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LUMINESCENT METAL CLUSTERS. SPECTROSCOPIC PROPERTIES AND X-RAY STRUCTURE OF A TRINUCLEAR GOLD(I) COMPLEX CONTAINING BIS(DIPHENYLPHOSPHINO)METHANE AND PHENYLACETYLIDE

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Abstract—The reaction of $[Au(C\equiv CPh)]_\infty$ with dppm [bis(diphenylphosphino)methane] in ethanol gave $[Au_3(\mu_2\text{-dppm})_2(C\equiv CPh)_2][Au(C\equiv CPh)_2]$. The complex has been characterized by X-ray crystal analysis. The structure consists of a trinuclear $[Au_3(\mu_2\text{-dppm})_2(C\equiv CPh)_2]^+$ cation with the three gold atoms arranged in an isosceles triangle. The intramolecular Au $\cdots$ Au separations are 3.083(2) and 3.167(2) Å. At room temperature, the $[Au_3(\mu_2\text{-dppm})_2(C\equiv CPh)_2][Au(C\equiv CPh)_2]$ complex is photoluminescent in the solid state and in solution.

Polynuclear d^{10} complexes have been shown to possess intriguing photophysical and photochemical properties.[1] Of particular interest to us are the polynuclear gold(I) complexes, for many of them are found to exhibit intense and long-lived solution emission at room temperature.[1c–g] In our laboratory, we have synthesized several luminescent polynuclear gold(I) complexes by using polydentate phosphines and isocyanides.[1c–g] Recent interest in organogold complexes in areas such as material science[2] and organic synthesis[3] prompted us to investigate the excited state properties of gold(I)–acetylide complexes such as $[Au_2(\mu_2\text{-dppe})(C\equiv CPh)_2]$ [dppe = bis(diphenylphosphino)ethane].[4] We anticipate that it is feasible to assemble organogold units by employing polydentate phosphine ligands. Herein is described the X-ray crystal structure and spectroscopic properties of a trinuclear Au^I complex, $[Au_3(\mu_2\text{-dppm})_2(C\equiv CPh)_2][Au(C\equiv CPh)_2]$ [dppm = bis(diphenylphosphino)methane].

EXPERIMENTAL

Synthesis

A solution of $[Au(C\equiv CPh)]_\infty$ (0.1 g) and excess dppm (0.1 g) in ethanol ($\sim$30 cm^3) was heated at $\sim$ 60°C until the solution became clear. The solution was filtered and a yellow solid appeared after reducing the solvent volume. The product was crystallized by diffusing diethyl ether into a dichloromethane solution.

Instrumentation

UV–vis absorption spectra were recorded with a Milton Roy 3000 array spectrophotometer. Emission spectra were measured with a Spex Fluorolog-2 Model F III A1 fluorescence spectrophotometer. Emission lifetimes were measured with a laser flash photolysis set-up equipped with a Quanta-Ray DCR-3 Nd:YAG pulsed laser and a Tektronix 2430 digital transient recorder.

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X-ray structure determination of [Au₃(μ_2-dppm)₂ (C≡CPh)₂][Au(C≡CPh)₂]

Crystals suitable for diffraction analysis were obtained by diffusing diethyl ether into a dichloromethane solution. A crystal was mounted on a glass fibre. Diffraction measurements were carried out on an Enraf–Nonius CAD4 fully automated four-circle diffractometer. The unit cell was determined and refined using setting angles of 24 randomly selected reflections, with angles in the range of 17.24–24.7°, obtained by using the CAD4 automatic search, centre, index and least-square routines. All data reduction and structure refinements were performed with the NRCC-SDP-VAX packages. The structure was solved by the Patterson method and refined by least-squares; all non-hydrogen atoms of the cation and gold atom of the anion were refined with anisotropic thermal parameters. There are serious disorders of the bisacetylide gold(I) anion; the gold atom is about 0.9 Å off the C_2-axis. Attempts to refine the structure with the space group C_c were unsuccessful due to the high correlation between the atoms of the cations. The crystal data and data collection parameters are summarized in Table 1. Selected bond distances and angles are given in Table 2. Positional parameters and thermal parameters are given as supplementary material.

