(*R*)-**6a–e**: The crude β-amino sulfones (*R*)-**5a–e** were dissolved in methanol (30 mL per mmol), and Boc_2O (10 equiv) and triethylamine (ca. 3 mL per mmol) were added at 0 °C. The reaction mixture was stirred for 2 d. The solvent was evaporated under reduced pressure, and the residue was diluted with diethyl ether. The mixture was washed with a saturated aqueous solution of NH_4Cl and then brine, and dried over $MgSO_4$. The solvent was evaporated, and the products were purified by chromatography (SiO_2, diethyl ether/pentane). The products (*R*)-**6a–e** were obtained as colorless solids.

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[26] All new compounds showed suitable spectroscopic data (IR, MS, NMR) and correct elemental analysis or high-resolution mass spectra.

A Novel High-Nuclearity Luminescent Gold(I)–Sulfido Complex**

Vivian Wing-Wah Yam,* Eddie Chung-Chin Cheng, and Kung-Kai Cheung

There has been growing interest in the study of Cu^I, Ag^I, and Au^I complexes, and in particular polynuclear systems. This stems from the tendency of these metal ions to form clusters and aggregates as a result of weak metal–metal interactions[1] and the recent demonstration that a number of these aggregates exhibit rich luminescence behavior.[2] Recently, our group showed[3] that unsubstituted chalcogenides, with their well-known ability to exhibit a variety of bridging

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modes and unusual stereochemistries,[4] could form soluble tetranuclear complexes of Cu^I and Ag^I with the formula $[M_4(\mu\text{-dppm})_4(\mu_4\text{-E})]X_2$ (M = Cu, Ag; E = S, Se, Te; X = PF_6, OTf; dppm = bis(diphenylphosphanyl)methane, Tf = trifluoromethanesulfonyl); all complexes were structurally characterized and shown to exhibit photophysical and photochemical properties. High-nuclearity chalcogenido clusters of Cu^I and Ag^I have also been reported by Fenske and co-workers.[5] On the other hand, Au^I–sulfido complexes are comparatively rare,[6] in particular those containing bridging phosphanes.[6g, 7] Examples of Au^I–sulfido species with monodentate phosphanes include the well-known $[S(AuPPh_3)_3]^+$,[6b, c] and more recently $[Au_4(\mu_4\text{-S})(PPh_3)_4]^{2+}$.[6f] As the dppm ligand has a higher tendency to bind metal centers in a bridging rather than a chelating mode, it has been used in an attempt to synthesize polynuclear Au^I–chalcogenido complexes. Herein are reported the synthesis and structural characterization of **1**, a high-nuclearity luminescent Au^I–μ_3-sulfido complex with bridging dppm ligands.

$[Au_{12}(\mu\text{-dppm})_6(\mu_3\text{-S})_4][PF_6]_4$ **1**

Reaction of $[Au_2Cl_2(dppm)]$[8] with H_2S in ethanol/pyridine, followed by removal of pyridinium chloride from the solid residue by washing with water, and subsequent metathesis reaction with NH_4PF_6 in methanol gave **1**. Recrystallization from acetone/diethyl ether afforded **1** as pale yellow crystals in 85% yield. The formulation of **1** was confirmed by elemental analyses, FAB and ESI mass spectrometry, and ^1H and ^{31}P NMR spectroscopy.[9]

The $^{31}P\{^1H\}$ NMR spectrum of **1** at ambient temperature shows two singlets at $\delta = 28.2$ and 29.8 in a ratio of 1:2, while three multiplets, which correspond to the methylene resonances of the dppm ligands, are observed in the ^1H NMR spectrum. The appearance of only two types of ^{31}P signals and three types of methylene resonances suggests that **1** is fluxional in solution. It probably undergoes a ring flipping of the $Au_2(\mu\text{-dppm})$ rings, as is commonly observed in other $[M_2(\mu\text{-dppm})_2]$ systems.[10] A proposed time-averaged structure of **1** in solution on the NMR time scale is depicted in Figure 1. The presence of local D_{2h} symmetry would account for the presence of two kinds of chemical environments for the P atoms and three for the methylene protons (labeled P_A and P_B, and H_A, H_B, and H_C).

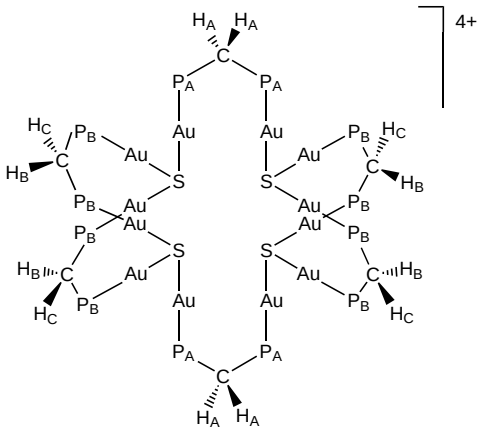

Figure 1. Proposed structure of the complex cation of **1** in solution on the NMR time scale.

The structure of **1** in the solid state was established by X-ray crystallography (Figure 2).[11] It consists of four Au_3S units linked together by six bridging dppm ligands to give a metallamacrobicyclic structure. A crystallographic center of inversion exists at the centroid of the four coplanar sulfur atoms.

