Cluster Compounds

DOI: 10.1002/ange.200800452

Self-Assembly of Supramolecular Luminescent Au^I–Cu^I Complexes: “Wrapping” an Au_6Cu_6 Cluster in a $[Au_3(diphosphine)_3]^{3+}$ “Belt”**

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Growing attention to alkynyl complexes of coinage metals, stimulated by their intriguing photophysical properties,[1–5] has substantially focused on polynuclear homo- and heterometallic compounds.[2,4–10] The versatile bonding mode of alkynes and metallophilic interactions resulted in the synthesis of numerous cluster complexes which display different structural motifs and emission properties.[5,6,9,11] However, in most cases assembly of the complexes occurs in an uncontrolled way[6,7,11] and therefore it is a challenge to find a synthetic approach which would allow directed modification of the structural and electronic properties of these compounds. One of the most attractive features of supramolecular construction is the possible tuning of the luminescent behavior through changes in the electron richness of the alkyne ligands by π coordination to different metal ions. This method has been successfully used to synthesize heterometallic complexes by coordination of phosphine–gold(I)–alkyne π-donor metalloligands to d^{10} metal centers.[5,10,12–14] These examples of alkynyl π coordination do not lead to ligand rearrangement, and the products formed obey the simple stoichiometry of the reaction. Composition and structure of the metal frameworks of these complexes are mainly determined by the steric properties of the phosphine ligands coordinated to the gold(I) center. This inspired our interest in probing rigid diphosphine ligands for the preparation of Au–alkynyl complexes containing spatially separated Au centers and studying their reactivity towards Cu^I ions. Herein we report the stepwise synthesis, structural characterization, and luminescence properties of Au–Cu supramolecular complexes self-assembled from simple Au^I and Cu^I precursors.

Complex $[Au_2(C{\equiv}CPh)_2(\mu\text{-}4,4'\text{-}Ph_2PC_6H_4C_6H_4PPh_2)]$ (**1**) was obtained by treating polymeric gold phenylacetylide $[AuC{\equiv}CPh]_n$ with the diphosphine. X-ray diffraction on **1** revealed a dimeric structure (Figure 1),[15] similar to that found for analogous gold complexes based on the 1,2-bis(diphenylphosphanyl)ethane ligand.[16] However, the spectroscopic data (see the Supporting Information) indicate dissociation of the Au–Au bonds in solution.

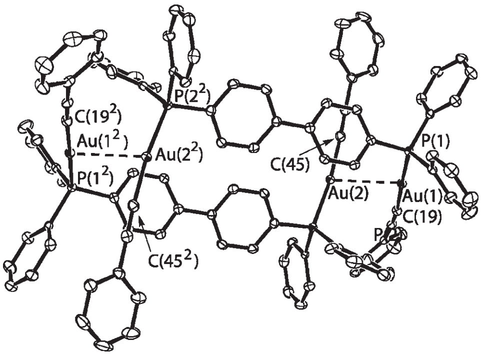

Figure 1. ORTEP view of the structure of **1**. Hydrogen atoms omitted for clarity. Au(1)–Au(2) 3.0812(2) Å.

Addition of one equivalent of $[Cu(NCMe)_4]PF_6$ to a colorless solution of **1** immediately turned it yellow-orange. The ^{31}P NMR spectrum of the reaction mixture displayed two major signals (43.2 and 43.0 ppm) with relative intensities of 1:1, which were later assigned to compounds **2** and **3** (see Scheme 1).

Optimization of the reaction conditions (Scheme 1) allowed selective preparation of $[Au_3(PPh_2(C_6H_4)_2PPh_2)_3\text{-}\{Au_6Cu_6(C_2Ph)_{12}\}](PF_6)_3$ (**3**). The composition of **3** was established on the basis of its ^1H, ^{13}C, and ^{31}P NMR and ESI-MS data. The structure of **3** proposed below was confirmed by X-ray crystallography. Unfortunately, poor diffraction due to crystals with multiple domains prevented high-quality refinement, but these data together with the detailed NMR investigation clearly support the structure shown in Figure 2. The ESI mass spectrum of **3** (Figure S1) displays a pattern for a triply charged cation at m/z 1645 that completely fits the stoichiometry given above.

