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A luminescent gold(I)–copper(I) cluster with unprecedented carbon-centered trigonal prismatic hexagold†

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An unprecedented trigonal prismatic (μ_6 -C)Au₆ structure has been found in a novel gold(I)–copper(I) cluster with a hypercoordinated carbon, [CAu₆Cu₂(dppy)₆](BF₄)₄; the incorporation of copper ions enhances the rigidity and integrity of the cluster and turns on the bright red solution luminescence.

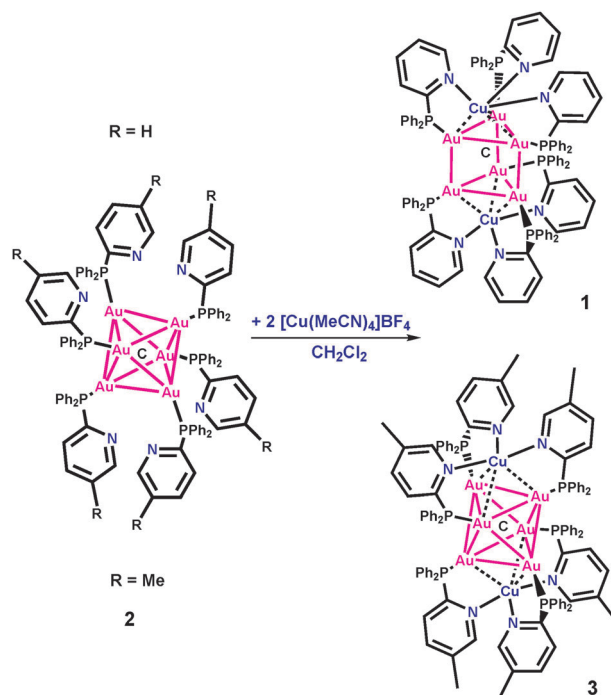
Gold chemistry has experienced amazing advances in the past decades.^{1–3} An interesting category of molecular gold compounds are those containing phosphino-gold(I) fragments clustering around a hypervalent main group atom, such as [C(AuPR₃)₆]²⁺, [N(AuPR₃)₅]²⁺ and [O(AuPR₃)₄]²⁺.⁴ These species are fascinating because of their importance in both structural and theoretical aspects. Auophilic attractions are thought to be significant in stabilizing these gold compounds with interstitial atoms. These gold clusters display a preference for forming as many short gold(I)–gold(I) contacts as possible along the edges of the polyhedra. Complexes of the type [C(AuPR₃)₆]⁺ have been extensively studied and a number of structures have been elucidated with tertiary phosphines and biphosphines.⁵ All these complexes contain a carbon-centered hexagold core adopting an octahedral configuration.

Our interest in molecular gold(I) systems containing interstitial atoms began with the effort to utilize them as molecular luminescent materials due to their spherical shape and stability in solution. Recently, we have shown that [CAu₆Ag₂(dppy)₆](BF₄)₄ (dppy = diphenylphosphino-2-pyridine) is able to display intense phosphorescence in solution at room temperature due to the rigidity enhancement caused by additional coordination and the protection supplied by peripheral phosphine ligands.⁶ To test the generality of the concept that rigidity enhances luminescence, we made efforts to check if the solution emission could be also turned on by introducing other ions such as copper(I) into the system. While bright luminescence was observed in the solid state and in solution, a surprising structural twist was found in the

formation of [CAu₆Cu₂(dppy)₆](BF₄)₄ (**1**). The trigonal prismatic CAu₆ core in **1** is unprecedented, because all known hexa-auriomethane CAu₆ moieties⁵ along with those theoretically predicted⁷ are all octahedral. Furthermore, we managed to assemble a bicapped octahedron CAu₆Cu₂ by applying a dppy derivative as the ligand, which is also a bright luminophore. Herein, we report the synthesis, structures and luminescence properties of these novel gold(I)–copper(I) clusters, and DFT calculation studies are also described.

The synthesis is summarized in Scheme 1. It is quite interesting that a subtle variation in the phosphine ligand can result in two distinct CAu₆Cu₂ arrangements.

