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[15] In **1** the cobalt ion occupies a general position thus lacking the trigonal symmetry. Its easy axis of magnetization can therefore be at any angle from the trigonal axis and the comparison with the mononuclear compound[9] suggests that this angle can be as large as 50°.

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A Novel Polynuclear Gold–Sulfur Cube with an Unusually Large Stokes Shift**

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The luminescence properties of polynuclear transition metal complexes with a d^{10} closed-shell electronic configuration have attracted much attention over the past few decades.[1] In view of the wide applicability of d^{10} transition metal chalcogenides in semiconducting materials, photovoltaics, and nanomaterials, and their intriguing optical behavior, their spectroscopic and photophysical properties are worthy of exploration. With our recent success in making soluble polynuclear copper(I), silver(I), gold(I), zinc(II), cadmium(II) and mercury(II) complexes with unsubstituted chalcogenide and chalcogenolate ligands and rich luminescence behavior,[2] we hope that, by systematic variation of the metal, chalcogen, and ancillary ligands, insights into the spectroscopic properties, the nature of the excited states, and the structure–property relationship can be obtained. This is particularly important, as many of the transition metal chalcogenides and chalcogenolates are insoluble, and this renders their structures and photophysical properties less amenable to study. Owing to the recent growing interest in the aurophilic nature of gold(I) centers and the scantiness of gold(I) chalcogenide aggregates,[3–5] we launched a program to investigate this class of compounds. A number of soluble dodecanuclear and decanuclear gold(I) sulfido complexes with bridging diphosphane ligands have been successfully synthesized by us.[2c,d] These complexes have the formulas $[Au_{12}(\mu\text{-dppm})_6(\mu_3\text{-}S)_4](PF_6)_4$ (dppm = bis(diphenylphosphanyl)methane) and $[Au_{10}\{\mu\text{-}Ph_2PN(n\text{Pr})PPh_2\}_4(\mu_3\text{-}S)_4](PF_6)_2$ and possess novel structures and interesting photophysical behaviors. Here we report an unprecedented hexanuclear gold(I) sulfido complex with bridging diphosphane ligands, namely, **1**, which has unusual photophysical properties.

$[Au_6\{\mu\text{-}Ph_2PN(p\text{-}CH_3C_6H_4)PPh_2\}_3(\mu_3\text{-}S)_2](ClO_4)_2$ **1**

Reaction of H_2S with a suspension of $[Au_2\{Ph_2PN(p\text{-}CH_3C_6H_4)PPh_2\}Cl_2]$ in ethanol/pyridine followed by metathesis reaction with $LiClO_4$ and recrystallization from acetone/dichloromethane/diethyl ether yielded **1** as colorless crystals in 50% yield. It was characterized by elemental analysis, positive-ion FAB mass spectrometry, positive- and negative-ion ESI mass spectrometry, and ^1H and ^{31}P NMR spectroscopy.[6]

The structure of the complex cation of **1** in the solid state was determined by X-ray crystallography.[7] The cation is hexanuclear, and the Au_6S_2 unit is arranged in a distorted heterocubane structure with the two sulfur atoms at opposite apices of the cuboid. Figure 1 shows a perspective drawing of the cation. Each sulfur atom is bonded to three gold(I) centers in a μ_3 bridging mode, and the two Au_3S units are interconnected by three diphosphanylamin ligands. Noticeable gold–gold interactions are present, and the Au···Au distances range from 2.939(3) to 3.3775(18) Å. The Au–S and Au–P bond lengths of 2.325(8)–2.346(8) and 2.256(9)–2.272(8) Å, respectively, and the P-Au-S angles of 168.4(3)–178.5(3)°, which are distorted from ideal linear geometry, are not uncommon.[2c–e, 8–10] The Au-S-Au angles at the μ_3-S atoms are in the range of 92.13–95.66° and thus deviate only slightly from the ideal 90° expected for bonding involving the sulfur 3p orbitals. The P-N-P angles are very close to 120°, indicative of sp^2 hybridization at the N center. Unlike other polynuclear gold(I) sulfido complexes with bridging diphosphane ligands,

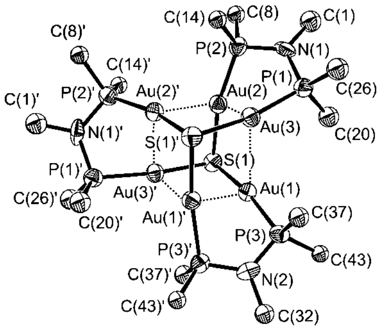

Figure 1. Perspective drawing of the structure of the complex cation of **1** in the crystal. Only the *ipso*-C atoms of the aromatic rings are shown for clarity. Thermal ellipsoids are drawn at the 30% probability level.