The molecule contains a central $[Au_6Cu_6(C_2Ph)_{12}]$ fragment, which is wrapped around by a $[Au(PPh_2(C_6H_4)_2PPh_2)]_3$ “belt”, anchored to the central part by Au–Au bonds. The

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[**] Financial support from the Academy of Finland (I.O.K.) and the Russian Foundation for Basic Research (grant 07-03-00908-a) is acknowledged.

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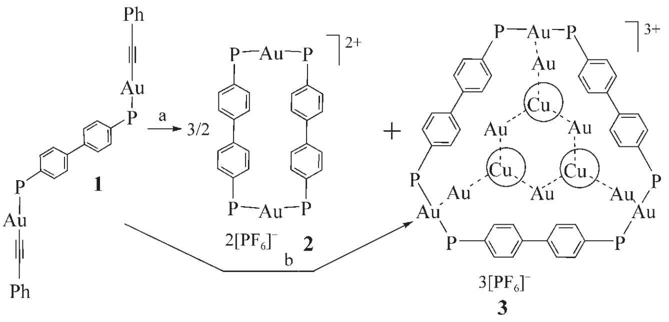


Scheme 1. Reaction of $[Cu(NCMe)_4]PF_6$ with **1**; conditions: a) $[Cu(NCMe)_4]PF_6$ (1 equiv), CH_2Cl_2; b) $[Cu(NCMe)_4]PF_6$ (2 equiv), PhC_2H, NEt_2H, $[AuC_2Ph]_n$, CH_2Cl_2.

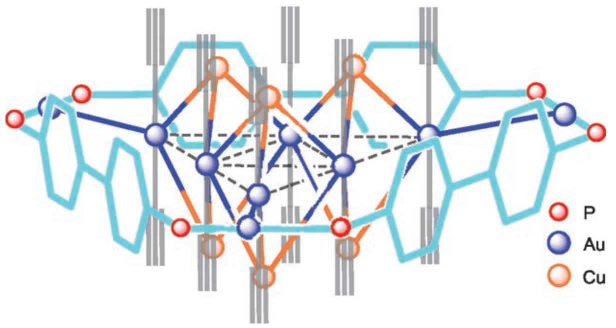
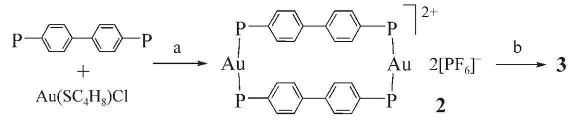


Figure 2. Schematic structure of trication **3**. Phenyl rings omitted for clarity.

central fragment consists of six $[PhC_2AuC_2Ph]$ rods held together by Cu–Au, π-C≡C–Cu, and Au–Au bonding. The gold atoms of this fragment together with those of the external $[Au(PPh_2(C_6H_4)_2PPh_2)]_3$ belt lie in one plane. Six Cu^I ions are disposed above and below the plane to form a trigonal prism, so that each is coordinated to three alkynyl units. Although a number of mixed Au–Ag and a few Au–Cu alkynyl compounds have been reported, the nuclearity and structure of the Au_9Cu_6 core of **3** are unprecedented.

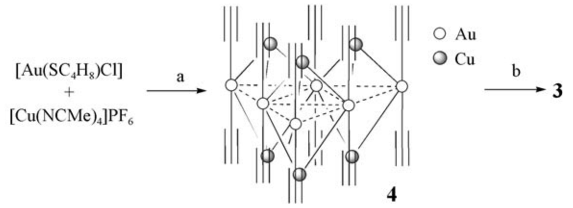
The ^1H NMR data of **3** completely fit the proposed structure. Complex **3** has four distinguishable groups of signals (^1H,^1H COSY spectrum; Figure S2) in the aromatic region of the ^1H NMR spectrum. Correlations observed in the low-field part (8.5–7.25 ppm) allow assignment of these signals to the phenyl rings and the biphenyl spacer of the diphosphine. Easily detected coupling of the *ortho*-protons to the phosphorus nuclei ($J = 13.2$ and 12.2 Hz, respectively) support the suggested assignment. Two high-field (7.25–6.5 ppm) sets of resonances with relative intensities 1(t):2(d):2(dd) can be assigned to *para*:*ortho*:*meta* protons of the $[PhC_2AuC_2Ph]$ moieties, which form two groups of inequivalent rods (Scheme 1 and Figure 2). Relative intensities of the signals corresponding to these aromatic rings fit exactly the number of protons in these organic moieties. The ^{31}P and ^{13}C NMR data are also in line with the proposed structure.

