghardt, Y-H. Tsay, C. Krüger, B. Nuber, and J. Weiss, *Angew. Chem.*, 1987, **99**, 583; *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 575.

9 J. Clarkson, R. Yagbasan, P. J. Blower, S. C. Rawle, and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, 1987, 950.

10 For example see: A. MacCragh and W. S. Koski, *J. Am. Chem. Soc.*, 1965, **87**, 2496; I. F. Warren and M. F. Hawthorne, *ibid.*, 1968, **90**, 4823; T. J. Bergendahl and E. M. Bergendahl, *Inorg. Chem.*, 1972, **11**, 638; R. L. Schlupp and A. H. Maki, *ibid.*, 1974, **13**, 44.

11 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

12 SHELX76, Program for Crystal Structure Determination, G. M. Sheldrick, University of Cambridge, 1976.

13 DIFABS, Program for Empirical Absorption Corrections, N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

14 A. J. Blake, R. O. Gould, G. Reid, and M. Schröder, *J. Organomet. Chem.*, 1988, **356**, 389.

15 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.

16 ORTEPII, interactive version, P. D. Mallinson and K. W. Muir, *J. Appl. Crystallogr.*, 1985, **18**, 51.

17 CALC, Fortran77 version, R. O. Gould and P. Taylor, University of Edinburgh, 1985.

18 D. T. Cromer and J. L. Mann, *Acta Crystallogr., Sect. A.*, 1968, **24**, 321.