Complex **1** was prepared by treatment of [CAu₆(dppy)₆](BF₄)₂⁶ with two equivalents of [Cu(MeCN)₄]BF₄ in dichloromethane solution. The incorporation of copper(I) into the cluster was confirmed by ³¹P NMR. Crystals of the composition 1·6CH₂Cl₂·*n*-hexane could be grown from a solution of **1** in CH₂Cl₂/MeOH/*n*-hexane, but the structure determination was laborious because of the extremely fast loss of solvent



Scheme 1

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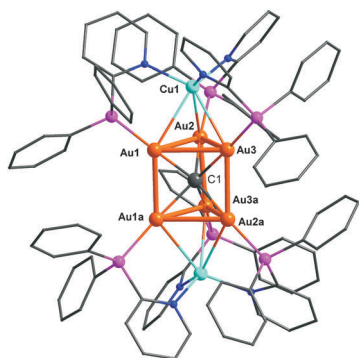


Fig. 1 Molecular structure of the cationic part of $[\text{CAu}_6\text{Cu}_2(\text{dppy})_6](\text{BF}_4)_4$ (**1**). Selected bond distances [\AA]: Au(1)–C(1) 2.137(13), Au(2)–C(1) 2.157(6), Au(3)–C(1) 2.168(7), Au(1)–Au(1)^a 2.7814(9), Au(1)–Au(2) 2.8604(7), Au(1)–Au(3) 2.8672(7), Au(2)–Au(3)^a 2.7529(6), Au(2)–Au(3) 2.8660(6), Au(1)–Cu(1) 2.907(2), Au(2)–Cu(1) 2.855(1), Au(3)–Cu(1) 2.885(1). Symmetry code: (a) $-x + 1/2, y, -z + 3/2$.

molecules from the crystals. Single crystal X-ray structural analysis[†] revealed that the core structure of **1** is a CAu_6Cu_2 bicapped trigonal prism as shown in Fig. 1. Six gold(i) ions form a trigonal prism with two copper atoms each capping one of the two opposite Au_3 triangles. The $\text{Au}^1 \cdots \text{Au}^1$ and $\text{Au}^1 \cdots \text{Cu}^1$ distances lie in the range of 2.7529(6)–2.8672(7) \AA and 2.855(1)–2.907(2) \AA , respectively, which suggests the presence of metallophilic interactions. A carbon tetra-anion sits in the middle of the cluster with Au–C bond lengths ranging from 2.137 to 2.168 \AA . Each gold(i)–copper(i) edge is bridged by one dppy ligand with the P atom bound to Au(i) and the pyridyl N atom coordinated to Cu(i). Compared with the starting material $[\text{CAu}_6(\text{dppy})_6](\text{BF}_4)_2$ in which the dppy ligands act as terminal ligands only, extra rigidity and integrity are conferred to **1** owing to the binding of the copper ions to the pyridyl of dppy and the additional $\text{Au}^1 \cdots \text{Cu}^1$ metallophilic interactions thus formed. There are 12 $\text{Au}^1 \cdots \text{Au}^1$ contacts in an octahedron while there are only 9 in a trigonal prism. The stability of **1** is not significantly affected by the missing of three gold(i)–gold(i) contacts because it is compensated with shorter gold(i)–gold(i) contacts in the trigonal prism. It was found by $^{31}\text{P}\{^1\text{H}\}$ NMR that the six P atoms in **1** are equivalent in solution even at -70°C .

To rationalize the formation of the unique configuration of CAu_6 , the relative stabilities of the octahedral and trigonal prismatic configurations of $[\text{CAu}_6\text{Cu}_2(\text{dppy})_6]^{4+}$ have been investigated using the density functional theory (DFT).⁸ The Perdew–Wang 91 exchange functional in combination with the Perdew local (PWC)^{9a} or the generalized gradient approximation (GGA-PW91)^{9a,b} was considered in density functional calculations with the all-electron relativistic double numerical basis set plus polarization functions implemented in the DMol3 program.^{9c,d} For comparison, DFT calculations with the GGA-PBE functional^{9e} were also performed. The $[\text{CAu}_6\text{Cu}_2(\text{dppy})_6]^{4+}$ cluster with the octahedral CAu_6 core is slightly more stable than its trigonal prismatic configuration by 5.4 kcal mol⁻¹ with GGA-PW91 or 4.5 kcal mol⁻¹ with GGA-PBE. However, PWC calculations show that $[\text{CAu}_6\text{Cu}_2(\text{dppy})_6]^{4+}$ with the trigonal prismatic CAu_6 core

is more stable than its configuration with the octahedral CAu_6 core by 1.2 kcal mol⁻¹. Although the predicted energy differences depend on the choice of methodology, the geometric shape of the CAu_6 core in $[\text{CAu}_6\text{Cu}_2(\text{dppy})_6]^{4+}$ might be sensitive to the experimental conditions as well as the structural environment of the metal core, due to the relatively small energy difference between the octahedral and trigonal prismatic configurations.

