tested. The use of methyl iodide, even in large excess, gave very slow and incomplete reactions. Very good results were obtained with methyl triflate. However, this method was found to be expensive and not practical to carry out. Thus, triethyloxonium tetrafluoroborate was preferred for a quick (1 or 2 h) and quantitative synthesis of sulfonium salts. Purifications of the salts were performed by trituration in ethanol/diethyl ether.

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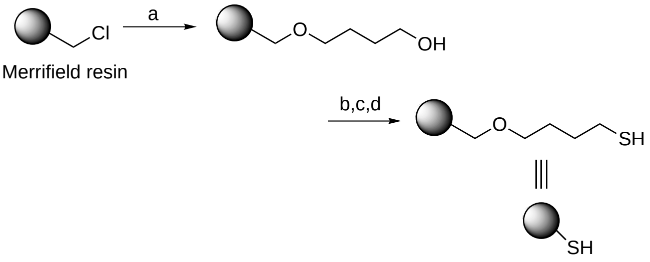
[11] This resin was prepared from commercially available Merrifield resin (1.2 mmol g^{-1}, 200–400 mesh) in four steps. a) 1,4-Butanediol (10 equiv), NaH (5 equiv), DMF, RT, 14 h (an analogous transformation is described in ref. [4f]; b) methanesulfonyl chloride (5 equiv), Et_3N (5 equiv), CH_2Cl_2, RT, 15 h; c) thiourea (5 equiv), DMF, 70 °C, 17 h; d) benzylamine (3 equiv), toluene, 70 °C, 14 h.



[12] Reagents and conditions for the grafting of the substrate on the solid support: 4-cyanobenzylbromide (3 equiv), DIEA (3 equiv), DMF, 70 °C, 14 h.

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A Highly Soluble Luminescent Decanuclear Gold(I) Complex with a Propeller-Shaped Structure[**]

Vivian Wing-Wah Yam,[*] Eddie Chung-Chin Cheng, and Zhong-Yuan Zhou

The chemistry of polynuclear d^{10} metal systems has attracted numerous studies in the past few decades, and many of them involved the investigation of their structure and their photoluminescent behavior.[1] These properties are often affected by the presence of weak metal–metal interactions as a result of a relativistic effect that leads to the contraction of the *n*s orbital of the d^{10} metal center.[2] This effect is most prominent for gold and leads to the phenomenon of aurophilicity commonly found in gold complexes, in which aggregation through short sub-van-der-Waals gold–gold contacts of around 3.05 Å occurs.[3] Chalcogenides, with their propensity to bridge metal atoms, could serve as ideal candidates for polynuclear metal complex formation. Although chalcogenido copper(I) and silver(I) clusters are known and a number of them have been structurally characterized, most are insoluble or have low solubility in common organic solvents.[4] Examples of soluble polynuclear d^{10} metal chalcogenides are scarce, especially those of gold.[5–7]

Recently, we reported the isolation of a series of soluble tetranuclear copper(I) and silver(I) chalcogenido complexes with the general formula $[M_4(\mu\text{-dppm})_4(\mu_4\text{-E})]X_2$ (M = Cu, Ag; dppm = bis(diphenylphosphanyl)methane; E = S, Se, Te; X = PF_6, OTf = trifluoromethanesulfonate),[8], as well as the dodecanuclear gold(I) sulfido complex $[Au_{12}(\mu\text{-dppm})_6(\mu_3\text{-S})_4](PF_6)_4$.[6] All were structurally characterized and shown to exhibit rich photophysical properties. Structurally related gold(I) complexes with the general formulas $[E(AuPPh_3)_3]^+$ (E = S, Se, Te) and $[E(AuPPh_3)_4]^{2+}$ (E = S, Se) were also reported.[7] Here we report the synthesis and the structural characterization of a novel soluble, high-nuclearity luminescent μ_3-sulfidogold(I) complex with bridging diphosphanylamine ligands, namely, $[Au_{10}(\mu\text{-PNP})_4(\mu_3\text{-S})_4](PF_6)_2$ (PNP = $Ph_2PN(n\text{Pr})PPh_2$).

