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New Co-ordination Mode of 4,5-Dimercapto-1,3-dithiole-2-thionate(2−) in Polynuclear Gold(I) Complexes. Crystal Structures of $[Au_3(\mu_3\text{-}C_3S_5)(PPh_3)_3]ClO_4$ and $[Au_4(\mu\text{-}C_3S_5)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]$

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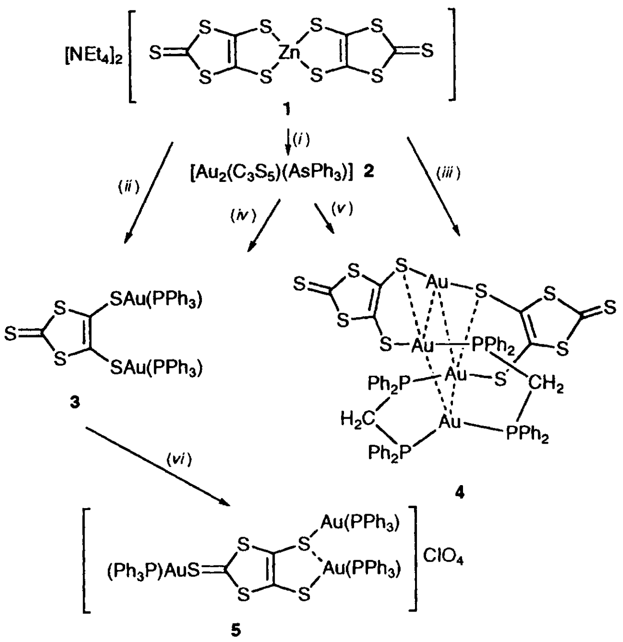
The ligand 4,5-dimercapto-1,3-dithiole-2-thionate(2−) ($C_3S_5^{2-}$) has been transferred from $[NEt_4]_2[Zn(C_3S_5)_2]$ to gold(I) centres, affording di-, tri- or tetra-nuclear complexes containing the $C_3S_5^{2-}$ ligand in unprecedented μ- or μ_3-bridging forms.

Metal complexes of the ligand 4,5-dimercapto-1,3-dithiole-2-thionate(2−) ($C_3S_5^{2-}$) have received considerable attention,[1,2] largely because some of them form good electrical conductors [1,2] or superconductors.[3-5]

The ligand $C_3S_5^{2-}$ is often capable of replacing all other ligands at a metal centre. The reaction of methanolic $C_3S_5^{2-}$ with metal salts thus generally leads to species $[M(C_3S_5)_n]^{m-}$, and consequently only a few heteroleptic $C_3S_5^{2-}$ complexes are known; previous studies have centred on homoleptic bis- or tris-chelate $C_3S_5^{2-}$ complexes.[6] Here we report on heteroleptic $C_3S_5^{2-}$ complexes of gold(I).[†]

The salt $[NEt_4]_2[Zn(C_3S_5)_2]$ **1** is a suitable reagent for transferring $C_3S_5^{2-}$ to other metal centres under very mild conditions. Thus reaction of **1** with chlorogold(I) complexes in a Zn:Au ratio of 1:4 affords the heteroleptic $C_3S_5^{2-}$ derivatives **2**–**4** (Scheme 1). Complex $[Au_2(C_3S_5)(AsPh_3)]$ **2** is noteworthy as it contains only one arsine ligand per two gold atoms and is thus a useful starting material for the preparation of **3** and **4** by addition of PPh_3 or $Ph_2PCH_2PPh_2$ (dppm). It could possess a dimeric structure analogous to those reported for $[\{Au_2(S\text{–}S)(PEt_3)\}_2]$ (S–S = $C_6H_4S_2$-1,2 or C_6H_3Me-1-S_2-3,4).[7,8]



Scheme 1 (*i*) $[AuCl(AsPh_3)]$; (*ii*) $[AuCl(PPh_3)]$; (*iii*) $[(AuCl)_2(\mu\text{-}dppm)]$; (*iv*) $2PPh_3$; (*v*) $Ph_2PCH_2PPh_2$; (*vi*) $[Au(OClO_3)(PPh_3)]$