Based on the theoretical analysis, a modified dppy ligand with a methyl substituent on the pyridyl group was used in attempts to obtain a bicapped octahedral configuration instead of a bicapped trigonal prism. The different packing forces might affect the final configuration of the gold cluster formed. The reaction of $[\text{OAu}_3\text{L}_3]\text{BF}_4$ (L = 5-methyl-diphenylphosphino-2-pyridine) with $\text{Me}_3\text{SiCHN}_2$ in CH_2Cl_2 solution led to the isolation of $[\text{CAu}_6\text{L}_6](\text{BF}_4)_2$ (**2**). Complex **2** is an octahedral cluster with an interstitial carbon as shown in Fig. 2a. Its structure is quite similar to that of $[\text{CAu}_6(\text{dppy})_6](\text{BF}_4)_2$. The reaction of **2** with two equivalents of $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ gave $[\text{CAu}_6\text{Cu}_2\text{L}_6](\text{BF}_4)_4$ (**3**), which was confirmed to have a bicapped octahedral configuration *via* X-ray structure determination. The molecular structure of **3** is shown in Fig. 2b.

The important average bond distances in **1** and **3** are summarized in Table 1. In comparison with **3**, **1** has shorter $\text{Au}^1 \cdots \text{Au}^1$ and $\text{Au}^1 \cdots \text{Cu}^1$ contacts along with longer Au^I–C bond lengths. It is plausible that stronger $\text{Au}^1 \cdots \text{Cu}^1$ interactions in **1** favor the formation of a trigonal prismatic CAu_6 moiety, which is constructed from 9 shorter $\text{Au}^1 \cdots \text{Au}^1$ contacts. The C–Au bond distances in **1** are significantly longer than those in **3** due to the twist from an octahedron to a trigonal prism, thus the Au–C–Au bond angles in **1** are

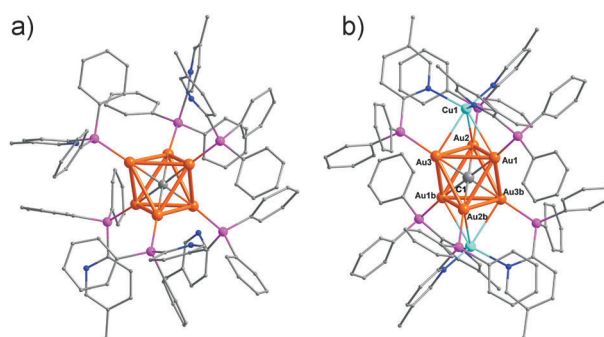


Fig. 2 (a) Molecular structure of the cationic part of $[\text{CAu}_6\text{L}_6](\text{BF}_4)_2$ (**2**). (b) Molecular structure of the cationic part of $[\text{CAu}_6\text{Cu}_2\text{L}_6](\text{BF}_4)_4$ (**3**). Selected bond distances [\AA] in **3**: Au(1)–C(1) 2.1076(2), Au(2)–C(1) 2.1219(2), Au(3)–C(1) 2.1184(2), Au(1)–Au(2) 2.9382(3), Au(1)–Au(3) 2.9891(3), Au(2)–Au(3) 2.9207(4), Au(1)–Au(2)^b 3.0423(4), Au(1)–Au(3)^b 2.9874(3), Au(2)–Au(3)^b 3.0741(3), Au(1)–Cu(1) 2.8914(7), Au(2)–Cu(1) 2.9712(7), Au(3)–Cu(1) 2.8567(8). Symmetry code: (b) $-x + 1, -y, -z$.

Table 1 Selected average bond distances in **1** and **3** [\AA]

	$\text{Au}^1 \cdots \text{Au}^1$	$\text{Au}^1 \cdots \text{Cu}^1$	Au ^I –C	$\text{Cu}^1 \cdots \text{N}$
1	2.8305	2.8825	2.154	2.102
3	2.9920	2.9064	2.116	2.168

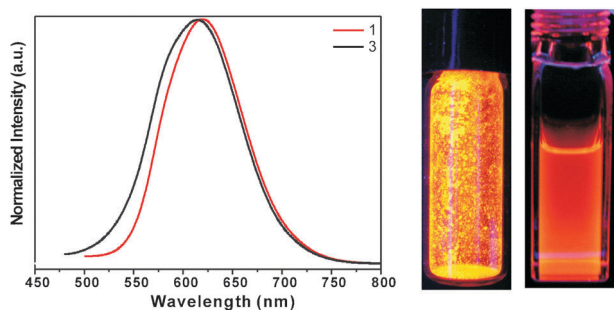


Fig. 3 (left) Normalized emission spectra of **1** and **3** in CH_2Cl_2 at room temperature. Excitation wavelengths (nm): 400 for **2**; 430 for **3**. (right) Photo of emissions from **1** in the solid state and in CH_2Cl_2 solution at room temperature (365 nm excitation).

about 83° and 138° rather than those values close to 90° or 180° in **3**.

