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COMMUNICATION

Syntheses, structures and theoretical investigations of $[\text{Au}_{10}\text{S}_2(\text{PPh}_2)_2(\text{dppma}2)_4(\text{dppma}3)] \cdot [\text{Au}_6\text{S}_2(\text{dppma}2)_2(\text{dppma}3)]^\dagger$

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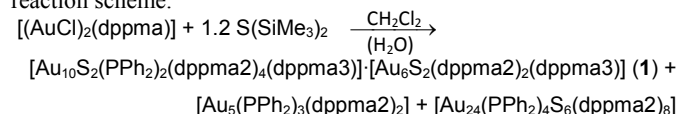
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The synthesis, crystal structure and theoretical studies of a high-nuclear gold(I) complex stabilized by bridging aromatic phosphane ligands are reported. The complex is composed of a neutral Au₁₀ complex unit with horseshoe-like structure around a neutral Au₆ complex unit with distorted cubane-like structure.

The chemistry of polynuclear gold(I) complexes has attracted increasing attention in the past decades. With a closed-shell electronic configuration of d¹⁰, gold(I) ions adopt a linear two-coordinate coordination geometry and tend to form weak metal...metal interactions,^{1,2} which have been termed “aurophilic interactions” by *Schmidbaur*.^{2,3} They are found in a huge number of polynuclear aggregates that possess a wide diversity of configurations and were successfully traced in several early theoretical investigations by extended Hückel quantum chemical calculations. Due to the high stability and the relatively good accessibility of synthetic routes, chalcogenide-based polynuclear gold(I) complexes, especially sulfide- and selenide-bridged gold(I) complexes, are among the most popular systems in the gold family. Many polynuclear gold(I) clusters of bridging phosphane ligands, with pyramidal [Au₃(μ₃-S)]⁺ units are linked via metal...metal interactions. Examples include clusters with the formulae [Au₅(PPh₂)₃(dppma2)]⁴, [Au₁₀Se₄(dppm)₄]²⁺ (dppm = bis(diphenylphosphino)methane),⁵ [Au₁₈Se₈(dpptph)₆]²⁺ (dpptph = 2,5-bis(diphenylphosphino)-thiophene)⁶ and series of decanuclear compounds recently published by *Yam* and co-workers, [Au₁₀S₄{(Ph₂P)₂NC_nH_{2n+1}}]²⁺ and [Au₁₀E₄{(Ph₂P)₂NC₆H₄X}]²⁺ (n = 8, 12, 14, 18; E = S, Se; X = H, Me, OMe, F, Cl, Br).^{7,8} In this work, we report on further extension of the investigations considering ligands that are based on maleic anhydride. In particular, we used a chlorogold(I) precursor containing the 2,3-bis(diphenylphosphino)maleic anhydride (dppma) ligand, [(AuCl)₂(dppma)], to form polynuclear gold(I) μ₃-sulfido clusters. The dppma ligand is known to assist the stabilization of mononuclear 19-electron complexes by electron delocalization into the low-lying π* orbital of the phosphane ligand,^{9,10} which led to the formation of a number of stable 19-electron complexes of Mn and Co, for example [(dppma)Co(CO)₃] and [(dppma)Mn(CO)₄], in which the odd electron appears to be ligand-centered.^{10,11} This

redox-active phosphane ligand seems to be an interesting point also for gold sulfide chemistry, as has been shown in some preliminary studies:

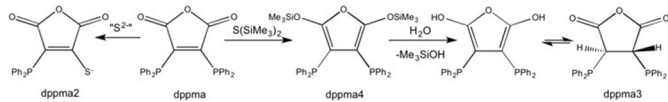
Both the ligand and the respective gold(I) precursor [(AuCl)₂(dppma)] were prepared according to literature methods and treated under inert conditions.⁴ Reaction of the latter with S(SiMe₃)₂ in CH₂Cl₂ (with traces of water) yielded a mixture of different complexes, [Au₅(PPh₂)₃(dppma2)]₂,⁴ [Au₂₄(PPh₂)₄S₆(dppma2)₈],^{4,12} reported recently, and the yet unknown compound [Au₁₀S₂(PPh₂)₂(dppma2)₄(dppma3)]·[Au₆S₂(dppma2)₂(dppma3)] (**1**, Figure 1), in single crystalline form according to the following reaction scheme:



