Synthesis of the first gold complex with a central μ_4-selenido ligand

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The first gold complex, $[\mathrm{Se(AuPPh_3)_4}](\mathrm{CF_3SO_3})_2$, with a μ_4-selenido ligand has been prepared; the crystal structure reveals a square pyramidal geometry with short gold–gold interactions.

The chemistry of complexes in which a main-group element is surrounded by several (phosphino)gold fragments was pioneered by Schmidbaur *et al.*,[1] who prepared fascinating hypercoordinated species of the type $[\mathrm{C(AuPR_3)_5}]^+$, $[\mathrm{C(AuPR_3)_6}]^{2+}$, $[\mathrm{N(AuPR_3)_5}]^{2+}$, $[\mathrm{P(AuPR_3)_5}]^{2+}$ and $[\mathrm{P(AuPR_3)_6}]^{2+}$.[2–6] Many of these heteroatom-centered complexes are electron-deficient, and gold–gold interactions provide a significant contribution to their stability. Such interactions between formally closed-shell (d^{10}) metal centres have been termed 'aurophilic attractions'[1] and their origin is still a matter of controversy;[7] Pyykkö *et al.* have presented theoretical evidence that these attractions are mainly correlation effects, strengthened by relativistic effects.[8–10]

Although the chemistry of the carbon-, nitrogen-, phosphorus- or arsenic-centered complexes was developed rapidly, the corresponding chalcogen-centered derivatives are still being studied. Recently the μ_4-sulfido[11] or μ_4-oxido[12] gold species were reported and shown to possess square pyramidal (apical sulfur) or tetrahedral geometry (central oxygen), respectively. Our previous work in the area of sulfur-centered complexes involved examples of gold(I) or gold(III) derivatives[13–17] with a μ_3- or μ_4-sulfur ligand. Selenium-centered compounds are limited to the species $[\mathrm{Se(AuPPh_3)_2}]$ and $[\mathrm{Se(AuPPh_3)_3}]\mathrm{PF_6}$;[18–20] here we report the synthesis and structural characterisation of the first μ_4-selenido gold derivative.

The reaction of $[\mathrm{Se(AuPPh_3)_2}]$ with 2 equiv. of $[\mathrm{Au(CF_3SO_3)(PPh_3)}]$ in dichloromethane affords a solution from which the colourless air- and moisture-stable solid $[\mathrm{Se(AuPPh_3)_4}](\mathrm{CF_3SO_3})_2$ **1** can be isolated.† Complex **1** behaves as a 1:2 electrolyte in acetone solution. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum shows only one signal corresponding to a unique phosphorus environment, shifted to high field in comparison with the starting material (δ 4) or the trinuclear compound $[\mathrm{Se(AuPPh_3)_3}](\mathrm{CF_3SO_3})$ (δ 1.3). In the liquid secondary positive-ion mass spectrum the monocationic peak $[\mathrm{Se(AuPPh_3)_4}]^+$ appears at *m/z* 1915 (35%).

Crystals of **1** suitable for X-ray structure analysis were obtained from dichloromethane–heptane.‡ Compound **1** crystallises with two molecules of dichloromethane and is isostructural with the analogous sulfido compound $[\mathrm{S(AuPPh_3)_4}](\mathrm{SO_3F_3})_2$[11] and its cation (Fig. 1) is also similar to that of $[\mathrm{As(AuPPh_3)_4}]\mathrm{BF_4}$.[21] It possesses a tetragonal pyramidal framework, with the selenium atom occupying the apical position. The Au atoms are not exactly coplanar, but arranged in a flattened butterfly form with a hinge angle of 27° about the Au1···Au2 diagonal; their deviations from the best $\mathrm{Au_4}$ plane are ±0.27 Å, and that of the Se atom is 1.4 Å. The $\mathrm{SeAu_4}$ core should be regarded as electron-deficient, considering the selenido ligand to serve as a six-electron donor. Therefore it still possesses a lone pair of electrons in the apical position, which means that further coordination of gold around the selenium atom is conceivable.

Complex **1** may be compared with the above-mentioned trinuclear selenide or the tetranuclear sulfide derivatives; observed differences are essentially as expected. The Au–Se–Au angles, which range from 70.45(4) to 72.59(4)° in **1**, are smaller than those in $[\mathrm{Se(AuPPh_3)_3}]\mathrm{PF_6}$ [77.7(1)–80.0(1)°][19] or the corresponding S–Au–S angles in the isostructural $[\mathrm{S(AuPPh_3)_4}](\mathrm{CF_3SO_3})_2$ [73.5(2)–75.6(2)°]. This difference may be associated with the presence of more diffuse 3p orbitals in the selenium derivative, allowing smaller angles, and/or a

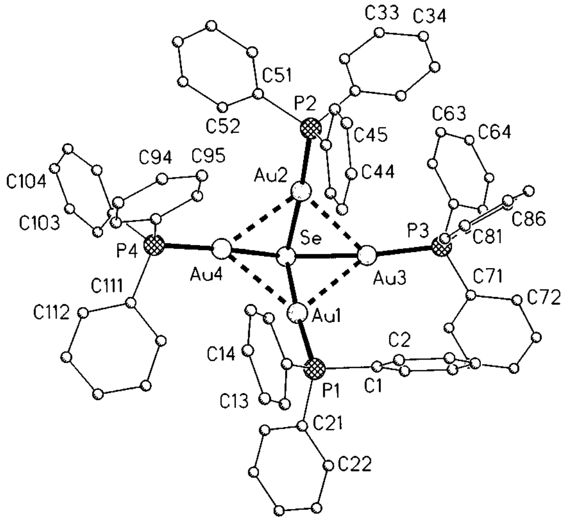

Fig. 1 The structure of the cation of complex **1** in the crystal. Hydrogen atoms have been omitted for clarity; radii are arbitrary.

