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tris(pentafluorophenyl)aurate(III)]**

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# Bis[bis(diphenylphosphinomethyl)-phenylphosphine]dichlorotetragold(I) bis[chlorotris(pentafluorophenyl)aurate(III)]

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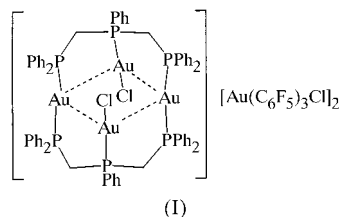
Data validation number: IUC0000260

The cation of the title compound,  $[\text{Au}_4(\text{PPh}_2\text{CH}_2\text{PPhCH}_2\text{-PPh}_2)_2\text{Cl}_2][\text{Au}(\text{C}_6\text{F}_5)_3\text{Cl}]_2$  or  $[\text{Au}_4\text{Cl}_2(\text{C}_{32}\text{H}_{29}\text{P}_3)_2][\text{AuCl}(\text{C}_6\text{F}_5)_3]_2$ , displays a rhomboidal geometry for the Au atoms, with short Au···Au distances of 3.104 (2) and 3.185 (1) Å; the linear coordination at the Au<sup>I</sup> atoms is distorted: P—Au—P 164.7 (2)° and P—Au—Cl 170.67 (11)°. The anion shows the expected square-planar geometry at Au<sup>III</sup>, with the Au atom 0.022 (5) Å out of the plane of the four donor atoms.

## Comment

Recently, we reported the synthesis of a series of trinuclear and tetranuclear gold(I) complexes with the triphosphine ligand dpmp [dpmp is bis(diphenylphosphinomethyl)phenylphosphine]. The molecular structure of the tetranuclear cationic complex  $[\text{Au}_4(\mu\text{-dpmp})_2\text{Cl}_2](\text{CF}_3\text{SO}_3)_2$  was described (Bardají *et al.*, 1998).

We report here the X-ray determination of the mixed gold(I)–gold(III) derivative  $[\text{Au}_4(\mu\text{-dpmp})_2\text{Cl}_2][\text{Au}(\text{C}_6\text{F}_5)_3\text{Cl}]_2$ , (I), which has the same cation; the structure of the chlorotris(pentafluorophenyl)aurate(III) anion was described previously (Usón *et al.*, 1983).



In the cation of the title compound, which displays crystallographic inversion symmetry, the four Au atoms exhibit a rhomboidal geometry with short metal–metal distances [Au—Au 68.96 (4) and 111.04 (4)°; Au···Au 3.104 (2) and

3.185 (1) Å]. The largest Au···Au distance, 3.185 (1) Å, is larger than those observed in the related derivative  $[\text{Au}_4(\mu\text{-dpmp})_2\text{Cl}_2](\text{CF}_3\text{SO}_3)_2$  [3.102 (1) and 3.106 (1) Å; Bardají *et al.*, 1998]. The diagonal Au···Au distances are 3.561 (2) Å (Au2···Au2<sup>i</sup>) and 5.184 (3) Å [Au1···Au1<sup>i</sup>; symmetry code: (i)  $-x, 1 - y, -z$ ]. This rhomboidal geometry has been observed for other loose Au<sub>4</sub><sup>I</sup> clusters (Chiari *et al.*, 1985; Beck & Strähle, 1986; Cerrada *et al.*, 1994), but it contrasts with that seen in related polynuclear gold(I) derivatives, such as  $[\text{Au}_4(\mu\text{-dpmp})_2(\text{SCN})_2](\text{SCN})\text{Cl}$  (Li *et al.*, 1993), where the Au atoms are in a nearly linear chain, or  $[\text{Au}_4(\mu\text{-dpma})_2\text{Cl}_2]\text{X}_2$  [X = PF<sub>6</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>; dpma is bis(diphenylphosphinomethyl)phenylarsine; Balch *et al.*, 1990], where the Au atoms are in a bent chain.

Ignoring the Au···Au contacts, the Au atoms exhibit a distorted linear coordination; the P—Au—P and P—Au—Cl angles [164.40 (9)° and 170.67 (11)°, respectively] are similar to those observed in the related derivative  $[\text{Au}_4(\mu\text{-dpmp})_2\text{Cl}_2](\text{CF}_3\text{SO}_3)_2$  [164.7 (2) and 169.1 (2)°; Bardají *et al.*, 1998].

The shortest Au···Au distances, 3.104 (2) Å, are of the same order as the values found in other polynuclear gold(I) complexes containing dpmp or related phosphine ligands, such as  $[\text{Au}_3(\mu\text{-dpmp})_2\text{Cl}_2]\text{Cl}$  [2.946 (3) and 2.963 (3) Å; Xiao *et al.*, 1997],  $[\text{Au}_3(\mu\text{-dpmp})_2](\text{SCN})_3$  [3.0137 (8) and 3.0049 (8) Å; Li *et al.*, 1993] or  $[\text{Au}_4(\mu\text{-dpma})_2\text{Cl}_2]\text{X}_2$  [X = PF<sub>6</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>; 2.965 (1)–3.110 (2) Å; Balch *et al.*, 1990]. The Au—Cl [2.285 (3) Å] and Au—P [2.237 (3) and 2.307 (3) Å (× 2)] bond lengths are somewhat shorter than in the related complex  $[\text{Au}_4(\mu\text{-dpmp})_2\text{Cl}_2](\text{CF}_3\text{SO}_3)_2$  [Au—Cl 2.306 (4) Å; Au—P 2.264 (4) 2.323 (4) and 2.326 (4) Å; Bardají *et al.*, 1998]; Au2—P2 of 2.237 (3) Å is shorter than the others, probably as a consequence of the minor *trans* influence of Cl.