Reaction of H_2S with a suspension of $[Au_2Cl_2(PNP)]$[9] in ethanol/pyridine followed by metathesis reaction with NH_4PF_6 in methanol and recrystallization from acetone/diethyl ether afforded $[Au_{10}(\mu\text{-PNP})_4(\mu_3\text{-S})_4](PF_6)_2$ (**1**) as yellow crystals in 72 % yield. The formulation of **1** was confirmed by elemental analyses, positive FAB and ESI mass spectrometry, ^1H and ^{31}P NMR spectroscopy, ^1H–^1H COSY experiments, and measurement of the molar conductivity.[10] The solid-state structure was established by X-ray crystallography (Figure 1).[11]

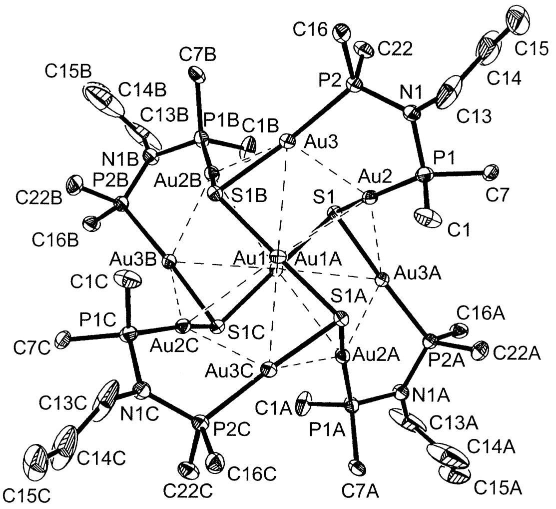

Figure 1. Perspective view of the complex cation of **1** with the atomic numbering scheme. Only the *ipso*-C atoms of the phenyl rings are shown and hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30 % probability level. Atoms with the notations A have coordinates at $(-y+\frac{1}{2}, x+\frac{1}{2}, -z+\frac{1}{2})$, B at $(y-\frac{1}{2}, -x+\frac{1}{2}, -z+\frac{1}{2})$, and C at $(-x, -y+1, z)$.

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Complex **1** is composed of four PNP-Au_2 units linked together by four S atoms, whereby opposite pairs of S atoms are bonded to the two Au1 and Au1A atoms at the core in a linear fashion. Significant intramolecular Au$\cdots$Au interactions exist; most of the Au–Au distances lie in the range of 3.026–3.278 Å, and the Au1–Au1A distance is 3.1553(5) Å. These values are comparable to those in $[Au\{S(AuPPh_3)_2\}_2][(CH_3)_3SnCl_2]$ (3.030(2)–3.213(2) Å)[12] and $[Au_{12}(\mu\text{-dppm})_6(\mu_3\text{-S})_4](PF_6)_4$ (2.905(2)–3.272(2) Å).[6] Exceptionally long Au–Au distances of 3.613 Å are found for Au1A–Au2, Au1–Au2B, Au1A–Au2C, and Au1–Au2A. The Au–S bond lengths of about 2.3 Å are in the range generally observed for Au^I–μ_3-S compounds.[6, 7a, 13] All the Au^I centers are two-coordinate, with P-Au-S angles of 165.60(3) and 173.88(3)°, and S-Au-S angles of 170.32(4)° that deviate from ideal linear geometry. The Au-S-Au angles range from 81.67(2) to 102.97(3)° and thus deviate from the 90° expected for bonding that involves sulfur 3p orbitals. Similar findings were reported for other related μ_3-sulfidogold(I) systems.[6, 7a, 13] The coordination geometry about the nitrogen atom of the diphosphanylamine ligand is almost trigonal-planar, and the atoms N1, P1, P2, and C13 all lie approximately on the same plane. Such a planar geometry is commonly found in compounds involving this class of ligands.[9, 14]

