# The PF6−/BF4− Mixed Salt of the Cluster Cation [Pt3(μ3-AuPPh3)(μ-dppm)3]+, dppm = Ph2PCH2PPh2

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## Abstract

Remarkably, the crystal structure of the title Pt3Au cluster compound, tris[bis(diphenylphosphino)methane]-2:3$\kappa^2$P:P';2:4$\kappa^2$P:P';3:4$\kappa^2$P:P'-(triphenylphosphine)-1$\kappa$P-tetrahedro-1-gold-2,3,4-triplatinum(3 *Au—Pt*, 3 *Pt—Pt*) 0.75-hexafluorophosphate 0.25-tetrafluoroborate, [AuPt3(C25H22P2)3(C18H15P)](BF4)0.25(PF6)0.75, is based on an *F*-centred cubic unit cell which contains 32 [Pt3(μ3-AuPPh3)(μ-dppm)3]+ cations, together with 24 PF6− and eight BF4− anions. Each cation straddles a crystallographic threefold axis and contains a triangular Pt3 unit whose edges are bridged by the three dppm ligands. The Pt3 triangle is capped by an AuPPh3+ fragment to form a tetrahedral Pt3Au cluster with a slight trigonal elongation. The Pt—Pt and Pt—Au bond lengths are 2.618 (2) and 2.707 (2) Å, respectively.

## Comment

Transition metal cluster complexes containing the $M_3$(μ-dppm)3 fragment have proved helpful in modelling chemisorption of small molecules and ions on metal surfaces (Puddephatt, Manojlović-Muir & Muir, 1990). Attachment of a second metal to the Pt3 core extends this idea to the modelling of heterogeneous bimetallic catalysts (Xiao, Puddephatt, Manojlović-Muir, Muir & Torabi, 1994).

We now report the structure of the title compound, (1), which was prepared by the reaction of [Pt3(μ3-CO)(μ-dppm)3][PF6]2 with [AuCl(PPh3)] and Na[BH4] in methanol (Payne, Ramachandran, Schoettel, Vittal & Puddephatt, 1991, hereinafter PR91).

(1)
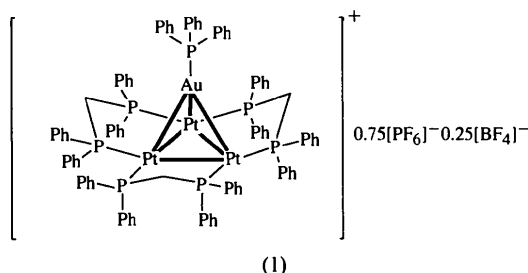
The structure of the complex cation in (1) (shown in Fig. 1) agrees with that proposed in PR91 on the basis of chemical and spectroscopic evidence. The cation possesses exact $C_3$ symmetry. It contains a triangle of Pt atoms capped by an AuPPh3+ unit to form a Pt3Au tetrahedron in which the Pt—Au distances are 0.089 (3) Å larger than the Pt—Pt distances. Each edge of the Pt3 triangle is bridged by a dppm ligand and, as is typical for Pt3(μ-dppm)3 complexes, the Pt2P2C rings adopt distorted envelope conformations with methylene C atoms (C1, C1A, C1B) at the flaps; the relevant ring torsion angles are given in Table 2. All three methylene C atoms lie on the same side of the Pt3 triangle as the Au atom; the conformation adopted by the Pt3P6C3 skeleton in (1) thus helps to minimize steric interactions between the dppm phenyl rings and the AuPPh3 unit (see Puddephatt, Manojlović-Muir & Muir, 1990).
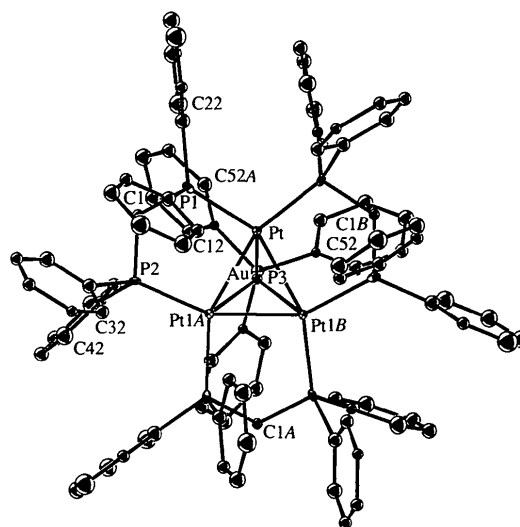
Fig. 1. The structure of the [Pt3(μ3-AuPPh3)(μ-dppm)3]+ cation viewed along a direction almost coincident with the threefold axis passing through the Au and P3 atoms. The operations of the threefold axis [symmetry codes (i) and (ii) in Table 2] are indicated by labels ending with *A* or *B*. The C atoms of the five independent phenyl rings are numbered in sequence, C$n$1–C$n$6 ($n$ = 1, 5), starting from the *ipso* C atom and only the labels of C atoms C$n$2 ($n$ = 1, 5) are shown. Non-H atoms are shown with 30% probability ellipsoids and H atoms are omitted.

