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 a horseshoe-like structure around a neutral Au6 complex unit with a distorted cubane-like structure.

The chemistry of polynuclear gold(I) complexes has attracted increasing attention in the past few decades. With a closed-shell electronic configuration of d10, gold(I) ions adopt a linear aurophilic...
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 a ligand in the formation of the cluster. In the other case, the second complex unit, [Au6S2(PPh2)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 μ₄-bridging mode, and the two [Au₅S₃] 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···Au contacts of 1a are in the range of 289.1(1) pm and 340.3(1) pm.

The larger complex unit, [Au₁₀S₆(PPh₂)₂(dppma2)₄(dppma3)] (1a), has a horseshoe-like structure with two [Au₅S₃] complex fragments linked together by a dppma3 ligand. Each of the [Au₅S₃] fragments consists of a distorted [Au₅S₆] tetrahedron (Au2–Au4, S3 and Au7–Au9, S4) and an [Au–(PPh2)–Au] unit (Au1, P2, Au5 and Au6, P7, Au10), which are linked by two dppma2 ligands. In the μ₄-bridging [Au₅S₃] units the Au–S–Au angles range from 81.7(1)° to 96.8(1)°, 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.

As shown in Fig. 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 (δ⁺–δ⁻–δ⁻) and the S7–Au11–S9 (δ⁻–δ⁺–δ⁺) moieties, or the Au8–S4–Au9 (δ⁺–δ⁻–δ⁻) and S8–Au14–S10 (δ⁻–δ⁺–δ⁺) moieties.

Quantum chemical calculations using the program system Turbomole V6.5 were undertaken to further explore the bonding within the complex, in particular to gain insight into the intramolecular Au···Au interactions and the intermolecular Au···S interactions. Density functional theory (DFT) methods were used, employing Grimme’s B97-D functional (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 C₂ 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 obser-
vation. 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 calculated from experimental values for bond angles was observed for S3–Au3–P4 (−5.5°); all other values are in agreement 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 the 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 Fig. S1–S8,‡ there is no indication of any bonding interaction between the quoted atoms even though the B97-D functional was used. Instead, we assume that a 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. 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 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). 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 the 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.

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 kJ mol\(^{-1}\).

Notes and references

† Crystal structure determination. Data collection at 150.15 K on a STOE Stadi Vari diffractometer with a Pilatus300 K detector using a Mo GeniX 3D HF micro focus X-ray source \( \lambda = 0.71073 \text{ Å} \). Structure solution by direct methods; full-matrix least-squares refinement on \( F^2 \) using SHELX22 and OLEX226 software. H atoms added at idealized positions. Crystal Data for C\(_{191}\)H\(_{156}\)Au\(_{16}\)Cl\(_{16}\)O\(_{24}\)P\(_{12}\)S\(_{10}\) (M 7246.05 g mol\(^{-1}\)): triclinic, space group P\(_1\) (no. 2), \( a = 15.464(3)\), \( b = 25.098(5)\), \( c = 27.090(4)\), \( \alpha = 92.194(1)\), \( \beta = 91.098(1)\), \( \gamma = 93.130(1)\); \( V = 10.4888(3)\) \( \text{Å}^3\), \( Z = 2\), \( \mu\text{(MoK}\_\alpha) = 11.596 \text{ mm}^{-1}\), \( \rho_{\text{calc}} = 2.294 \text{ g cm}^{-3}\), 79 203 refl. meas. \((3.01° < \Theta < 52.2°)\), 40 454 unique \((R_{\text{ave}} = 0.0653, R = 0.0644)\) 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 V6.5,25 RIIIPTF;27 B97-D functional,22 (grid size m3), dispersion correction by DFT-D3+\( \ddagger \) with B9-damping,29 def2-TZVP basis sets,28 effective core potential (au def-ecp)31 at Au atoms. Mulliken,28 NPA,28 and PABOON analyses and Boys localization of MOs,28 as implemented in TURBOMOLE V6.5.


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