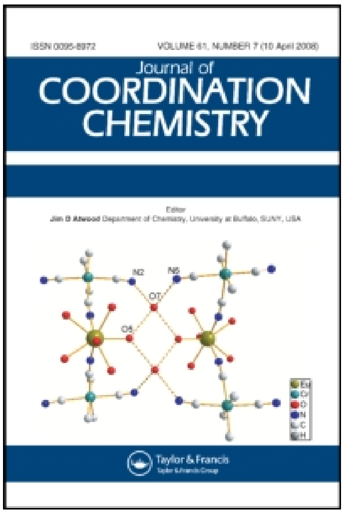

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Synthesis, characterization and luminescence of the tetranuclear gold cluster: $[Au_4\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2(PPh_3)_2]$

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A tetranuclear gold cluster has been synthesized by the reaction of $[Au(PPh_3)NO_3]$ with the *closo* carborane diphosphine $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ in THF, and characterized by elemental analysis, FT-IR, ^{1}H and ^{13}C NMR spectroscopy and X-ray structure determination. The cluster crystallizes in the triclinic $P\bar{1}$, $a = 15.118(8)$ Å, $b = 16.057(9)$ Å, $c = 24.284(13)$ Å, $\alpha = 80.822(9)^\circ$, $\beta = 79.624(8)^\circ$, $\gamma = 81.938(8)^\circ$, $Z = 2$, $R_1 = 0.0626$, $wR_2 = 0.1894$. A single crystal structure determination showed that four gold atoms form a tetrahedral framework. Among these four gold atoms, two were chelated by two *nido* carborane diphosphine $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ anions coming from the degradation of the initial *closo* ligand $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, while the other two were ligated to two PPh_3 groups. The luminescence of this cluster was also investigated in dichloromethane solution at room temperature.

Keywords: Synthesis and characterization; Au cluster; $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$; Luminescence

1. Introduction

The chemistry of homo- or heteropolynuclear gold clusters attracts interest with many examples of different nuclearities described [1–5]. All the gold atoms in these clusters, except for the central one, are ligated by monophosphine ligands. Reports on purely gold clusters containing diphosphine ligands were very poor [6–8]. As part of our studies on carborane chemistry, we were interested in the *closo* diphosphine derivatives $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ and *nido* $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$. These two moieties have been widely used in transition metal chemistry as chelating diphosphine ligands [9–12]. Here we report the synthesis and crystal structure of a tetranuclear gold cluster containing the *nido* carborane diphosphine ligand $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ and PPh_3.

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2. Experimental

2.1. *Materials and measurement*

The reaction was carried out under an atmosphere of dry, oxygen-free dinitrogen. Solvents were dried with appropriate drying agents and distilled under dinitrogen prior to use. [Au(PPh$_3$)NO$_3$] was synthesized as described in the literature [13]. *Bis*(diphenyl phosphino)-1,2-dicarba-*closo*-dodecaborane was prepared according to the literature procedure [14]. All chemicals were purchased and used as received.

Infrared spectra were obtained from KBr pellets on a Nicolet-460 FT-IR spectrophotometer. Elemental analysis (C, H) was performed with a Perkin-Elemer 2400 II elemental analyzer. The ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Mercury 400 spectrometer in CDCl$_3$ solution with tetramethylsilane (TMS) as internal standard at 400.15 and 100.63 MHz, respectively. The ^{13}C spectra were broadband proton decoupled. The chemical shifts are reported in parts per million with respect to the references and are stated relative to external TMS for ^{1}H and ^{13}C NMR.

2.2. *Synthesis procedure*

[Au(PPh$_3$)NO$_3$] (104.2 mg, 0.20 mmol) was added to a solution of 1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (51.2 mg, 0.10 mmol) in THF (10 mL). The mixture was heated to 50°C, and continuously stirred for 3 h at this temperature under dry N$_2$. After cooling to room temperature, the suspension was filtered. The filtrate was concentrated to 5 mL, and excess *n*-hexane was added to precipitate the solid (40.6 mg, 35.1%). M.p. 194–195°C. The crystal suitable for X-ray diffraction was grown from a tetrahydrofuran solution after partial evaporation of the solvent. FT-IR ν_{KBr} (cm^{-1}): 3054s, 2590s, 1630m, 1400m, 1095m, 725m. ^{1}H NMR (400.15 MHz, CDCl$_3$): −2.1 ppm (2H, B–H–B); ^{13}C NMR (100.63 MHz, CDCl$_3$): 77.1 ppm (4C). Anal. Calcd for C$_{88}$H$_{90}$Au$_4$B$_{18}$P$_6$: C, 45.64; H, 3.92; Found: C, 45.68; H, 3.87%.