The Pt—Pt and Pt—Au bond lengths in (1) [2.618 (2) and 2.707 (2) Å] are slightly shorter than the corresponding mean distances of 2.639 and 2.742 Å in [Pt3(μ3-AuPPh3)2(μ-dppm)3]2+, (2) (PR91). The greater length of the metal–metal bonds in (2), compared with those in (1), is consistent with a bonding scheme (PR91) which assumes that the HOMO of a Pt3(μ-dppm)3 fragment, a Pt3-based orbital of $a_1'$ symmetry, can donate an electron pair to the vacant $a_1'$ sp-hybrid orbital of a single AuPPh3+ unit to give (1), or to an $a_1'$ combination from two such units to give (2). We also note that in [Pt3(μ3-CO)(μ-dppm)3]2+, which can be formally derived from

(1) by replacement of AuPPh$_3^+$ with the more strongly electrophilic CO$^{2+}$, the mean Pt—Pt distance of 2.634 Å (Ferguson, Lloyd & Puddephatt, 1986) is longer than in (1). In (2), where in contrast to (1) no threefold symmetry is imposed on the cluster cation, the individual Pt—Pt bond lengths vary slightly [2.635 (1)–2.642 (1) Å] but the Pt—Au distances are markedly irregular [2.678 (1)–2.843 (1) Å], thus providing a good illustration of the known sensitivity of metal–metal bond lengths to crystal packing forces. Other bond lengths and angles in the dppm ligands and in the counteranions (Table 2) agree with accepted values (Orpen *et al.*, 1992).

The crystal structure of (1) is unusual for a large cluster complex. The cubic *F* cell contains 32 cations straddling triad axes (Wyckoff site *e*) which pass through the Au and P3 atoms. 16 ordered PF$_6^-$ anions with near-octahedral and exact $\bar{3}$ symmetry (site *c*) are defined by the atoms P11 and F1; the eight *a* sites of 23 (*T*) symmetry are occupied by the B3 atoms of ordered BF$_4^-$ anions, presumably derived from the reaction of PF$_6^-$ and BH$_4^-$ present during synthesis. Finally, a further eight PF$_6^-$ anions have their P atoms (P21) on *b* sites of 23 symmetry and their F atoms (F21, F22 and F23) are disordered.

## Experimental

The title compound was prepared as described in PR91 (see *Comment*).

### Crystal data

[AuPt₃(C₂₅H₂₂P₂)₃-
(C₁₈H₁₅P)](BF₄)₀.₂₅-
(PF₆)₀.₇₅
$M_r = 2328.03$
Cubic
$Fd\bar{3}$ (origin at $\bar{3}$)
$a = 40.302\,(4)$ Å
$V = 65461\,(11)$ Å³
$Z = 32$
$D_x = 1.890$ Mg m$^{-3}$

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 14.1–16.9°$
$\mu = 7.112$ mm$^{-1}$
$T = 130\,(2)$ K
Block
$0.20 \times 0.18 \times 0.15$ mm
Red

### Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from $\Delta F$ (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.22$, $T_{max} = 0.38$
3723 measured reflections
3361 independent reflections

1692 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.036$
$\theta_{max} = 22°$
$h = 0 \rightarrow 27$
$k = 0 \rightarrow 29$
$l = 2 \rightarrow 42$
3 standard reflections frequency: 120 min intensity decay: none

### Refinement

Refinement on $F^2$
$R(F) = 0.0499$
$wR(F^2) = 0.1256$
$S = 1.086$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.11$ e Å$^{-3}$ (near P2)
$\Delta\rho_{min} = -1.02$ e Å$^{-3}$

1692 reflections
115 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0809P)^2 + 1055P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\mathring{A}^2$)*

$U_{iso}$ for C and F; $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for Au, Pt and P.

| | *x* | *y* | *z* | $U_{iso}/U_{eq}$ |
|---|---|---|---|---|
| Au | 0.22906 (2) | *x* | *x* | 0.0142 (5) |
| Pt | 0.25963 (2) | 0.23556 (2) | 0.28853 (2) | 0.0115 (3) |
| P1 | 0.3024 (2) | 0.2001 (2) | 0.2975 (2) | 0.0143 (15) |
| P2 | 0.3273 (2) | 0.2199 (2) | 0.2301 (2) | 0.015 (2) |
| P3 | 0.1969 (2) | *x* | *x* | 0.020 (3) |
| C1 | 0.3178 (6) | 0.1849 (6) | 0.2562 (5) | 0.014 (6) |
| C11 | 0.3383 (3) | 0.2217 (4) | 0.3153 (4) | 0.025 (7) |
| C12 | 0.3348 (3) | 0.2556 (4) | 0.3206 (4) | 0.021 (7) |
| C13 | 0.3617 (4) | 0.2742 (3) | 0.3318 (4) | 0.039 (8) |
| C14 | 0.3920 (4) | 0.2588 (4) | 0.3377 (4) | 0.046 (9) |
| C15 | 0.3955 (3) | 0.2249 (4) | 0.3323 (4) | 0.033 (8) |
| C16 | 0.3686 (4) | 0.2064 (3) | 0.3211 (4) | 0.020 (6) |
| C21 | 0.2977 (5) | 0.1617 (3) | 0.3212 (4) | 0.028 (7) |
| C22 | 0.2807 (4) | 0.1354 (4) | 0.3067 (3) | 0.043 (9) |
| C23 | 0.2773 (4) | 0.1057 (4) | 0.3238 (4) | 0.039 (8) |
| C24 | 0.2908 (5) | 0.1022 (3) | 0.3554 (4) | 0.036 (8) |
| C25 | 0.3077 (4) | 0.1285 (4) | 0.3698 (3) | 0.053 (9) |
| C26 | 0.3112 (4) | 0.1583 (4) | 0.3527 (4) | 0.018 (6) |
| C31 | 0.3717 (3) | 0.2258 (4) | 0.2375 (4) | 0.024 (6) |
| C32 | 0.3823 (3) | 0.2571 (3) | 0.2474 (4) | 0.023 (7) |
| C33 | 0.4148 (3) | 0.2619 (3) | 0.2577 (4) | 0.014 (6) |
| C34 | 0.4369 (3) | 0.2353 (4) | 0.2581 (4) | 0.019 (6) |
| C35 | 0.4263 (3) | 0.2040 (3) | 0.2482 (4) | 0.020 (6) |
| C36 | 0.3938 (4) | 0.1993 (3) | 0.2378 (4) | 0.029 (7) |
| C41 | 0.3270 (4) | 0.2009 (4) | 0.1888 (3) | 0.013 (6) |
| C42 | 0.3517 (3) | 0.2090 (4) | 0.1662 (4) | 0.041 (8) |
| C43 | 0.3500 (4) | 0.1970 (4) | 0.1339 (4) | 0.027 (7) |
| C44 | 0.3237 (4) | 0.1769 (4) | 0.1243 (3) | 0.028 (7) |
| C45 | 0.2991 (4) | 0.1688 (4) | 0.1469 (4) | 0.034 (8) |
| C46 | 0.3007 (4) | 0.1808 (4) | 0.1792 (4) | 0.024 (6) |
| C51 | 0.1540 (3) | 0.1973 (4) | 0.2105 (4) | 0.010 (6) |
| C52 | 0.1418 (4) | 0.2259 (3) | 0.2252 (4) | 0.027 (7) |
| C53 | 0.1099 (4) | 0.2263 (3) | 0.2384 (4) | 0.022 (6) |
| C54 | 0.0902 (3) | 0.1980 (4) | 0.2367 (4) | 0.033 (7) |
| C55 | 0.1025 (3) | 0.1694 (3) | 0.2220 (4) | 0.030 (7) |
| C56 | 0.1344 (4) | 0.1690 (3) | 0.2088 (4) | 0.022 (7) |
| P21 | 3/8 | 3/8 | 3/8 | 0.038 (7) |
| F21† | 0.3971 (10) | *x* | *x* | 0.030 (18) |
| F22† | 0.3515 (12) | *x* | *x* | 0.05 (2) |
| F23† | 0.3739 (16) | 0.3515 (16) | 0.3434 (16) | 0.039 (17) |
| P11 | 0 | 1/4 | 1/4 | 0.052 (6) |
| F1 | 0.0102 (4) | 0.2123 (4) | 0.2590 (4) | 0.054 (5) |
| F3 | 0.1054 (6) | *x* | *x* | 0.128 (18) |
| B3 | 1/8 | 1/8 | 1/8 | 0.03 (3) |