RESULTS AND DISCUSSION

Figure 1 shows a perspective view of the [Au₃(μ_2-dppm)₂(C≡CPh)₂]⁺ cation, which possesses the crystallographic C_2 symmetry. The structure is composed of an isosceles triangle of gold atoms with Au—Au separations of 3.083(2) and 3.167(2) Å. These Au—Au distances are similar to those found in other phosphine-bridged gold(I) complexes such as [Au₂(μ_2-dppm)₂](BF₄)₂[1d] and [Au₃(μ_3-tpm)₂(Cl)]²⁺ [tpm = tris(diphenylphosphino)methane][1e]. The Au(2) atom is coordinated with two phosphorus atoms each from the two bridging dppm ligands in a distorted linear fashion, with a P(2)—Au(2)—P(2a) angle of 166.4(3)°. On the other hand, both Au(1a) and Au(1) are coordinated to one phosphorus atom from dppm and phenylacetylide in such a way that the two phenylacetylides are opposing each other. The coordination geometries of Au(1) and Au(1a) are almost linear, with a P(1)—Au(1)—C(1) angle of 174.5(9)°. The anion [Au(C≡CPh)₂]−, which is heavily disordered, is linear in geometry.

Figure 2 shows the UV–vis absorption spectrum of [Au₃(μ_2-dppm)₂(C≡CPh)₂][Au(C≡CPh)₂] measured in acetonitrile. The spectrum exhibits an intense absorption band at 276 nm (ε_{max} = 6.9 × 10⁴ M⁻¹ cm⁻¹). This absorption band is similar to the metal (Au) perturbed intraligand transition of

Table 1. Crystal data

Formula	[Au₃P₄C₆₆H₅₄]⁺[AuC₁₆H₁₀]⁻
Crystal system/space group	monoclinic/$C2/c$
M	1961.33
a (Å)	22.827(12)
b (Å)	13.170(3)
c (Å)	25.398(5)
β (°)	108.56(3)
V (Å³)	7239(4)
D_{calc} (g cm⁻³)	1.800
Z	4
$F(000)$	3728
Temperature (K)	298
Data collection parameters	
λ(Mo-K_α) (Å)	0.7107
Scan method	2θ–θ
Scan range	$2(0.80 + 0.35\tan(\theta))$
Scan speed (° min⁻¹)	2.35–8.24
Crystal size (mm)	0.30 × 0.40 × 0.50
Transmission factor: max, min	1.000, 0.608
Number of unique reflections	4720
Number of atoms and parameters refined	77,385
Δ/σ_{max}	1.3961
R, R_w	0.068, 0.051
G. O. F.	4.05

Table 2. Selected bond lengths (Å) and angles (°) of $[Au_3(\mu_2\text{-dppm})_2$
$(C\equiv CPh)_2][Au(C\equiv CPh)_2]$

Au(1)—Au(2)	3.167(2)	Au(1)—Au(1a)	3.083(2)
Au(1)—P(1)	2.293(6)	Au(1)—C(1)	2.01(3)
Au(2)—P(2)	2.328(6)		
Au(1a)—Au(1)—Au(2)	60.88(3)	Au(1)—Au(2)—Au(1a)	58.25(5)
P(1)—Au(1)—C(1)	174.5(9)	P(2)—Au(2)—P(2a)	166.4(3)
Au(2)—Au(1)—P(1)	81.0(2)	Au(2)—Au(1)—C(1)	104.4(9)
Au(1)—Au(2)—P(2)	92.1(2)	Au(1)—Au(2)—P(2a)	99.8(2)
Au(1)—C(1)—C2	174(3)	P(1)—C—P(2)	113.9(11)

$PhC\equiv C^-$ found in the absorption spectra of $[NBu_4][Au(C\equiv CPh)_2]$ and $[Au(C\equiv CPh)(PPh_3)]$,[5] and is assigned to it accordingly. Apart from the 276 nm band, there is an intense absorption shoulder $(\varepsilon = 10^4\text{--}10^3 \ M^{-1} \ cm^{-1})$ at 315–375 nm. This absorption feature is absent in the spectrum of $[NBu_4][Au(C\equiv CPh)_2]$ and hence should arise from the $[Au_3(\mu_2\text{-dppm})_2(C\equiv CPh)_2]^+$ cation. Because the complex $[Au(C\equiv CPh)(PPh_3)]$ does not show any significant absorption at $\lambda > 300$ nm (see also Fig. 2), the broad absorption shoulder in Fig. 2 should arise from weak Au$\cdots$Au interaction, as revealed in the crystal structure. For the analogous trinuclear complex $[Au_3(\mu_3\text{-tpm})_2(Cl)]^{2+1e}$, extended Huckel molecular orbital calculation has shown that the HOMO is the $d\delta^*$ orbital and the LUMO is the $p\sigma$ orbital, which arises from the interaction

of the $6p$ orbitals of the gold(I) ions. Similarly, the LUMO and HOMO of $[Au_3(\mu_2\text{-dppm})_2(C\equiv CPh)_2]^+$ are expected to be $p\sigma$ and $d\delta^*$, respectively, both of which, however, must acquire certain ligand character (phenylacetylide). The 315–375 nm shoulder is tentatively assigned to the $d\delta^* \rightarrow p\sigma$ transition.