2.3. *X-ray structure determination*

The collection of crystallographic data for the cluster was carried out on a Bruker Smart-1000 CCD diffractometer, using graphite-monochromatized Mo-Kα ($\lambda = 0.71073$ Å) at 298(2) K. The structure was solved by direct methods and expanded using Fourier difference techniques with the SHELXTL-97 program package [15]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. All the H atoms were located in a difference Fourier map and thereafter refined isotropically, except the bridge H atoms, which were refined isotropically with fixed U. Details of the crystal parameters, data collection and refinement are summarized in table 1.

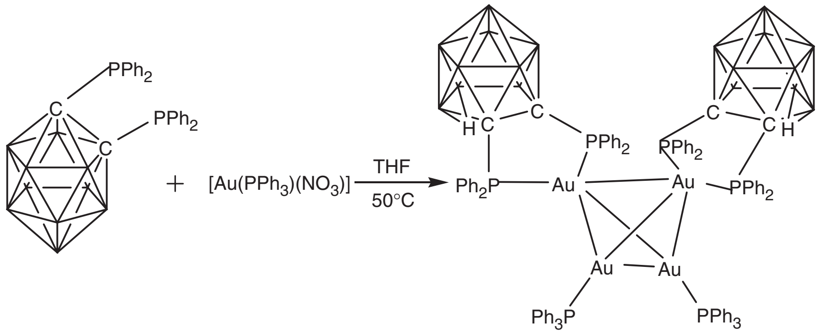
3. Result and discussion

3.1. *Synthesis and spectral characterization*

Large gold clusters, such as [Au$_9${P(C$_6$H$_4$OMe-*p*)$_3$}$_3$]$_8$](NO$_3$)$_3$ [16], [Au$_9${(PPh$_3$)$_3$}$_8$] (NO$_3$)$_3$ [17], could be synthesized by reaction of [AuL(NO$_3$)] ($L = $ PPh$_3$,

Table 1. Details of the crystal parameters, data collection and refinement for cluster.

Empirical formula	$C_{88}H_{90}Au_4B_{18}P_6$
Formula weight	2315.87
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	15.118(8)
b (Å)	16.057(9)
c (Å)	24.284(13)
α (°)	80.822(9)
β (°)	79.624(8)
γ (°)	81.938(8)
V (Å^3)	5686(5)
Z	2
Absorption coefficient (mm^{-1})	5.263
D (Mg m^{-3})	1.353
$F(000)$	2228
Crystal size (mm^3)	0.17 × 0.15 × 0.13
Theta range (°)	1.74–25.01
Limiting indices	$-17 \le h \le 17$, $-18 \le k \le 19$, $-20 \le l \le 28$
Independent reflection	19747
Max. and min. transmission	0.5478 and 0.4682
Goodness-of-fit on F^2	1.012
$R[I > 2\sigma(I)]$	$R_1 = 0.0626$, $wR_2 = 0.1894$
R(all data)	$R_1 = 0.1429$, $wR_2 = 0.2391$
Largest diff. peak and hole ($\times 10^2$ e Å^{-3})	2.123 and −1.203



Scheme 1. Synthesis of the cluster.

$P(C_6H_4OMe\text{-}p)_3)$ with $NaBH_4$, whose function was to reduce the Au(I) to form Au–Au bonds. One of the methods for preparation of heterometallic polynuclear gold clusters, in which the gold atoms are chelated by diphosphine ligands, was through ligand exchange [18]. In this article, we revised the synthesis method that was conventionally used to obtain gold clusters. The reaction was carried out directly between $[Au(PPh_3)NO_3]$ and the *closo* carborane diphosphine ligand $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ with a ratio 2 : 1 in THF at 50°C under stirring. The mixture was stirred for 3 h at 50°C, then filtered and concentrated to afford the title tetranuclear gold cluster $[Au_4\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2(PPh_3)_2]$ as a yellow solid (scheme 1).

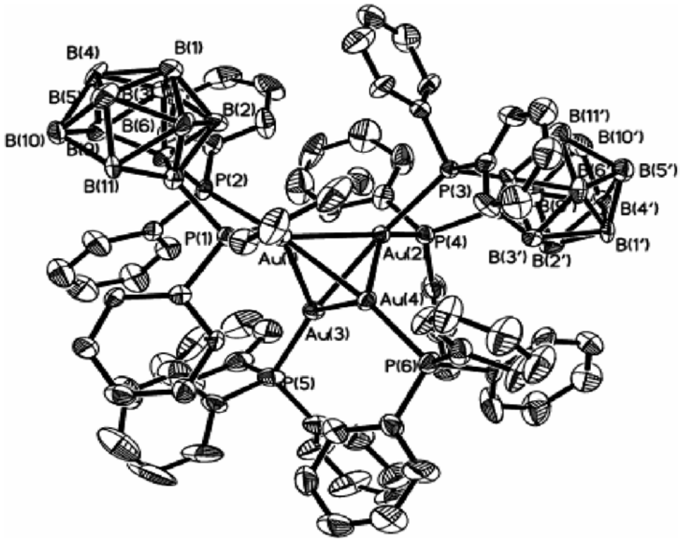


Figure 1. The crystal structure of the title cluster. The H atoms were omitted for clarity.