The $^{31}P\{^1H\}$ NMR spectrum of **1** at ambient temperature showed a pair of doublets at $\delta = 83.1$ and 85.5 ($J_{P,P} = 115$ Hz), and this indicates the presence of two different phosphorus environments, P_A and P_B. The observation of a two-spin AB pattern is in line with the results predicted when the difference in chemical shifts has the same order of magnitude as the coupling constant $J_{P,P}$.[15a] The inequivalence of the two P environments supports the assignment of a local S_4 symmetry in solution, with the principal symmetry axis coincident with the Au1–Au1A bond axis, such that the two P environments could not be interchanged by any symmetry operations of the S_4 point group. The four *n*Pr groups are magnetically equivalent in solution. From the room-temperature ^1H NMR spectrum, five multiplets at $\delta = 2.80$, 2.33, 0.85, 0.27, and 0.04 with integral ratios of 1:1:1:1:3 were observed for the protons of the *n*-propyl groups, namely, $\{H_A, H_B\}$, $\{H_C, H_D\}$, and H_E, respectively (Figure 2). The splitting of the H_A–H_B and H_C–H_D signals may be explained by their diastereotopic relationship, which is induced by the slow inversion at the nitrogen atom. Similar findings were reported for a number of compounds with a chiral nitrogen center or a ring structure with restricted rotation.[15] The H_E protons are much less affected on the NMR timescale simply as a result of their greater distance from the nitrogen atom. A ^1H–^1H COSY experiment confirmed the diastereotopic relationship between the protons rather than the presence of two different *n*-propyl environments, as the five proton environments are correlated with the protons on the adjacent carbon atoms (Figure 3). It further suggests that, in solution, the nitrogen atom may have a nonplanar geometry that allows an inversion process to occur and is different from that in the solid state.

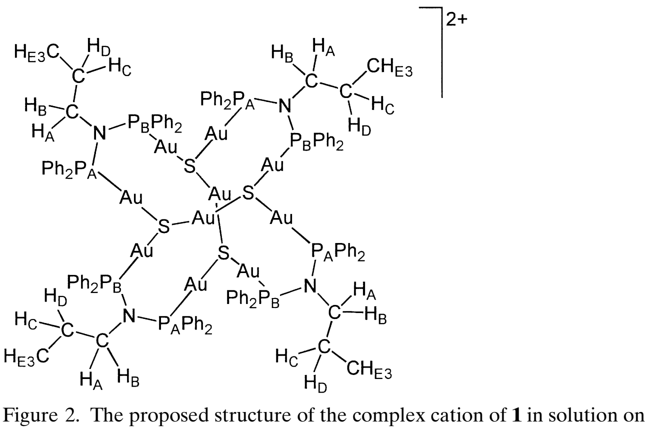

Figure 2. The proposed structure of the complex cation of **1** in solution on the NMR timescale.

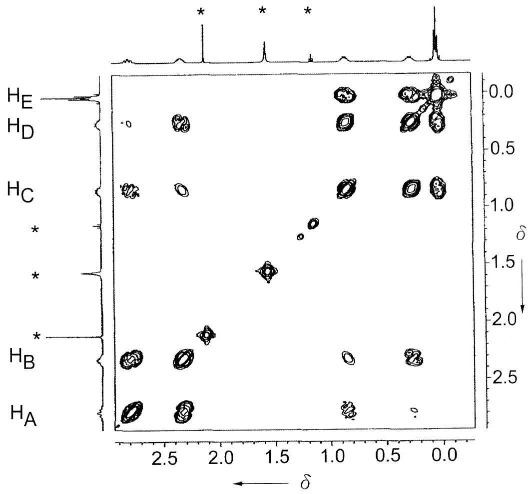

Figure 3. The ^1H–^1H COSY spectrum of **1** at 298 K in CD_2Cl_2, showing the correlations between the *n*-propyl protons. * = solvent peak.

The electronic absorption spectrum of **1** in CH_2Cl_2 shows low-energy absorption bands at about 336 and 400 nm (Table 1). The low-energy band at 400 nm, which is absent in the Au^I precursor $[Au_2Cl_2(PNP)]$, is likely to originate from a ligand-to-metal charge transfer transition modified by an Au$\cdots$Au interaction (LMMCT; S$\rightarrow$Au). The higher energy absorptions at about 268 and 336 nm, which are also exhibited by the PNP ligand and $[Au_2Cl_2(PNP)]$, are assigned to an intraligand transition and a metal-perturbed intraligand transition, respectively. Excitation of **1** in the solid state or in solution with visible light at room temperature and at 77 K results in intense dual luminescence in the green and orange-red regions. The radiative lifetimes in the microsecond range are suggestive of a triplet parentage. With reference to previous spectroscopic work on d^{10} chalcogenido systems,[6, 8, 9] the low-energy emission is tentatively assigned to originate

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

λ_{abs} [nm] (ε [$dm^3mol^{-1}cm^{-1}$])	Medium	T [K]	λ_{em} [nm]	τ_0 [µs]
268 (71620), 336 (24920), 400 (3930)	CH_2Cl_2	298	510, 759	0.10
	$(CH_3)_2CO$	298	509, 768	0.11
	Solid	298	522, 657	0.23, 1.28[a]
	Solid	77	526, 662	3.77

[a] Biexponential decay.

from triplet states of a ligand-to-metal charge transfer character that mix with metal-centered (ds/dp) states modified by Au ⋯ Au interactions (LMMCT; S → Au), whereas the high-energy emission at ca. 500 nm is attributed to metal-perturbed intraligand phosphorescence.