The $^{31}P\text{-}\{^1H\}$ NMR spectra show a single resonance at δ 36.5 for **3** and an AA′BB′ system for **4** (δ_A 37.5, δ_B 24.3, $^2J_{AA'}$ 310, $^2J_{AB}$ 98.5, $^2J_{A'B'}$ 101.2 Hz) (complex **2** was too insoluble to record NMR data). The FAB mass spectra of **3** and **4** show the dinuclear fragments $[Au_2(C_3S_5)L_2]^+$ (L_2 = $2PPh_3$ or dppm) at *m*/*z* 1114 (26%) and 974 (8%) respectively, but the NMR data for **4** are incompatible with a dinuclear formulation. A signal at *m*/*z* 1573 (7%) for **3**, assignable to $[M + Au(PPh_3)]^+$, seemed to indicate that a further $Au(PPh_3)$ fragment could be incorporated into complex **3**.

The reaction of **3** with $[Au(OClO_3)(PPh_3)]$ affords **5** in good yield (76%). Its $^{31}P\text{-}\{^1H\}$ NMR spectrum shows a broad singlet at δ 35.7 both at room temperature and at −70 °C, presumably because of fluxional processes. The mass spectrum shows the parent ion at *m*/*z* 1573 (32%).

The structures of complexes **4** and **5** were determined by single-crystal X-ray diffraction analysis and reveal the $C_3S_5^{2-}$ ligand in hitherto unprecedented μ- or μ_3-bridging forms. The tetranuclear complex $[Au_4(\mu\text{-}C_3S_5)_2(\mu\text{-}dppm)_2]$ **4**[‡] is shown in

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[†] Preparation of **2**, **3** and **4**: [AuClL] (0.2 mmol) (L = $AsPh_3$ or PPh_3) or $[(AuCl)_2(\mu\text{-}dppm)]$ (0.1 mmol) was added to a solution of $[NEt_4]_2[Zn(C_3S_5)_2]$ (0.05 mmol) in acetone; after stirring for 3 h the product **2** was filtered off (82%). The solvent was evaporated to 5 cm^3, whereupon addition of diethyl ether (20 cm^3) afforded orange **3** (76%) or yellow **4** (41%). The complexes were washed with water (2 × 5 cm^3) and dried. They could also be obtained by addition of PPh_3 (0.1 mmol) or dppm (0.05 mmol) to an acetone suspension of **2** (0.1 mmol); after stirring for 2 h and work-up as above the yields were 90% (**3**) and 78% (**4**). Preparation of **5**: complex **3** (0.1 mmol) was added to a dichloromethane solution of $[Au(OClO_3)(PPh_3)]$ (0.1 mmol). After stirring for 2 h, the solution was evaporated to 5 cm^3, whereupon addition of diethyl ether (20 cm^3) afforded **5** (76%). All the complexes were satisfactorily characterised by elemental analyses (C, H, N, S), IR and NMR spectroscopy (^1H, ^{31}P) and FAB mass spectrometry.

[‡] Compound **4**·Me_2CO: $C_{59}H_{50}Au_4OP_4S_{10}$, M_r = 2007.3, monoclinic, space group *C*2/*c*, $a = 36.777(8)$, $b = 14.961(5)$, $c = 23.366(7)$ Å, $\beta = 102.85(3)°$, U = 12 535 $Å^3$, $Z = 8$, $D_c = 2.127$ Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ = 9.8 mm^{-1}, $F(000) = 7584$, $T = -100$ °C. Orange prism 0.2 × 0.1 × 0.1 mm, Siemens R3 diffractometer, 9131 intensities to 2θ 45° (absorption corrected, 8211 unique, R_{int} 0.042). Refinement on F^2 for all reflections (SHELXL 93 [9]), hydrogen atoms with riding model. The solvent molecule was poorly resolved. The final $wR(F^2)$ was 0.146, conventional $R(F)$ 0.048, for 403 parameters and 141 restraints; $S = 1.02$, max. Δ/σ 0.002, max. Δρ 2.1 e $Å^{-3}$.