Compound **1** possesses an overall near C₂ symmetry and is composed of two separate units, namely [Au₁₀S₂(PPh₂)₂(dppma2)₄(dppma3)] (**1a**) containing Au⁺, S²⁻, (PPh₂)⁻, and (dppma2)⁻ ions, besides [Au₆S₂(dppma2)₂(dppma3)] (**1b**) containing Au⁺, S²⁻, and (PPh₂)⁻ ions, and neutral dppma3. It is worth noting that the two clusters that co-exist in **1** are neutral, which is rare and reminds of self-recognition of carbonyl clusters,¹³ concerning gold sulfide cluster chemistry, it was observed for the first time and prompted us to undertake further investigations on their intermolecular interaction.

Further, during the formation of complex **1** the initially reacted dppma ligand underwent various transformations led to the generation of ligands dppma2 and dppma3, respectively. Replacement of a PPh₂ fragment of dppma with a sulfide ligand yielded the negatively charged dppma2 ligand, thereby releasing a (PPh₂)⁻ group to be involved in the formation of the cluster. In the other case, hydrogenation of the ring, presumably via intermediate silylation of the anhydride's enol form by S(SiMe₃)₂ and release of Me₃SiOH in the presence of traces of water, led to the formation of the neutral ligand dppma3 (Scheme 1). The suggested route was indeed rationalized by detection of a mono-silylated intermediate acting as ligand in [Au₁₂(PPh₂)₂S₄(dppma4)₄](BPh₄)₂.¹² These kinds of transformations have only been observed in the presence of gold(I), whereas analogous reactions with silver(I) or copper(I) do not yield any changes of the initial ligands. According to single-

crystal X-ray structure analyses,[†] **1** (triclinic space group $P\bar{1}$, $Z = 2$) crystallizes along with 14 molecules of dichloromethane per unit cell.



Scheme 1. Suggested derivatization of dppma yielding the ligands dppma2 and dppma3 alongside the synthesis of compound **1**.

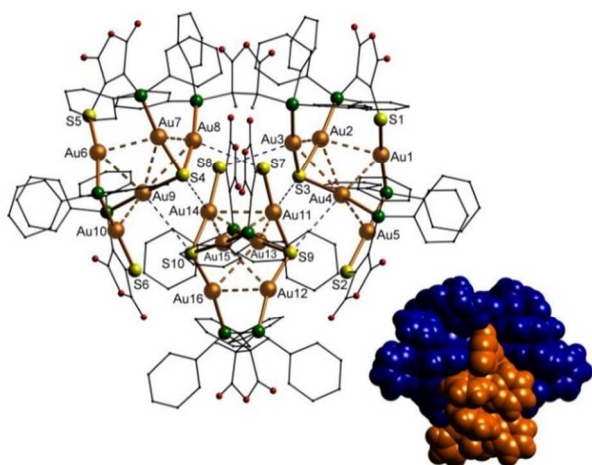


Figure 1. Molecular structure of **1** in the crystal. Closest Au...Au distances within each complex unit and closest Au...S interactions between **1a** and **1b** are indicated by dashed golden or blue lines. For clarity, only H atoms of the central cycle of the dppma3 ligands are shown; Au: gold, S: yellow, P: green, O: red, C: black, H: light grey; inset: size-reduced space-filling model of **1** with **1a** in blue and **1b** in gold.

The larger complex unit, $[Au_{10}S_2(PPh_2)_2(dppma2)_4(dppma3)]$ (**1a**), has a horseshoe-like structure with two $\{Au_5\}$ complex fragments linked together by a dppma3 ligand. Each of the $\{Au_5\}$ fragments consists of a distorted $[Au_3S]$ tetrahedron (Au2–Au4, S3 and Au7–Au9, S4) and an $[Au-(PPh_2)-Au]$ unit (Au1, P2, Au5 and Au6, P7, Au10), which are linked by two dppma2 ligands. In the μ_3 -bridging $[Au_3S]$ units the Au–S–Au angles range from $81.7(1)^\circ$ to $96.8(1)^\circ$, thus pretty close to the expected 90° for essential 3p-bonding of sulfur atoms. The Au–S and Au–P bond lengths in **1a** range from 230.5(3) pm to 233.9(3) pm and 225.3(3) to 229.0(3) pm, respectively. The Au...Au contacts of **1a** are in the range of 289.1(1) pm and 340.3(1) pm.