† Partial occupancy (see below).

Table 2. *Selected geometric parameters ($\mathring{A}$, °)*

| | | | |
|---|---|---|---|
| Au—P3 | 2.244 (12) | P2—C31 | 1.830 (12) |
| Au—Pt | 2.707 (2) | P2—C41 | 1.831 (13) |
| Pt—Pt$^i$ | 2.618 (2) | P3—C51 | 1.813 (12) |
| Pt—P2$^{ii}$ | 2.250 (6) | P21—F21 | 1.54 (7) |
| Pt—P1 | 2.266 (7) | P21—F22 | 1.64 (8) |
| P1—C21 | 1.828 (14) | P21—F23 | 1.59 (7) |
| P1—C11 | 1.836 (13) | P11—F1 | 1.61 (2) |
| P1—C1 | 1.88 (2) | B3—F3 | 1.37 (5) |
| P2—C1 | 1.80 (2) | | |
| P3—Au—Pt | 146.06 (3) | C1—P2—C41 | 101.7 (9) |
| Pt$^i$—Au—Pt | 57.83 (5) | C31—P2—C41 | 102.1 (8) |
| P2$^{ii}$—Pt—P1 | 111.7 (2) | C1—P2—Pt$^i$ | 110.8 (8) |
| P2$^{ii}$—Pt—Pt$^i$ | 156.9 (2) | C31—P2—Pt$^i$ | 124.8 (6) |

| | | | |
|---|---|---|---|
| P1—Pt—Pt$^i$ | 91.5 (2) | C41—P2—Pt$^i$ | 112.4 (6) |
| P2$^{ii}$—Pt—Pt$^{ii}$ | 97.1 (2) | C51$^i$—P3—C51 | 107.0 (6) |
| P1—Pt—Pt$^{ii}$ | 150.0 (2) | C51—P3—Au | 111.8 (6) |
| Pt$^i$—Pt—Pt$^{ii}$ | 60.0 | P2—C1—P1 | 109.3 (12) |
| P2$^{ii}$—Pt—Au | 106.3 (2) | C12—C11—P1 | 116.5 (9) |
| P1—Pt—Au | 115.2 (2) | C16—C11—P1 | 123.3 (9) |
| Pt$^i$—Pt—Au | 61.09 (2) | C22—C21—P1 | 118.5 (10) |
| C21—P1—C11 | 106.2 (8) | C26—C21—P1 | 121.5 (10) |
| C21—P1—C1 | 102.7 (10) | C32—C31—P2 | 117.7 (9) |
| C11—P1—C1 | 103.8 (10) | C36—C31—P2 | 121.7 (9) |
| C21—P1—Pt | 122.6 (7) | C42—C41—P2 | 119.6 (9) |
| C11—P1—Pt | 111.3 (6) | C46—C41—P2 | 120.2 (9) |
| C1—P1—Pt | 108.5 (8) | C52—C51—P3 | 118.2 (9) |
| C1—P2—C31 | 102.5 (10) | C56—C51—P3 | 121.6 (9) |
| | | | |
| Au—P3—C51—C52 | 31.3 (9) | C1—P2—Pt$^i$—Pt | 12.8 (8) |
| Pt—P1—C1—P2 | 53.6 (13) | P2—Pt$^i$—Pt—P1 | 13.4 (2) |
| P1—C1—P2—Pt$^i$ | −40.9 (13) | Pt$^i$—Pt—P1—C1 | −37.1 (8) |