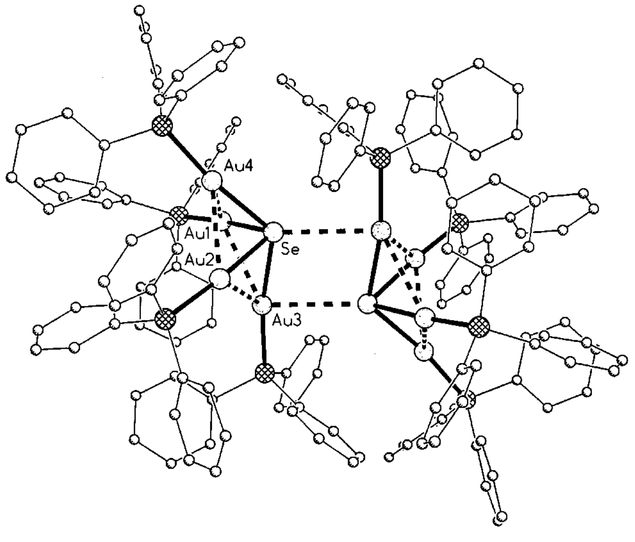

Fig. 2 Association of two cations of **1** in the crystal. The $\mathrm{CF_3SO_3}^-$ ions and the $\mathrm{CH_2Cl_2}$ molecules have been omitted.

greater electron repulsion of the lone pair of electrons. The Au–Se distances, 2.4654(13)–2.5347(14) Å, in **1** are longer than in [Se(AuPPh$_3$)$_3$]$^+$ [2.425(2)–2.451(2) Å] or (than Au–S) in [S(AuPPh$_3$)$_4$]$^{2+}$ [2.362(5)–2.429(5) Å]. Gold–gold distances between adjacent gold atoms in the pyramid base are short, 2.8959(8) to 2.9605(8) Å [the diagonal distances are 3.6 Å for Au(1)···Au(2) and 4.5 Å for Au(3)···Au(4)]. These contacts are longer than those found in the tetranuclear sulfide derivative, 2.883(2)–2.938(2) Å. The Au–P bond lengths in **1** [2.265(3)–2.282(3) Å] lie in the expected range for two-coordinate gold(I) complexes and are very similar to those found in [Se(AuPPh$_3$)$_3$]PF$_6$ [2.257(6)–2.283(5) Å].

The cations of **1** are paired across symmetry centres to form loose dimers (Fig. 2), the shorter intermolecular distances being Se···Au3′ 3.248 Å and Au3···Au3′ 4.45 Å.

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Notes and references

† *Preparation*: [Au(CF$_3$SO$_3$)(PPh$_3$)] (0.2 mmol, 0.121 g) was added to a solution of [Se(AuPPh$_3$)$_2$] (0.1 mmol, 0.100 g) in dichloromethane (20 mL) and the mixture was stirred for 30 min and then the solvent removed under vacuum to *ca.* 5 mL. Addition of diethyl ether (10 mL) gave complex **1** as a white solid. Yield 81%. (Found: C, 39.45; H, 2.60; S, 2.70. Calc. for $C_{74}H_{60}Au_4F_6O_6P_4S_2Se$; C, 39.0; H, 2.7; S, 2.8%). Λ_M = 165 Ω^{-1} cm^2 mol^{-1}. NMR: $^{31}P\{^1H\}$ (121 MHz, CDCl$_3$, reference 85% H$_3$PO$_4$), δ 31.0 (s); ^{1}H (300 MHz, CDCl$_3$, reference SiMe$_4$), δ 7.3–7.5 (m, Ph). Mass spectrum (LSIMS+): *m/z* 1915 ([Se(AuPPh$_3$)$_4$]$^+$, 35%).

‡ *Crystal data* for **1**·2CH$_2$Cl$_2$: $C_{74}H_{60}Au_4F_6O_6P_4S_2Se\cdot 2CH_2Cl_2$, M_r = 2383.90, monoclinic, space group $P2_1/n$, a = 16.410(2), b = 23.353(3), c = 20.352(2) Å, β = 91.593(8)°, V = 7796.4(17) Å^3, Z = 4, D_c = 2.031 Mg m^{-3}, μ(Mo-Kα) = 8.31 mm^{-1}, F(000) = 4528, Siemens P4 diffractometer, λ(Mo-Kα) = 0.71073 Å, T = −100 °C. A colourless tablet 0.20 × 0.20 × 0.15 mm was used to collect 11096 intensities to $2\theta_{max}$ = 46°, of which after absorption corrections (transmission 0.685–0.873) 10820 were unique (R_{int} 0.0499). Scan type: ω. The structure was solved by direct methods and subjected to anisotropic refinement on F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen). H atoms were included using a riding model. The final $wR(F^2)$ was 0.0536 for 10820 reflections, 928 parameters and 1206 restraints (to local ring symmetry and light atom displacement factors), conventional $R(F)$ = 0.0386, $S(F^2)$ = 0.743, max. $\Delta\rho$ 0.84 e Å^{-3}.

CCDC 182/1190. See http://www.rsc.org/suppdata/cc/1999/679/ for crystallographic files in .cif format.

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