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such as $[Au_{12}(\mu\text{-dppm})_6(\mu_3\text{-S})_4](PF_6)_4$ and $[Au_6(\mu\text{-dppf})_3(\mu_3\text{-S})_2](OTf)_2$ (dppf = 1,1′-bis(diphenylphosphanyl)ferrocene), in which the sulfur atoms of the SAu_3 pyramids are adjacent to each other in an open structure,[2c, 4d] **1** assumes a *closo*-cuboidal structure in which the two sulfur atoms of the SAu_3 pyramids are further apart and occupy opposite corners of the cuboid. This configuration is assumed to be more sterically demanding. However, it is likely that the presence of Au ⋯ Au interactions in the complex together with the small bite angle of the diphosphane ligands may overcome the steric effects and give rise to the observed structure.

The $^{31}P\{^1H\}$ NMR spectrum of **1** in $[D_6]$acetone shows a sharp singlet at $\delta = 82.7$. The presence of only one ^{31}P environment is in line with the D_3 symmetry of the molecule, in which the C_3 symmetry axis passes through the two sulfur atoms, and each of the three perpendicular C_2 axes bisects the diphosphane ligands.

The photophysical data of **1** are summarized in Table 1. The electronic absorption spectrum of **1** shows two absorption shoulders and a low-energy absorption band. With reference to previous spectroscopic studies on related polynuclear gold(I) compounds,[2c–e, 8, 9] the low-energy absorption at 346 nm, which is absent in the gold(I) precursor complex $[Au_2\{Ph_2PN(p\text{-}CH_3C_6H_4)PPh_2\}Cl_2]$, is likely to originate from a ligand-to-metal charge transfer transition modified by Au ⋯ Au interactions (LMMCT; S → Au). The higher-energy absorption shoulders, which are also found in the electronic absorption spectra of the corresponding ligand $Ph_2PN(p\text{-}CH_3C_6H_4)PPh_2$ and the gold(I) precursor complex $[Au_2\{Ph_2PN(p\text{-}CH_3C_6H_4)PPh_2\}Cl_2]$, are assigned to the diphosphane intraligand and the metal-perturbed intraligand transitions, respectively. Excitation of the hexanuclear complex in the solid state with visible light at room temperature and at 77 K results in intense orange emission. The radiative lifetimes in the microsecond range are suggestive of a triplet parentage. Excitation bands of **1** in dichloromethane solution at 298 K (monitored at 810 nm) are observed at about 333 and 365 nm, which closely resemble that of the low-energy absorption bands, indicative of their similar origin (Figure 2). The emission is therefore tentatively assigned to originate from the triplet states of a ligand-to-metal charge-transfer character that are mixed with metal-centered (ds/dp) states modified by Au ⋯ Au interactions (LMMCT; S → Au). Assignments based on similar grounds were made for related gold(I) sulfido and thiolato complexes.[2c–e, 8–10] An energy difference of about 1.87 eV (15 052 cm^{-1}) was observed between the lowest energy excitation maximum (365 nm) and the emission maximum in fluid solutions at room temperature (810 nm). Such an abnormally large Stokes shift may suggest that the excited-state structure is highly distorted from that of the ground state. When compared with the orange emission observed in solid **1** at room temperature ($\lambda_{em} = 635$ nm), the red shift for the luminescence in solution ($\lambda_{em} = 810$ nm in dichloromethane) can be ascribed to the larger structural changes that may occur in solution than in the rigid lattice of the solid. Blue shifts in emission energy upon lowering the temperature have also been observed in the solid state, and more prominently in fluid solutions, and may be attributed to rigidochromic effects, similar to those observed in the tetranuclear copper(I) cubane clusters reported by the groups of Vogler and Ford[11] and the gold(I) thiolato complexes by Eisenberg et al.[9] The increased rigidity of the system in the glass state compared to that in fluid solutions would restrict the extent of the distortions in the excited state and hence give rise to a smaller red shift in the emission energy. Alternatively, attribution of the large red shift to the rearrangement or decomposition of the complex in solution, or solvent–exciplex formation was not favored, in view of the establishment of the identity of **1** in solution by positive-ion ESI-MS, as well as the lack of solvent dependence in the emission energy of **1** in methanol and dichloromethane (see Table 1).