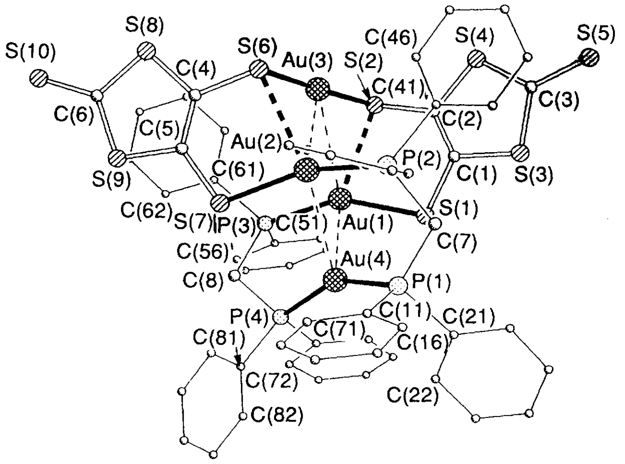

Fig. 1 Molecule of complex **4** in the crystal. Radii are arbitrary; hydrogen atoms are omitted. The weaker Au–S and Au • • • Au interactions are represented as dashed bonds. Selected bond lengths (Å) and angles (°): Au(1)–P(3) 2.270(5), Au(1)–S(1) 2.364(5), Au(1)–S(2) 2.735(5), Au(1)–Au(4) 3.0950(13), Au(1)–Au(3) 3.240(2), Au(2)–P(2) 2.280(5), Au(2)–S(7) 2.347(5), Au(2)–S(6) 2.793(5), Au(2)–Au(3) 2.9721(13), Au(2)–Au(4) 3.100(2), Au(3)–S(2) 2.312(5), Au(3)–S(6) 2.325(5), Au(4)–P(4) 2.302(6), Au(4)–P(1) 2.312(5); P(3)–Au(1)–S(1) 151.3(2), P(3)–Au(1)–S(2) 120.5(2), S(1)–Au(1)–S(2) 85.6(2), Au(4)–Au(1)–Au(3) 105.90(3), P(2)–Au(2)–S(7) 154.1(2), P(2)–Au(2)–S(6) 110.5(2), S(7)–Au(2)–S(6) 85.7(2), Au(3)–Au(2)–Au(4) 112.76(4), S(2)–Au(3)–S(6) 177.4(2), Au(2)–Au(3)–Au(1) 70.38(3), P(4)–Au(4)–P(1) 151.2(2), Au(1)–Au(4)–Au(2) 70.75(3), Au(3)–S(2)–Au(1) 79.4(2), Au(3)–S(6)–Au(2) 70.32(13)

Fig. 1. The gold atoms are coplanar (mean deviation 0.05 Å) and form a trapezium *via* short gold–gold contacts (2.97–3.24 Å), as has been observed for other loose Au^{I}_{4} clusters.[10,11] They are bridged by two $C_3S_5^{2-}$ and two dppm ligands, one of each above and below the metal plane. Considering only the shortest metal–ligand interactions, all gold atoms are two-co-ordinate [Au(1) and Au(2) S,P-, Au(3) S_2-, Au(4) P_2-co-ordinated]; the Au–S and Au–P bond lengths (av. 2.34, 2.29 Å) are similar to those reported for $[Au_4(S_2CMe)_4]$[10] or other dithiolate derivatives $[Au_2(C_6H_4S_2\text{-}1,2)(PPh_3)_2]$[8,12] and $[Au_2\{S(CH_2)_3S\}(dppm)]$.[8] However, only Au(3) shows the expected linear co-ordination; at the other gold atoms angles of 151–154° are subtended. Closer inspection reveals that Au(1) and Au(2) are involved in weaker interactions to S(2) and S(6) respectively (Au • • • S *ca.* 2.7–2.8 Å), thus leading to distorted three-co-ordination (similar Au • • • S contacts were observed in some other dithiolate complexes[7,8,12]); the making and breaking of such contacts could be associated with the fluxional nature of the NMR spectra (see above). The non-linearity at Au(4) has no such obvious cause [Au(4) • • • S(1) 3.17 Å is the shortest such contact] and may be a result of the Au • • • Au interactions.