The second complex unit, $[Au_6S_2(dppma2)_2(dppma3)]$ (**1b**), is hexanuclear, with a distorted cubane-like structure and the two sulfur atoms are at opposite apexes. Each sulfur atom coordinates to three gold(I) ions in a μ_3 -bridging mode, and the two $[Au_3S]$ units are connected by two dppma2 ligands and one dppma3 ligand. The Au...Au distances range from 297.1(1) pm to 437.6(1) pm. The Au–S and Au–P bond lengths in **1b** range from 228.2(3) pm to 233.6(3) pm and 227.4(3) to 228.4(3) pm, respectively, and the Au–S–Au angles are between $86.8(1)^\circ$ and $107.2(1)^\circ$; deviations from the ideal value of 90° are often observed in gold(I) μ_3 -sulfido complexes.^{5–8,14}

As shown in Figure 1, **1a** and **1b** interdigitate, reminding of a lock-and-key like arrangement of both subunits. The shortest, yet non-bonding distances between **1a** and **1b** are 347 pm (Au8...S7), 360 pm (Au3...S8), 404 pm (Au9...S10), 414 pm (Au4...S9), 456 pm (Au11...S3), and 459 pm (Au14...S4). We thus inferred that dipole-dipole interactions between the two complex units trigger the organization of the intriguing structure, which was further studied by means of quantum

chemical investigations (*vide infra*). Very obviously, an opposite alignment of reverse polarizations is favored, as can be seen in the relative orientation of the Au3–S3–Au4 ($\delta^+-\delta^--\delta^+$) and the S7–Au11–S9 ($\delta^--\delta^+-\delta^-$) moieties, or the Au8–S4–Au9 ($\delta^+-\delta^--\delta^+$) and S8–Au14–S10 ($\delta^--\delta^+-\delta^-$) moieties.

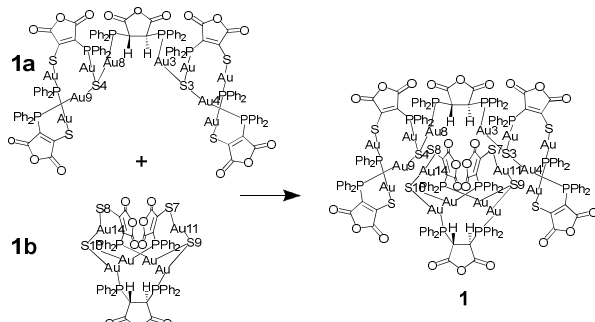
Quantum chemical calculations using the program system TURBOMOLE V6.5¹⁵ were undertaken to further explore the bonding within the complex, in particular to get insight in the intramolecular Au...Au interactions¹⁶ and the intermolecular Au...S interactions. Density functional theory (DFT) methods^{17–21} were used, employing Grimme's B97-D functional²² (for further technical details, see below and the ESI[†]). Simultaneous optimization of the electronic and geometric structure was performed to rationalize the experimental results and to examine possible interactions within the two parts of the complex. For reduction of the computational effort, we symmetrized the complex to adopt C_2 symmetry, which is only barely missed in the crystal structure. During the geometry optimization, all the Au–S bond lengths were constantly increased by ca. 4 pm with respect to the experiment, as typical and expected for DFT calculations. The calculated Au–S bond lengths in **1b** (230.8–237.5 pm) span a slightly wider range than the bond lengths in **1a** (235.4–237.8 pm), in accordance with the experimental observation. The calculated S–Au–P angles range from 164.6° to 177.2° . The S–Au–S angles in **1b** amount to 170.9° . Some angles show a clear deviation from the expected ideal linear coordination of the Au(I) atoms, both in the experiment and the calculations. The largest deviation of calculated from experimental values for bond angles was observed for S3–Au3–P4 (-5.5°); all other values agree with the experimentally found ones within less than 5° . All calculated and experimentally obtained values are listed in the ESI (Tables S1–S7). Based on the good agreement of experimental and calculated structures, we state that the chosen method is appropriate to model the compound and thus to comment on the bonding situation.