The IR spectra of the cluster exhibited absorptions characteristic of terminal B–H vibrations at 2590 cm^{-1}, within the normal range of B–H vibrations from 2625 to 2450 cm^{-1} [19]. The absorption at 3054 cm^{-1} may be attributed to the $\nu_{\mathrm{C-H}}$ stretching vibration of benzene rings. Several peaks are found from 1630 to 1410 cm^{-1}, which may be assigned to $\nu_{\mathrm{C=C}}$ stretching vibrations. The peak at ca 1400 cm^{-1} is the inplane deformation mode of the benzene ring, and the peak at ca 1095 cm^{-1} is the absorption of $\nu_{\mathrm{C(phenyl)-P}}$, which is slightly shifted in keeping with phosphorus coordination to the carborane moiety. The absorption at approximately 725 cm^{-1} shows deformation of the cage. The ^{1}H NMR (400.15 MHz) show a resonance at ca −2.1 ppm, which can be attributed to the bridging H atoms of B–H–B [20]. The resonance at ca 77.1 ppm in the ^{13}C NMR spectra (100.63 MHz) is assigned to the carbon atoms of the carborane cage [21].

3.2. *Crystal structure*

The structure of the cluster was determined by X-ray crystal analysis (shown in figure 1) Selected bond distances and angles are listed in table 2. The structure of this cluster is similar to that of the other two clusters, $[\mathrm{Au_4\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2(AsPh_3)_2}]$ and $[\mathrm{Au_4\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2(P(C_6H_4OMe\text{-}}p)_3)_2]$ [22, 23]. As shown in figure 1, a tetrahedral gold core can be found in the structure of the cluster. The Au–Au–Au angles are within the range 54.11(3) to 65.43(3)°, indicating that these four Au atoms form a slightly distorted tetrahedron. The Au–Au bond distances are in the range of 2.6211(16) to 2.9606(16) Å, which is comparable to the corresponding range 2.6036(7)–2.9148(8) Å and 2.6291(3)–2.8722(3) Å in the above two clusters. These bond lengths can be classified into three groups: short (Au(1)–Au(4) 2.6211(16), Au(2)–Au(3) 2.6498(15) and Au(1)–Au(2) 2.6694(13) Å), medium (Au(1)–Au(3) 2.8459(16) and Au(2)–Au(4) 2.8619(14) Å) and long (Au(3)–Au(4) 2.9606(16) Å). The reason for the longest Au–Au

Table 2. Selected bond lengths (Å) and angles (°).

Au(1)–P(1)	2.374(4)	P(1)–C(7)	1.859(17)
Au(1)–P(2)	2.387(4)	P(2)–C(8)	1.840(16)
Au(1)–Au(4)	2.6211(16)	C(7)–C(8)	1.59(2)
Au(1)–Au(2)	2.6694(13)	C(7′)–C(8′)	1.61(2)
Au(1)–Au(3)	2.8459(16)	P(1)–Au(1)–P(2)	87.29(14)
Au(2)–P(4)	2.368(5)	P(1)–Au(1)–Au(4)	94.95(10)
Au(2)–P(3)	2.406(4)	P(2)–Au(1)–Au(4)	172.71(11)
Au(2)–Au(3)	2.6498(15)	P(1)–Au(1)–Au(2)	152.10(10)
Au(2)–Au(4)	2.8619(14)	P(2)–Au(1)–Au(2)	114.69(10)
Au(3)–P(5)	2.299(5)	Au(4)–Au(1)–Au(2)	65.49(3)
Au(4)–P(6)	2.296(5)	P(5)–Au(3)–Au(2)	165.24(14)
Au(3)–Au(4)	2.9606(16)	P(5)–Au(3)–Au(1)	136.20(14)
P(1)–Au(1)–Au(3)	134.36(11)	Au(2)–Au(3)–Au(1)	57.99(3)
P(2)–Au(1)–Au(3)	108.18(11)	P(5)–Au(3)–Au(4)	128.00(14)
Au(4)–Au(1)–Au(3)	65.43(3)	Au(2)–Au(3)–Au(4)	61.05(3)
Au(2)–Au(1)–Au(3)	57.32(3)	Au(1)–Au(3)–Au(4)	53.62(4)
P(4)–Au(2)–P(3)	85.89(16)	P(6)–Au(4)–Au(1)	168.90(13)
P(4)–Au(2)–Au(3)	97.24(12)	P(6)–Au(4)–Au(2)	133.02(13)
P(3)–Au(2)–Au(3)	173.13(12)	Au(1)–Au(4)–Au(2)	58.07(3)
P(4)–Au(2)–Au(1)	150.26(12)	P(6)–Au(4)–Au(3)	123.78(13)
P(3)–Au(2)–Au(1)	114.88(11)	Au(1)–Au(4)–Au(3)	60.95(3)
Au(3)–Au(2)–Au(1)	64.69(4)	Au(2)–Au(4)–Au(3)	54.11(3)
P(4)–Au(2)–Au(4)	139.33(12)	C(8)–C(7)–P(1)	117.8(11)
P(3)–Au(2)–Au(4)	108.90(12)	C(7)–C(8)–P(2)	116.7(11)
Au(3)–Au(2)–Au(4)	64.84(4)	C(8′)–C(7′)–P(3)	118.0(10)
Au(1)–Au(2)–Au(4)	56.44(4)	C(7′)–C(8′)–P(4)	115.8(11)