We have investigated the luminescence properties of **1** and **3**. Complex **1** is brightly emissive in the solid state and in solution at room temperature. As shown in Fig. 3, complex **1** exhibits red emission with a $\lambda_{\text{em}}^{\text{max}}$ value of 619 nm in dichloromethane, and the quantum yield in CH_2Cl_2 is 4.3% as measured with Rhodamine B in absolute ethanol as the standard (0.69).¹⁰ The lifetime at the microsecond scale (2.1 μs) and the large Stokes shift indicate that the emission is of triplet parentage. At room temperature, while $[\text{CAu}_6(\text{dppy})_6](\text{BF}_4)_2$ is non-emissive in solution, **1** is brightly red emissive, and similarly complex **2** is not emissive in solution while **3** displays strong red luminescence in solution. These observations confirm that the increase of rigidity is important for the solution luminescence. The vibration and rotation of the pyridyl groups of the phosphines are limited because of the coordination of silver ions, which favors the radiative pathway and turns on the luminescence in solution.

In summary, a brightly luminescent gold(i)–copper(i) cluster having a unique trigonal prismatic CAu_6 moiety is reported for the first time. Clusters with different geometries could be obtained by applying modified ancillary phosphine ligands. The observed trigonal prismatic geometry presents a new model for the consideration of the electronic structures.

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Notes and references

† Crystal data for $1\cdot 6\text{CH}_2\text{Cl}_2\cdot \text{C}_6\text{H}_{14}$, $\text{C}_{103}\text{H}_{84}\text{B}_4\text{N}_6\text{F}_{16}\text{P}_6\text{Cu}_2\text{Au}_6\cdot 6\text{CH}_2\text{Cl}_2\cdot \text{C}_6\text{H}_{14}$, $a = 17.5733(3)$, $b = 17.4274(5)$, $c = 21.4717(4)$ Å, $\beta = 90.610(2)^\circ$, $V = 6575.5(3)$ Å³, monoclinic space group $P2_1/n$, $Z = 2$, $T = 173(2)$ K, 48 447 reflections measured, 17 103 unique

($R_{\text{int}} = 0.0865$), final $R_1 = 0.0505$, $wR_2 = 0.1192$ for 7357 observed reflections [$I > 2\sigma(I)$]. Crystal data for $2\cdot \text{CH}_2\text{Cl}_2\cdot \text{Et}_2\text{O}$, $\text{C}_{109}\text{H}_{96}\text{B}_2\text{N}_6\text{F}_8\text{P}_6\text{Au}_6\cdot \text{CH}_2\text{Cl}_2\cdot \text{Et}_2\text{O}$, $a = 15.3693(2)$, $b = 26.7614(6)$, $c = 27.7995(5)$ Å, $\alpha = 85.822(2)$, $\beta = 79.850(1)$, $\gamma = 87.051(2)^\circ$, $V = 11216.5(4)$ Å³, triclinic space group $P1$, $Z = 4$, $T = 173(2)$ K, 187 271 reflections measured, 61 813 unique ($R_{\text{int}} = 0.0916$), final $R_1 = 0.0536$, $wR_2 = 0.0966$ for 22 470 observed reflections [$I > 2\sigma(I)$]. Crystal data for $3\cdot 6\text{CH}_2\text{Cl}_2$, $\text{C}_{109}\text{H}_{96}\text{B}_4\text{N}_6\text{F}_{16}\text{P}_6\text{Cu}_2\text{Au}_6\cdot 6\text{CH}_2\text{Cl}_2$, $a = 15.7378(3)$, $b = 24.8385(7)$, $c = 16.3084(4)$ Å, $\beta = 94.301(2)^\circ$, $V = 6357.1(3)$ Å³, monoclinic space group $P2_1/n$, $Z = 2$, $T = 173(2)$ K, 72 151 reflections measured, 17 626 unique ($R_{\text{int}} = 0.0492$), final $R_1 = 0.0437$, $wR_2 = 0.1018$ for 11 678 observed reflections [$I > 2\sigma(I)$].

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