We therefore investigated the named short Au...S distances between the two subunits by inspection of canonical and localized molecular orbitals (MOs and LMOs). However, as illustrated in Figures S1–S8, there is no indication for any bonding interaction between the quoted atoms even though the B97-D functional was used. Instead, we assume that the large number of short S...H and O...H distances are involved, as the respective lone pairs at the sulfide and oxide ligands clearly direct towards the hydrogen atoms. All distances are close to the sum of the van der Waals radii of hydrogen and oxygen or sulfur atoms, respectively (see Table S7). Besides, the calculated O...H distances also correspond well to the normal range of CH...O contact distances in organic crystal structures.²³

As **1a** and **1b** do not represent an ion pair, the total interaction energy between the two subunits in **1** is based exclusively on dispersive interactions. It was possible to estimate this energy value by comparison of the total energy calculated for **1** with the sum of total energies calculated for the separated subunits in their original geometric structure. Scheme 2 illustrates the procedure that yielded $E_{\text{interaction}} = E_1 - [E_{1a} + E_{1b}] = -649.5 \text{ kJ mol}^{-1}$. Considering the twelve S...H and O...H interactions, this yields an interaction energy of $-54.1 \text{ kJ mol}^{-1}$ per contact on average.

To examine possible aurophilic interactions within the subunits, shared electron numbers (SEN) were calculated via population analysis based on occupation numbers (PABOON).²⁴ The obtained values vary largely, from 0.09 (Au4...Au5,

Au9...Au10) to 0.56 (Au11...Au15, Au13...Au14), indicating some interaction at least for the contacts with largest SEN. It should be noted that the observed Au...Au distances do not correlate in a strict way with the SEN values obtained (see Table S6), both in **1a** and **1b**. A possible explanation might be that the Au atoms are forced into these confirmations by the surrounding structures without actual bonding interactions.



Scheme 2. Formal division of compound **1** into its two neutral subunits under specification of according total energies, summing up to $E = -649.5 \text{ kJ}\cdot\text{mol}^{-1}$.

In conclusion, we showed the successful preparation and characterization of a high-nuclearity gold(I) sulfido complex containing derivatives of bis(diphenylphosphino)maleic anhydride. The complex possesses a lock-and-key like structure as revealed by X-ray diffraction studies. According to DFT calculations, the two neutral subunits are held together mainly by S...H and O...H hydrogen bonds, reminiscent of the key interactions in bio-organic compounds, with a total interaction energy of about $-650 \text{ kJ}\cdot\text{mol}^{-1}$.

Notes and references

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† *Crystal structure determination.* Data collection at 150.15 K on a STOE StadiVari diffractometer with Pilatus300K detector using a Mo GeniX 3D HF micro focus X-ray source ($\lambda = 0.71073 \text{ \AA}$). Structure solution by direct methods; full-matrix least-squares refinement on F^2 using SHELX²⁵ and OLEX2²⁶ software. H atoms added on idealized positions. *Crystal Data* for $\text{C}_{191}\text{H}_{156}\text{Au}_{16}\text{Cl}_{16}\text{O}_{24}\text{P}_{12}\text{S}_{10}$ (M 7246.05 g/mol): triclinic, space group $P\bar{1}$ (no. 2), a , b , c 15.4644(3), 25.0982(5), 27.0905(4) Å, α , β , γ 92.194(1), 91.098(1), 93.130(1)°, V 10488.8(3) Å³, Z 2, $\mu(\text{MoK}\alpha) = 11.596 \text{ mm}^{-1}$, $\rho_{\text{calc}} = 2.294 \text{ g/cm}^3$, 79203 refl. meas. ($3.01^\circ \leq 2\theta \leq 52.2^\circ$), 40454 unique ($R_{\text{int}} = 0.0653$, $R_\sigma = 0.0644$) used in all calculations. Final R_1 0.0634 ($I > 2\sigma(I)$) and wR_2 0.1770 (all data). CCDC 1046523 The low yield of **1** (ca. 5%), its insolubility and the quoted co-crystallization hampered further analytical studies.

Quantum chemical methods. TURBOMOLE V6.5,¹⁵ RIDFT,¹⁷ B97-D functional,²² (grid size m3), dispersion correction by DFT-D3¹⁸ with BJ-damping,¹⁹ def2-TZVP basis sets,²⁰ effective core potential (au def-ecp)²¹

at Au atoms. Mulliken,²⁷ NPA,²⁸ and PABOON²⁴ analyses and Boys localization of MOs,²⁹ as implemented in TURBOMOLE V6.5.

Electronic Supplementary Information (ESI) available: Details of syntheses, analyses and quantum chemistry. See DOI: 10.1039/c000000x/

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