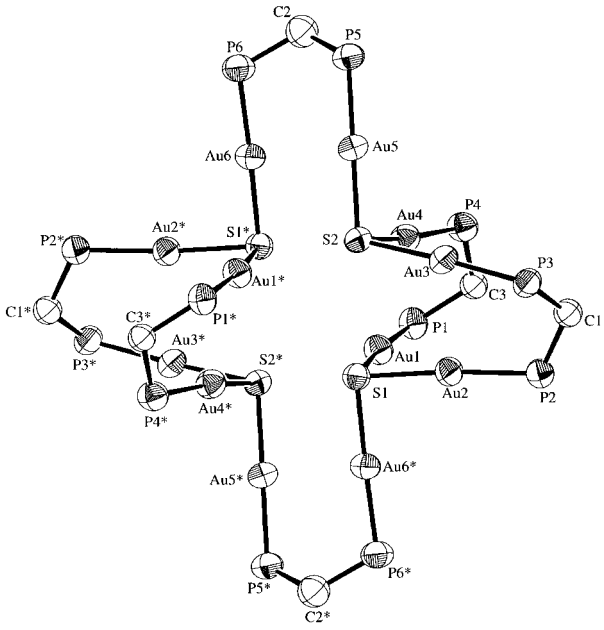

Figure 2. Crystal structure of the complex cation of **1**. Phenyl rings and hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Au1–Au2 3.050(1), Au1–Au4 3.065(1), Au1–Au6* 3.342(1), Au2–Au3 3.176(1), Au2–Au6* 3.239(1), Au3–Au4 3.001(1), Au3–Au5 3.728(1), Au4–Au5 3.152(1), Au5–Au6 3.188(2), Au1–S1 2.334(5), Au2–S1 2.327(5), Au3–S2 2.319(5), Au4–S2 2.345(5), Au5–S2 2.309(5), Au6*–S1 2.297(5); Au1-S1-Au6* 92.4(2), Au1-S1-Au2 81.8(2), Au2-S1-Au6* 88.9(2), Au3-S2-Au4 80.1(2), Au3-S2-Au5 107.3(2), Au4-S2-Au5 85.2(2), S1-Au1-P1 170.8(2), S1-Au2-P2 175.5(2), S2-Au3-P3 177.5(2), S2-Au4-P4 168.1(2), S2-Au5-P5 176.8(2), S1-Au6*-P6* 175.3(2). Starred atoms have coordinates at $1-x, 1-y, -z$.

The Au–S bond lengths are about 2.3 Å, which is in the range generally observed for Au^I–μ_3-sulfido complexes,[6b, e, h] but longer than those found in μ_2-sulfido systems[6d] and shorter than those in μ_4-sulfido systems.[6f] Short intramolecular Au···Au contacts are present, and most are in the range of 3.001(1) to 3.342(1) Å. This is comparable to the intramolecular Au···Au distances observed in $[S(AuPPh_3)_3]PF_6$ (3.071–3.409 Å)[6b] and $[(\mu\text{-}Au_2dppf)\{S(Au_2dppf)\}_2][OTf]_2$ (2.905(2)–3.272(2) Å; dppf = bis(diphenylphosphanyl)ferrocene).[7] An exceptionally long Au···Au distance of 3.728(1) Å is observed between Au3 and Au5. The Au-S-Au angles range from 80.1(2) to 107.3(2)°; most deviate from the 90° expected for bonding involving sulfur 3p orbitals. A smaller deviation of the Au-S-Au angle from 90° has been reported in Au^I–μ_3-sulfido systems containing monodentate phosphane ligands, such as $[S(AuPPh_3)_3]PF_6$ (Au-S-Au 82.9(3)–95.0(3)°).[6b] The presence of a long Au3–Au5 distance (3.728(1) Å) and a large Au3-S2-Au5 angle (107.3(2)°) may be a result of the steric demands of the dppm ligands. All the Au^I centers are two-

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coordinate, and the P-Au-S angles range from 168.1(2) to 177.5(2)° and thus are slightly distorted from a linear coordination geometry. Similar deviation has also been observed in $[S(AuPPh_3)_3]PF_6$[6b] and $[NEt_4]_2[S(AuC_6F_5)_3]\cdot 0.5\,MeC(O)Et$.[6h]

The UV/Vis spectrum of **1** in MeCN shows an intense absorption at 266 nm and an absorption shoulder at about 332 nm (Table 1). The intense absorption at 266 nm is

Table 1. Photophysical data for complex **1**.

λ_{abs} [nm] (ε)	Medium	T[K]	λ_{em} [nm]	τ_0[μs]
266 (94310) 332 (26150)	MeCN	298	546	0.25 ± 0.02
	solid[a]	298	648	2.7 ± 0.2 0.3 ± 0.02[b]
	solid[a]	77	634	–

assigned to a dppm intraligand transition. The absence of the absorption shoulder in the spectra of $[Au_2Cl_2(dppm)]$ and $[Au_2(dppm)_2]^{2+}$ may suggest that it is characteristic of the Au^I–sulfido system. Unlike $[S(AuPPh_3)_3]^+$, which only emits in the solid state at low temperature ($\lambda_{em} = 640$ nm, 77 K), excitation of **1** in the solid state and in solution at room temperature at wavelengths greater than 350 nm produce long-lived orange-red and green luminescence, respectively. The relatively long radiative lifetime in the microsecond range is suggestive of emission from a triplet state. With reference to previous spectroscopic work on related polynuclear d^{10} metal–chalcogenido complexes,[3] the emission is tentatively assigned as derived from triplet states of a ligand-to-metal charge transfer (LMCT; S → Au) character that mix with metal-centered (ds/dp) states which are modified by $Au^I \cdots Au^I$ interactions.

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