Complex **2** was obtained individually by another synthetic route (Scheme 2). Its composition was established on the basis of its ESI mass spectrum (Figure S3) and ^1H, ^{31}P NMR data. The former displays one major signal that can be unambiguously assigned to a dimeric structure, and its isotopic pattern fits the calculated one. The spectroscopic patterns observed both in the ^1H and DEPT-135 NMR spectra indicate that this structure remains unchanged in solution. The solution of **2** is stable in the dark and does not show the presence of other species such as monomeric or trimeric forms of the complex. Complex **2** can be converted to **3** in good yield by treatment with stoichiometric amounts of $[AuC_2Ph]_n$ and $[Cu(NCMe)_4](PF_6)$ in the presence of phenylacetylene and base.



Scheme 2. Stepwise synthesis of **2** and **3**; conditions: a) $AgPF_6$ (1 equiv), CH_2Cl_2/acetone; b) $[Cu(NCMe)_4]PF_6$ (4 equiv), PhC_2H (4 equiv), NEt_2H (4 equiv), $[AuC_2Ph]_n$ (4 equiv), CH_2Cl_2.

Preparation of **2** as a precursor for the $[Au(PPh_2(C_6H_4)_2PPh_2)]_3$ belt of **3** prompted us to investigate the possibility of synthesizing its central $[Au_6Cu_6(C_2Ph)_{12}]$ fragment as an individual complex. Indeed, reaction of $[Au(SC_4H_8)Cl]$ with $[Cu(NCMe)_4]PF_6$ in the presence of phenylacetylene and base results in formation of bright orange light-sensitive cluster $[Au_6Cu_6(C_2Ph)_{12}]$ (**4**) in moderate yield (Scheme 3). Complex **4** was characterized by X-ray crystallography, ^1H NMR spectroscopy, and elemental analysis. Composition and geometry of cluster **4** (Figure 3) exactly match those of the central $[Au_6Cu_6(C_2Ph)_{12}]$ fragment of **3**.



Scheme 3. Synthesis of **4**; reaction conditions: a) PhC_2H (excess), NEt_3 (2 equiv), acetone; b) **2** (1.5 equiv), CH_2Cl_2.

Complex **4** is unstable in solution both in the dark and particularly under irradiation. Nevertheless, its ^1H NMR spectrum is completely compatible with the structure found in the solid state.

A remarkable interaction between complexes **4** and **2** occurs unassisted and leads to fast formation of **3** in nearly quantitive yield (Scheme 3).

"Wrapping" neutral cluster **4** in an Au–diphosphine cationic "belt" significantly increases the stability of the Au_6Cu_6 unit, particularly under irradiation. Self-assembly of the relatively simple precursors into a supramolecular aggregate is the most interesting feature of this chemistry, which proved to have an extension to be reported elsewhere.