As expected for Au<sup>III</sup>, the metal atom in the anion displays a square-planar coordination; it lies only 0.022 (5) Å out of the plane of the four donor atoms (mean deviation 0.03 Å). Au—C bond lengths [2.013 (11), 2.064 (11) and 2.071 (10) Å] are similar to the values of 2.028 (2), 2.06 (2) and 2.07 (3) Å for the pentafluorophenyl groups of the  $[\text{Au}(\text{C}_6\text{F}_5)_3\text{Cl}]^-$  of the complex  $[\text{Au}_3(\mu\text{-dppm})_2\text{Cl}_2][\text{Au}(\text{C}_6\text{F}_5)_3\text{Cl}]$ , previously reported (Usón *et al.*, 1983).

## Experimental

Crystals of the title compound were obtained by slow diffusion of ethanol/pentane into a dichloromethane solution of the trinuclear gold(I)–gold(III) complex  $(\text{C}_6\text{F}_5)_3\text{AuPPh}_2\text{CH}_2\text{PPh}(\text{AuCl})\text{CH}_2\text{PPh}_2\text{Au}(\text{C}_6\text{F}_5)_3$  (Bardají *et al.*, 1998).

### Crystal data

$[\text{Au}_4(\text{C}_{32}\text{H}_{29}\text{P}_3)_2\text{Cl}_2][\text{AuCl}(\text{C}_6\text{F}_5)_3]_2$	Z = 1
$M_r = 3338.88$	$D_x = 2.207 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 12.193 (6) \text{ \AA}$	Cell parameters from 52 reflections
$b = 14.439 (8) \text{ \AA}$	$\theta = 9\text{--}11.5^\circ$
$c = 16.531 (9) \text{ \AA}$	$\mu = 9.033 \text{ mm}^{-1}$
$\alpha = 65.93 (2)^\circ$	$T = 173 (2) \text{ K}$
$\beta = 86.36 (3)^\circ$	Prism, colourless
$\gamma = 71.46 (3)^\circ$	$0.34 \times 0.30 \times 0.23 \text{ mm}$
$V = 2512 (2) \text{ \AA}^3$	

Data collection

Siemens—Stoe AED-2 diffractometer  
 $\omega/\theta$  scans  
 Absorption correction:  $\psi$  scan (XEMP; Siemens, 1990)  
 $T_{\min} = 0.039$ ,  $T_{\max} = 0.125$   
 12 573 measured reflections  
 8863 independent reflections  
 6194 reflections with  $I > 2\sigma(I)$

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.104$   
 $S = 0.977$   
 8863 reflections  
 658 parameters

$R_{\text{int}} = 0.060$   
 $\theta_{\text{max}} = 25.02^\circ$   
 $h = -14 \rightarrow 4$   
 $k = -17 \rightarrow 17$   
 $l = -19 \rightarrow 19$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 4.5%

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0493P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 2.44 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.92 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Au1—P3	2.307 (3)	Au2—Au1 <sup>i</sup>	3.1037 (15)
Au1—P1	2.307 (3)	Au3—C81	2.014 (11)
Au1—Au2 <sup>i</sup>	3.1037 (15)	Au3—C91	2.065 (10)
Au1—Au2	3.1850 (14)	Au3—C71	2.071 (10)
Au2—P2	2.237 (3)	Au3—Cl1	2.330 (3)
Au2—Cl2	2.285 (3)		
P3—Au1—P1	164.40 (9)	P2—Au2—Au1	92.77 (8)
P3—Au1—Au2 <sup>i</sup>	80.43 (8)	Cl2—Au2—Au1	94.03 (9)
P1—Au1—Au2 <sup>i</sup>	114.89 (7)	Au1 <sup>i</sup> —Au2—Au1	111.04 (4)
P3—Au1—Au2	112.15 (8)	C81—Au3—C91	89.1 (4)
P1—Au1—Au2	77.84 (8)	C81—Au3—C71	89.6 (4)
Au2 <sup>i</sup> —Au1—Au2	68.96 (4)	C91—Au3—C71	178.3 (4)
P2—Au2—Cl2	170.67 (11)	C81—Au3—Cl1	178.6 (3)
P2—Au2—Au1 <sup>i</sup>	93.89 (8)	C91—Au3—Cl1	90.6 (3)
Cl2—Au2—Au1 <sup>i</sup>	89.63 (9)	C71—Au3—Cl1	90.8 (3)

Symmetry code: (i)  $-x, 1 - y, -z$ .

The significant residual electron density is in the heavy-atom region; the distance of the maximum peak to the nearest atom (Au2) is 1.04  $\text{\AA}$ . H atoms were refined using a riding model (C—H = 0.95 and 0.99  $\text{\AA}$ ). A total of 40 restraints were applied, involving local phenyl-ring symmetry (FLAT/SAME).

Table 2

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C32—H32 $\cdots$ F11 <sup>i</sup>	0.95	2.51	3.412 (14)	159
C52—H52 $\cdots$ F14	0.95	2.50	3.417 (17)	163

Symmetry code: (i)  $-x, 2 - y, -z$ .

Data collection: DIF4 (Stoe & Cie, 1988); cell refinement: DIF4; data reduction: REDU4 (Stoe & Cie, 1988); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); software used to prepare material for publication: SHELXL97.

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