Table 1. Photophysical properties of **1**.[a]

Medium (T [K])	Emission λ [nm] (τ_0 [μs])	Medium (T [K])	Emission λ [nm] (τ_0 [μs])
solid (298)	635 (14.3, 2.5)[a]	CH_2Cl_2 (77)	562 (23.2, 3.2)[a]
solid (77)	603	MeOH (298)	808 (3.1)
CH_2Cl_2 (298)	810 (3.6)	EtOH/MeOH (4/1) (77)	564 (37.6)

[a] Absorption λ_{max} [nm] in CH_2Cl_2 (ε [$dm^3mol^{-1}cm^{-1}$]): 264 sh (83 280), 304 sh (24 290), 346 (6320). [b] Biexponential decay.

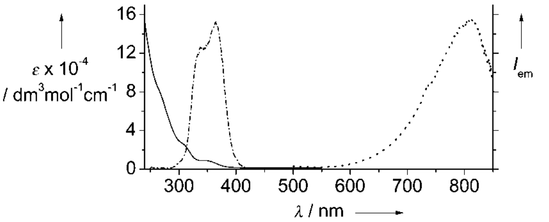

Figure 2. Electronic absorption (——, ε) spectrum, and emission (••••, I_{em}) spectrum with excitation at 365 nm, and excitation spectrum (•–•–, I_{ex}), monitored at 810 nm, of **1** in dichloromethane solution at 298 K.

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[7] Crystal data for **1**: C$_{93}$H$_{81}$Au$_6$Cl$_2$N$_3$O$_8$P$_6$S$_2$, $M_r = 2871.25$, cubic, space group $I2_13$ (No. 199), $a = 36.465(4)$ Å, $V = 48487(9)$ Å^3, $Z = 12$, $\rho_{\mathrm{calcd}} = 1.180$ g cm^{-3}, $\mu(\mathrm{Mo}_{K\alpha}) = 5.576$ mm^{-1}, $F(000) = 16248$, $T = 301$ K. 43580 reflections measured, of which 8604 were unique ($R_{\mathrm{int}} = 0.1570$) and were used in all calculations. Final $R = 0.0842$ (for observed data with $I > 2\sigma(I)$). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155449. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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First Diastereomerically Controlled Aggregation of L-Cysteinato Cobalt(III) Octahedra, Assisted by Silver(I) Ions

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During the past decade considerable progress has been made in the design and creation of supramolecular systems.[1] While the majority of supramolecular species have been constructed from organic ligands and metal ions by spontaneous self-assembly, our strategy is to use metal thiolate complexes as building blocks which can aggregate by forming S-bridged structures with a variety of metal ions.[2] In particular, we are interested in the aggregation of tris(chelate)-type octahedral complexes with simple bidentate *N,S*-thiolate ligands such as 2-aminoethanethiolate (aet = NH$_2$CH$_2$CH$_2$S$^-$) and L-cysteinate (L-cys = NH$_2$CH(COO$^-$)CH$_2$S$^-$), with the aim of creating chiral supramolecular architectures.[3] To date, a number of chiral aggregates based on the octahedral [M(aet)$_3$] unit (M = Co$^{\mathrm{III}}$, Rh$^{\mathrm{III}}$, Ir$^{\mathrm{III}}$) with three thiolate donors, such as trinuclear [Co$^{\mathrm{III}}${M(aet)$_3$}$_2$]$^{3+}$,[4] pentanuclear [Ag$^{\mathrm{I}}_3${M(aet)$_3$}$_2$]$^{3+}$,[5] and octanuclear [Zn$^{\mathrm{II}}_4$O{M(aet)$_3$}$_4$]$^{6+}$,[6] as well as analogous aggregates based on the [M(L-cys-*N,S*)$_3$]$^{3-}$ unit, have been prepared, and their unique stereochemical, spectroscopic, and redox properties have been extensively studied. In contrast, the aggregation of octahedral complex units with a single thiolate donor has been studied far less; only a few trinuclear and tetranuclear species such as [Co(aet)(en)$_2$]$^{2+}$ or [Co(SCH$_2$COO)(en)$_2$]$^+$ (en = NH$_2$CH$_2$CH$_2$NH$_2$) have been reported.[7]