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[10] **1**: Elemental analysis calcd for $[Au_{10}(\mu\text{-PNP})_4(\mu_3\text{-S})_4](PF_6)_2 \cdot (CH_3)_2CO$ (found): C 32.08 (32.34), H 2.76 (2.75), N 1.38 (1.43); positive FAB-MS: m/z: 1903 $[M-2\,PF_6]^{2+}$; positive ESI-MS: m/z: 1903 $[M-2\,PF_6]^{2+}$; ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): $\delta = 0.04$ (m, 12 H, CH_3), 0.27 (m, 4 H, CCH_2C), 0.85 (m, 4 H, CCH_2C), 2.33 (m, 4 H, NCH_2), 2.80 (m, 4 H, NCH_2), 6.83 (m, 8 H, Ph), 7.12–7.83 (m, 72 H, Ph); ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 298 K): $\delta = 83.1$, 85.5 (dd, $J_{P,P} = 115$ Hz); molar conductivity (acetone, 298 K): $\Lambda_M = 262\ \Omega^{-1}\,cm^2\,mol^{-1}$ (1:2 electrolyte).

[11] a) Crystal data for **1**: $Au_{10}S_4(C_{27}H_{27}P_2N)_4 \cdot 2\,PF_6$, $M_r = 4097.59$, tetragonal, space group $I\bar{4}$ (no. 82), $a = 18.9950(14)$, $c = 17.7282(19)$ Å, $V = 6396.5(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.127$, $\mu(Mo_{K\alpha}) = 11.670$ mm^{-1}, $F(000) = 3792$, $T = 293$ K; $R = 0.0347$, $wR = 0.0870$ for 7314 reflections with $I > 2\sigma(I)$. Crystal dimensions $0.20 \times 0.14 \times 0.12$ mm; Bruker CCD area detector diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); collection range $2\theta = 3$–$55°$; Phi and Omega oscillation frames 0–180°; 1321 frames taken in four shells. Absorption correction applied by using the program SADABS[11b]; the structure was determined by direct methods and subsequent difference Fourier syntheses, and refined by full-matrix least-squares on F^2 by using the programs of the Bruker Smart and Bruker Shelxtl package[11b]. All non-hydrogen atoms were refined anisotropically. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138838. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).; b) SADABS, Bruker Smart and Bruker Shelxtl Package, Bruker AXS GmbH, **1998**.

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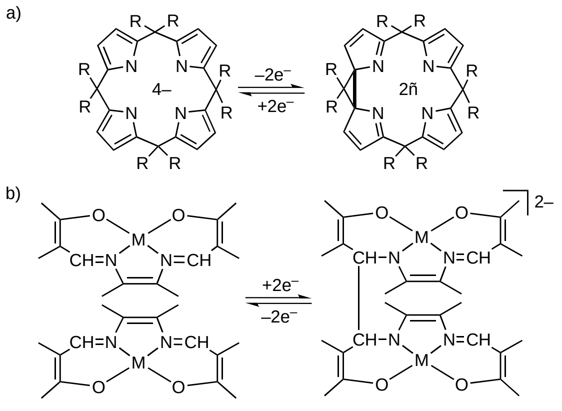
Metal-Mediated Transfer of Electrons between Two Different C−C Single Bonds That Function as Electron-Donor and Electron-Acceptor Units[**]

Federico Franceschi, Euro Solari, Rosario Scopelliti, and Carlo Floriani[*]

Two complementary electron-storage and -releasing units are the fundamental constituents of storage cells[1] and molecular devices devoted to long-range electron-transfer processes.[2] The C−C single bonds formed by oxidative (Scheme 1 a)[3] or reductive coupling[4] (Scheme 1 b) can be



Scheme 1. Reversible two-electron oxidative (a) and reductive coupling (b) to form C−C bonds. R = Et.

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