Symmetry codes: (i) $z,x,y$; (ii) $y,z,x$.

Data collection and cell refinement were performed with CAD-4 EXPRESS (Enraf–Nonius, 1992). GX (Mallinson & Muir, 1985) was used for data reduction. The structure was solved by Patterson and Fourier methods (SHELXS86; Sheldrick, 1985). Refinement was performed on $F^2$ for unique reflections with $I > 3\sigma(I)$. $wR$ factors and all goodnesses of fit $S$ are based on $F^2$, conventional $R$ factors are based on $F$. Preliminary studies at 296 K established that at ambient temperature (1) crystallizes in an $F$-centred cubic cell, space group $Fd\bar{3}$, with $a = 40.69$ (1) Å. Using 890 unique observed reflections [$I > 3\sigma(I)$] the structure was refined to $R = 0.057$. This refinement revealed a cation structure indistinguishable from that reported here, but it accounted for only 16 of the 32 anions necessary for charge balance. Accordingly, the crystal was cooled to 130 K (Oxford Cryosystems Cryostream Cooler; Cosier & Glazer, 1986) and a second data set (unique reflections only) was collected after it had been established that no change in structure occurred on cooling. This data set allowed the remaining anions to be located. In the final calculations anisotropic displacement parameters were refined only for Pt, Au and P atoms; the five phenyl rings were constrained to be rigid hexagons of side 1.39 Å. H atoms rode on the parent C atoms with the constraints C—H $= 0.95$ Å and $U$(H) $= 1.2U_{eq}$(C). The disorder of the six F atoms attached to P21 was accounted for by assigning fixed site occupancies of 3/8, 3/8 and 1/4 for F21, F22 and F23, respectively. The GX package was used for most of the refinement calculations, but the final cycles of refinement and CIF preparation were performed with SHELXL93 (Sheldrick, 1993). Molecular graphics were prepared using ORTEP (Johnson, 1965).

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# Dichloro(ethylenediaminetetraacetic acid-$N,N'$)platinum(II)–Water (1/6)

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## Abstract

The Pt atom of the title compound, [PtCl$_2$(C$_{10}$H$_{16}$N$_2$O$_8$)].6H$_2$O, sits on a twofold axis and exhibits square-planar coordination geometry. Two Cl$^-$ ions are bound to the Pt atom, as are the two N atoms of ethylenediaminetetraacetic acid. The distances and angles are typical.

## Comment

Ethylenediaminetetraacetic acid (H$_4$edta) is widely recognized as a metal complexing agent and generally binds to metals in either a penta- or hexadentate fashion (Anderegg, 1987). However, in 1956 H$_4$edta was first reported to bind to Pt$^{II}$ and Pd$^{II}$ in a bidentate fashion, and H$_2$edta$^{2-}$ was reported to bind to these same metal ions in a tetradentate fashion (Busch & Bailar, 1956). These types of complexes have continued to attract the interest of chemists, as evidenced by the fact that various Pt$^{II}$ and Pd$^{II}$ edta complexes have been the subject of numerous NMR studies (Erickson, McDonald, Howie & Clow, 1968; Smith & Sawyer, 1969; Appleton, Hall