The structure of the cation of $[Au_3(\mu_3\text{-}C_3S_5)(PPh_3)_3]ClO_4$ **5**[*] (Fig. 2) shows that the $C_3S_5^{2-}$ ligand bridges three $Au(PPh_3)$ units. The co-ordination at Au(2) is approximately linear but the non-linearity at Au(1) and Au(3) is again associated with longer contacts Au(1) • • • S(2) 2.934, Au(1) • • • Au(2) 3.072 Å, and additionally with an interionic contact Au(2) • • • $Au(3^{I})$ 2.957 Å that links the molecules into centrosymmetric, hexanuclear dimers. The Au–P and Au–S (thiolate) bond lengths are similar to those of **4**, but the Au(3)–S(5) (thione) bond is somewhat longer (2.370 Å).

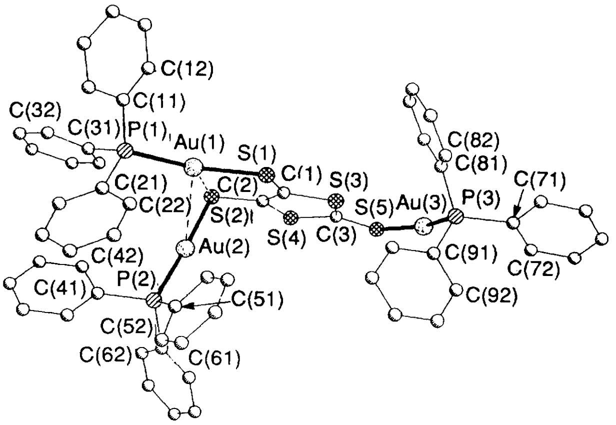

Fig. 2 Cation of complex **5** in the crystal. Radii are arbitrary; hydrogen atoms are omitted. The weaker Au–S and Au • • • Au interactions are represented as dashed bonds. Selected bond lengths (Å) and angles (°): Au(1)–P(1) 2.262(2), Au(1)–S(1) 2.336(2), Au(1)–S(2) 2.934(3), Au(1)–Au(2) 3.0720(13), Au(2)–P(2) 2.288(2), Au(2)–S(2) 2.338(2), Au(2)–$Au(3^{I})$ 2.9565(13), Au(3)–P(3) 2.280(3), Au(3)–S(5) 2.370(2), P(1)–Au(1)–S(1) 155.26(9), P(1)–Au(1)–S(2) 121.41(8), S(1)–Au(1)–S(2) 83.33(8), P(2)–Au(2)–S(2) 176.28(8), $Au(3^{I})$–Au(2)–Au(1) 137.91(3), P(3)–Au(3)–S(5) 162.17(8), Au(2)–S(2)–Au(1) 70.25(6), C(3)–S(3)–C(1) 98.5(4), C(3)–S(4)–C(2) 98.1(4), C(3)–S(5)–Au(3) 97.5(3). Symmetry transformation: I $-x, -y+1, -z+1$

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[*] Compound **5**: $C_{57}H_{45}Au_3ClO_4P_3S_5$, $M_r = 1673.5$, triclinic, space group $P\bar{1}$, $a = 10.988(4)$, $b = 15.789(6)$, $c = 17.650(6)$ Å, $\alpha = 88.39(3)$, $\beta = 89.85(3)$, $\gamma = 75.11(3)°$, $U = 2958$ Å^3, $Z = 2$, $D_c = 1.879$ Mg m^{-3}, $\mu = 7.8$ mm^{-1}, $F(000) = 1596$, $T = -100$ °C. Orange tablet 0.45 × 0.2 × 0.08 mm, $2\theta_{max}$ 50°, 11 882 intensities, 10 414 unique, R_{int} 0.038, refinement as above to $wR(F^2)$ 0.114, $R(F)$ 0.038, 658 parameters, 552 restraints, $S = 1.01$, max. $\Delta/\sigma < 0.001$, max. $\Delta\rho = 2.2$ e Å^{-3}. Details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote the full literature citation and the reference numbers CSD 400646 (**4**), 400645 (**5**).

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