bond may be attributed to the larger PPh_3 groups, which can lengthen the Au···Au interaction. Among the four gold atoms, two are coordinated to two chelating diphosphine ligands $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ coming from the degradation of the initial *closo* ligand $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, and the other two are bonded to two PPh_3 groups. The distances of Au atoms to P of the PPh_3 groups are slightly shorter than those to the diphosphine ligands with the mean value 2.298 cf 2.383 Å. This phenomenon can be also found in another gold complex $[Au(PPh_3)\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}]\cdot CH_2Cl_2$ [24]. The distances of P–Cc (carbon atom of the carborane skeleton) and Cc–Cc are all comparable to those in the same complex. But an obvious difference must be noticed for the Cc–Cc bond length in the title cluster and in the *closo* ligand $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$. In the former its average value is 1.60 Å, while in the latter it is 1.694(4) Å [25]. The two angles of P(1)–Au(1)–P(2) and P(3)–Au(2)–P(4) are 87.29(14) and 85.89(16)°, respectively. In general, this P–M–P bite angle in the transition metal complexes containing this type of coordination mode is usually about 90° [26].

4. Luminescence study

Luminescence studies of gold compounds, especially polynuclear clusters, received continuous attention during the past years for potential applications in synthesis, energy conversion and pharmacology [27]. The three-coordinate gold complexes of *nido*-diphosphine $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ show luminescence, with the emissions

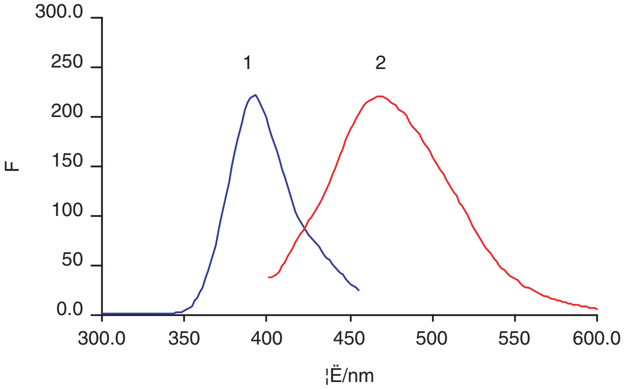


Figure 2. Emission and excitation spectra in CH_2Cl_2 solution at room temperature: emission spectrum ($\lambda_{max} = 468$ nm); excitation spectrum ($\lambda_{max} = 392$ nm).

assigned to a metal-perturbed intraligand transition (IL) and a mainly metal-to-ligand charge transfer (MLCT) transition [28]. The luminescence study of the title cluster was also carried out using LS-55 luminescence spectrometer in dichloromethane solution at room temperature. The emission and excitation spectra are shown in figure 2. Unlike the mononuclear three-coordinate gold complexes above mentioned, this cluster is a mixed valence cluster. Two of the gold atoms, which are bonded to the monophosphine ligand, are formally assigned oxidation state +1, and the other two zero [23]. Two Au (+1) centers are responsible for the observed light emission, although the environment around the centers cannot be neglected. This conclusion is supported by other d^{10} gold(I) centers responsible for luminescence [23, 29]. This type of phosphorescent emission originating from a metal centered (MC) state is common in other polynuclear Au(I) phosphine derivatives [30].

Supplementary material

Crystallographic data for the structural analysis (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC no. 603293. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44) 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

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