The UV/Vis spectra of gold complexes **1** and **2** in CH_2Cl_2 display strong absorption in the near-UV region (230–

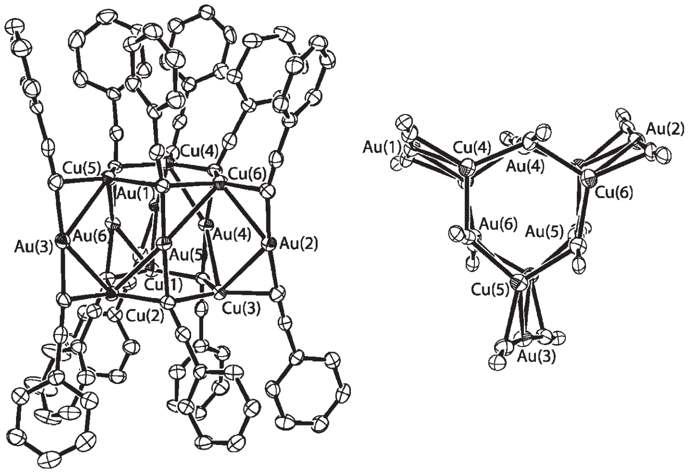


Figure 3. Two ORTEP projections of the structure of **4**. Hydrogen atoms omitted for clarity.

300 nm). The spectrum of **2** has a clear-cut band with maximum at 289 nm together with a higher-energy (HE) UV absorption at shorter wavelength. The band at 289 nm can be assigned to the transition from the σ(Au−P) orbital to an empty π* antibonding orbital located at the phosphine ligand, whereas HE absorption is usually associated with intraligand transitions. The spectrum of **1** has a more complicated pattern in the near-UV region (240–295 nm sh) along with the HE absorption observed for all the complexes studied. In this case the series of near-UV bands may be associated with transitions from the σ(Au−P) orbital to the π* antibonding orbital centered at aryl fragments of either phosphine or alkyne. The lowest-energy (LE) absorptions in both complexes could also correspond to metal-centered transitions. In addition to the near-UV absorption bands at 286 and 284 nm, mixed-metal complexes **3** and **4** show absorptions in the visible region, in the form of a well-separated band at 399 nm for **3** and a shoulder at 330 nm for **4**. These LE bands in **3** and **4** may be associated either with cluster-centered transitions or with the Cu–π-alkynyl fragment.

All compounds studied herein exhibit luminescence at room temperature (Figure 4). Binuclear complex **2** displays an intense emission band at 354 nm and much weaker luminescence at 681 nm in solution. The similar solid-state emission spectrum of complex **2** indicates similar structures in solution and in the crystal. The lifetime of HE emission of this complex at room temperature of less than 30 ns points to singlet origin of the emissive excited state, which can be assigned to π*(aryl phosphine) orbitals.

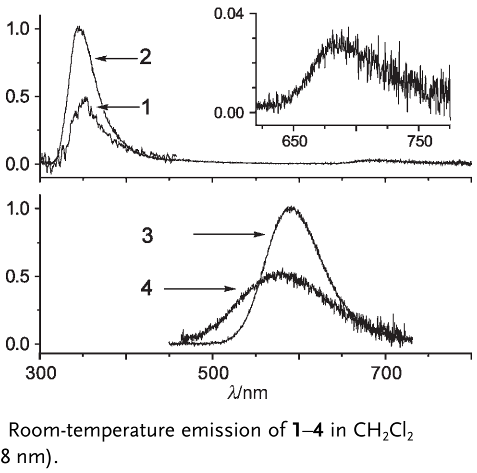


Figure 4. Room-temperature emission of **1**–**4** in CH$_2$Cl$_2$ (λ_{exc} = 308 nm).

The emission spectrum of dinuclear complex **1** in solution consists of a main band at 344 and a very weak band at about 480 nm. The HE emission is a short-lived fluorescence, whereas the lifetime of the LE emissive state of 2.8 μs points to its triplet parentage. The solid-state luminescence spectrum of **1** shows a combination of two intense bands at 509 and 550 nm. Substantial difference in the luminescence characteristics of **1** in the solid state and in solution is in line with dimer-to-monomer transformation of this complex in fluid media (for example, see reference [16]). The luminescence behavior of **1** is similar to that of its analogue $[(\mathrm{RC_2Au})_2(\mathrm{Ph_2PC_6H_4PPh_2})]$,[17] which in dichloromethane solution gives two main emission bands at 395 and 628 nm; the lifetime of the latter is 0.27 μs.