To expand the range of chiral supramolecular architectures based on octahedral complex units with thiolate donors, it is desirable to find the key factors that control their aggregation by studying the fundamental [Co$^{\mathrm{III}}$(thiolato-*S*)(amine-*N*)$_5$] system. We therefore started by investigating the aggregation of [Co(aet)(en)$_2$]$^{2+}$ and [Co(L-cys-*N,S*)(en)$_2$]$^+$ assisted by metal ions. Recently, we found that the reaction of racemic [Co(aet)(en)$_2$]$^{2+}$ with AgNO$_3$ in a 1:1 ratio gives an S-bridged Co$^{\mathrm{III}}$Ag$^{\mathrm{I}}$ coordination polymer having a one-dimensional infinite zigzag chain structure, namely, {[Ag{Co(aet)(en)$_2$}](NO$_3$)$_3$}$_\infty$.[8] Interestingly, the chain structure discriminated the chiral configuration (Λ or Δ) of [Co(aet)(en)$_2$]$^{2+}$ to give exclusively the enantiomeric (Λ-Co$^{\mathrm{III}}$Ag$^{\mathrm{I}}$)$_\infty$ and (Δ-Co$^{\mathrm{III}}$Ag$^{\mathrm{I}}$)$_\infty$ chains, which separate from one another as homochiral crystals. Given this result, we expected that similar (Co$^{\mathrm{III}}$Ag$^{\mathrm{I}}$)$_\infty$ chiral chain structures would be formed on using the Λ_{L} or Δ_{L} diastereomer of [Co(L-cys-*N,S*)(en)$_2$]$^+$ instead of racemic [Co(aet)(en)$_2$]$^{2+}$. Indeed, we found that the reactions of Λ_{L}- or Δ_{L}-[Co(L-cys-*N,S*)(en)$_2$]$^+$ with AgNO$_3$ lead to the formation of fascinating chiral supramolecular structures, which are markedly dependent on whether the Λ_{L} or Δ_{L} diastereomer is used (Scheme 1).

Treatment of a dark brown aqueous solution of Λ_{L}-[Co(L-cys-*N,S*)(en)$_2$](ClO$_4$)[9] with AgNO$_3$ in a 1:1 ratio at room temperature gave a dark red solution, from which red plate crystals of **1** were isolated by adding an aqueous solution of NaNO$_3$. The electronic absorption spectrum of **1** in water is characterized by an intense S-to-Co charge-transfer (CT) band at 288 nm and a first d–d absorption band at 497 nm. The disappearance of a distinct shoulder at ca. 560 nm in the first d–d band of the starting material Λ_{L}-[Co(L-cys-*N,S*)(en)$_2$]$^+$ is indicative of coordination of the thiolate S atom to an Ag$^{\mathrm{I}}$ ion.[7b, 8] Plasma emission spectral analysis indicated that **1** contains Co and Ag atoms in a 1:1 ratio, and the elemental analysis was consistent with the 1:1 stoichiometry of [Co(L-cys)(en)$_2$](NO$_3$) · AgNO$_3$.

The crystal structure of **1**, determined by X-ray analysis, revealed the presence of an asymmetric unit consisting of one octahedral Λ_{L}-[Co(L-cys-*N,S*)(en)$_2$]$^+$ unit and one Ag$^{\mathrm{I}}$ ion

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