Both solid state and solution of $[Au_3(\mu_2\text{-dppm})_2(C\equiv CPh)_2][Au(C\equiv CPh)_2]$ are emissive. Figure 3 shows the emission spectrum of a degassed acetonitrile of the complex. The room temperature emission spectrum is composed of two bands centred at 425 and ~600 nm. The 425 nm band is more intense than that at 600 nm, and the emission lifetimes are 0.45 and 8.7 μs, respectively. It is noted that both $[Au(PPh_3)(C\equiv CPh)]$ and $[NBu_4][Au(C\equiv CPh)_2]$ exhibit intense intraligand $(-C\equiv CPh)$

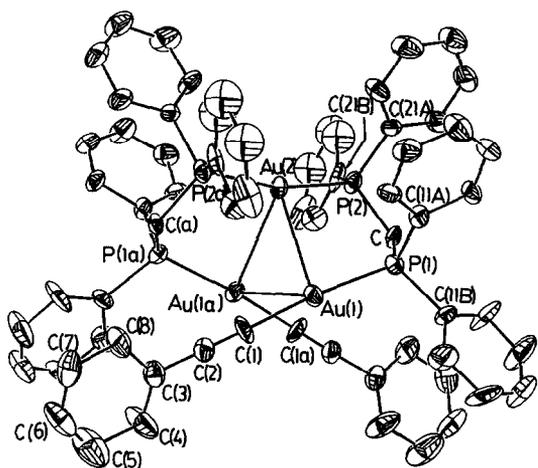Fig. 1. Perspective view of the $[Au_3(\mu_2\text{-dppm})_2(C\equiv CPh)_2]^+$ cation; only the bonded carbon atoms of the dppm phenyls are labelled; the C_2-related atoms of the coordination sphere are labelled by "a".
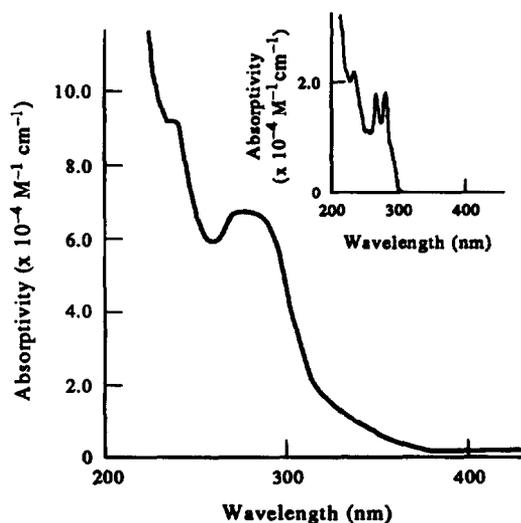

Fig. 2. Room temperature UV–vis absorption spectrum of $[Au_3(\mu_2\text{-dppm})_2(C\equiv CPh)_2][Au(C\equiv CPh)_2]$ in acetonitrile; inset: absorption spectrum of $[Au(PPh_3)(C\equiv CPh)]$ in acetonitrile.
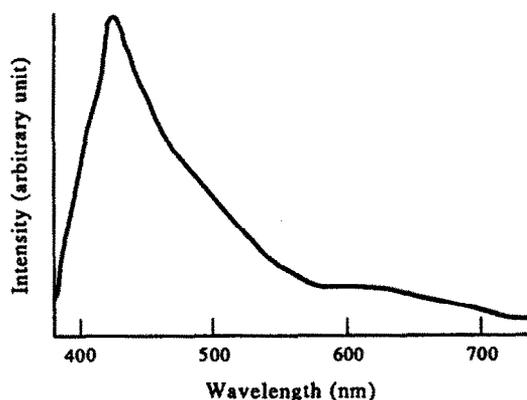
Fig. 3. Emission spectrum of a degassed acetonitrile solution of [Au₃(μ₂-dppm)₂(C≡CPh)₂][Au(C≡CPh)₂] at 298 K.

emission at about 430 nm at room temperature.[5] Thus, the 425 nm emission of [Au$_3$(μ_2-dppm)$_2$(C≡CPh)$_2$][Au(C≡CPh)$_2$] is logically assigned to come from the anion. The long-lived 600 nm emission is attributed to come from the trinuclear [Au$_3$(μ_2-dppm)$_2$(C≡CPh)$_2$]$^+$ cation and is tentatively assigned to $^3(d\delta^*p\sigma)$ emission. The redshift of this emission from the emission spectrum of [Au(PPh$_3$)(C≡CPh)] is therefore attributed to

the weak Au···Au interaction in [Au$_3$(μ_2-dppm)$_2$(C≡CPh)$_2$]$^+$.

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