This similarity suggests an analogous assignment of the emissive excited states for complex **1**, namely, π→π*[Ph(P)] and σ→π*[Ph(P)] or MLCT [d(Au)→π*(C≡Ph)] for HE and LE luminescence, respectively.

The Au–Cu complexes **3** and **4** show much more intense luminescence than the homometallic compounds. The luminescence spectrum of **4** displays long-wavelength emission bands at 590 and 580 nm in the solid state and in solution, respectively. The emission lifetime in solution of 1.26 μs points to its triplet origin. The origin of the LE luminescence in the mixed-metal complexes is evidently the “Au$_6$Cu$_6$” core, because the mononuclear gold analogues [Au(C$_2$R)$_2$]$^-$ do not display luminescence in the spectral range below 450 nm.[16] Complex **3** is the strongest luminophore among the compounds studied. The emission spectra of this complex in solution and in the solid state have a very strong band centered at 590 nm. The emission lifetime in CH$_2$Cl$_2$ of 3.9 μs is indicative of triplet parentage of the emissive excited state. The similar luminescence parameters of **3** and **4** stem from the presence of the Au$_6$Cu$_6$ cluster core in both compounds, the contribution of the diphosphine belt to emission is evidently negligible.

In summary, we have demonstrated the possibility of preparing luminescent supramolecular gold–copper complexes using simple precursors. Successful isolation of the structural fragments of these compounds as individual species demonstrates a stepwise approach to building up multinuclear aggregates. This allows for better understanding of the unique photophysical properties of this type of complexes and may provide the basis for future design and synthesis of supramolecular luminescent compounds.

Received: January 28, 2008

Keywords: alkyne ligands · cluster compounds · gold · luminescence · P ligands

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[15] Crystal data for **1**: $C_{152}H_{124}Au_4P_4$, $M = 2862.26$, colorless block, $0.42 \times 0.28 \times 0.19$ mm, triclinic, space group $P\bar{1}$ (No. 2), $a = 14.6612(3)$, $b = 15.1969(3)$, $c = 15.8798(3)$ Å, $\alpha = 87.1160(10)$, $\beta = 72.2500(10)$, $\gamma = 64.1000(10)°$, $V = 3017.00(10)$ Å^3, $Z = 1$, $\rho_{\text{cald}} = 1.575$ g cm^{-3}, $F_{000} = 1412$, Nonius KappaCCD, $\text{Mo}_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{\max} = 55.0°$, 59454 reflections collected, 13814 unique ($R_{\text{int}} = 0.0357$). Final GoF = 1.068, $R1 = 0.0242$, $wR2 = 0.0368$, R indices based on 10814 reflections with $I > 2\sigma(I)$ (refinement on F^2), 692 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 4.954$ mm^{-1}. Crystal data for **4**: $C_{96}H_{60}Au_6Cu_6$, $M = 2776.48$, orange block, $0.34 \times 0.11 \times 0.08$ mm, monoclinic, space group $P2_1/n$ (No. 14), $a = 16.7459(2)$, $b = 22.6803(3)$, $c = 20.3365(3)$ Å, $\beta = 99.9980(10)°$, $V = 7606.55(18)$ Å^3, $Z = 4$, $\rho_{\text{cald}} = 2.424$ g cm^{-3}, $F_{000} = 5136$, Nonius KappaCCD, $\text{Mo}_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{\max} = 52.0°$, 105275 reflections collected, 14951 unique ($R_{\text{int}} = 0.0802$). Final GoF = 1.043, $R1 = 0.0298$, $wR2 = 0.0553$, R indices based on 11615 reflections with $I > 2\sigma(I)$ (refinement on F^2), 973 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 13.211$ mm^{-1}. Both structures were solved by direct methods. In **1** one of the phenyl rings (C59–C64) was disordered over two sites with occupancies of 0.59 and 0.41. The disordered phenyl C atoms were fitted to a regular hexagon. The carbon atoms of each disordered ring were constrained to have equal anisotropic displacement parameters. Both in **1** and in **4** the hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms. CCDC-674106 (**1**) and CCDC-674107 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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