

Structure of a Pt/Re cluster complex: aggregation of ions in crystals of $[\text{Pt}_3\{\text{Re}(\text{CO})_2\text{P}(\text{OMe})_3\}\{\mu_3\text{-O}\}_2(\mu\text{-dppm})_3][\text{AsF}_6]^-$ ¹

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Abstract

The crystal structure of the molecular salt $[\text{Pt}_3\{\text{Re}(\text{CO})_2\text{P}(\text{OMe})_3\}\{\mu_3\text{-O}\}_2(\mu\text{-dppm})_3][\text{AsF}_6]$, dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, has been determined by X-ray diffraction. The crystals are monoclinic, space group $P2_1/c$, $a = 15.614(2)$, $b = 21.550(2)$, $c = 24.810(2)$ Å, $\beta = 93.518(10)^\circ$, $V = 8332.5(13)$ Å³, $Z = 4$, $R = 0.0501$ for 7403 reflections with $I \geq 2\sigma(I)$. The structure of the cation contains a $\text{Pt}_3\text{Re}(\mu_3\text{-O})_2$ core with a tetrahedral arrangement of the metal atoms. One Pt atom is not directly involved in metal–metal bonding, which is limited to a triangle containing one Re and two Pt atoms [Pt–Pt 2.815(1), Pt–Re 2.779(1) and 2.835(1) Å]. The packing of ions in the crystal is governed by their relative size: the large cations self-assemble into one-dimensional aggregations, leaving the anions to occupy the cavities in the cationic substructure. Crystal cohesion is enhanced by hydrogen bonding of C–H \cdots O type, involving carbonyl oxygen atoms, and by C–H \cdots F interactions. © 1997 Elsevier Science S.A.

Keywords: Platinum; Rhenium; Cluster; Crystal structure; X-ray diffraction

1. Introduction

The growing interest in heteronuclear metal clusters, notably those containing at least one platinum atom, stems mostly from their relevance to catalysis [1]. In industrial bimetallic catalysis much attention is centred on the oxide-supported Pt–Re/Al₂O₃ catalysts extensively used in petroleum reforming processes [2]. Attempts to obtain some insight into the reactivity of these catalysts have stimulated interest in complexes containing Pt–Re bonds [3] and led to the development of an extensive chemistry of the coordinatively unsaturated cluster $[\text{Pt}_3\{\text{Re}(\text{CO})_3\}(\mu\text{-dppm})_3]^+$ (**1**) (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) [4,5]. Numerous products of ligand addition, oxidation and sulphidation reactions of **1** have been structurally characterised and considered as models mimicking Pt–Re interactions in catalytic processes [3,6–12].

Of particular interest is the unique reaction of **1** with oxygen and oxygen-donors, which has produced a series

of oxo clusters $[\text{Pt}_3\{\text{Re}(\text{CO})_3\}(\mu_3\text{-O})_n(\mu\text{-dppm})_3]^+$, $n = 1, 2$ or 3 , $[\text{Pt}_3\{\text{ReO}_3\}(\mu_3\text{-O})_3(\mu\text{-dppm})_3]^+$ [4,10] and $[\text{Pt}_3\{\text{ReO}_3\}(\mu\text{-dppm})_3]^+$ [11,12]. Further oxidation of the last complex, a remarkable cluster with metal atoms in widely different oxidation states (Pt(0), Re(VII)), has led to formation of the $[\text{ReO}_4]^-$ ion [10]. The conversion of **1** into $[\text{Pt}_3\{\text{Re}(\text{CO})_3\}(\mu_3\text{-O})_2(\mu\text{-dppm})_3]^+$ (**2**) has provided the first example of oxidative addition of dioxygen to a metal cluster to form a bis(μ_3 -oxo) species, and the first model for dissociative chemisorption of O₂ on a metal surface. Metal cluster complexes with oxo ligands are still relatively uncommon for the later transition metals [13].

It has been shown recently that **2** reacts with neutral ligands, such as phosphites $\text{P}(\text{OR})_3$, R = Me or Ph, to form new dioxo-cluster complexes, and their $[\text{PF}_6]^-$ salts have been characterised spectroscopically [10]. We now report an X-ray diffraction study of the $[\text{AsF}_6]^-$ salt of $[\text{Pt}_3\{\text{Re}(\text{CO})_2\text{P}(\text{OMe})_3\}(\mu_3\text{-O})_2(\mu\text{-dppm})_3]^+$ (**3**).

The factors which control crystal formation, stability and assembly of ions in molecular salts containing ionic Pt₃ and Pt₃Re cluster nuclei stabilised by dppm ligands, have not previously been studied. As a first step towards the understanding of these factors we have investigated the interactions of the ions and their organisation in the crystal structure of the $[\text{AsF}_6]^-$ salt of **3**.

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¹ We dedicate this paper to the memory of Professor Yuri T. Struchkov in recognition of his great contribution to organometallic structural chemistry and as a token of our personal respect.

2. Results and discussion

2.1. The cluster cation $[Pt_3\{Re(CO)_2P(OMe)_3\}(\mu_3-O)_2(\mu-dppm)_3]^+$ (**3**)

The structure of **3** in crystals of its $[AsF_6]^-$ salt, characterised by the bond lengths and angles listed in Table 1, is shown in Fig. 1. It contains a $Pt_3Re(\mu_3-O)_2$ core in which the metal atoms form a distorted tetrahedral arrangement, with two faces of the tetrahedron capped by triply bridging oxygen atoms. The edges of the Pt_3 triangle are spanned by the dppm ligands to form a $Pt_3(\mu-dppm)_3$ fragment, a structural feature commonly found in Pt_3 complexes stabilised by dppm ligands [4–12,14,15]. The environments of the Pt(1) and

Table 1
Selected bond lengths [Å] and angles [°] in $3[AsF_6]$

Pt(1)–O(1)	2.042(10)	Pt(1)–P(1)	2.204(4)
Pt(1)–P(6)	2.293(4)	Pt(1)–Re	2.7794(9)
Pt(1)–Pt(2)	2.8150(8)	Pt(2)–O(2)	2.032(10)
Pt(2)–Pt(2)	2.225(4)	Pt(2)–P(3)	2.306(4)
Pt(2)–Re	2.8353(9)	Pt(3)–O(2)	2.025(10)
Pt(3)–O(1)	2.031(10)	Pt(3)–P(4)	2.232(4)
Pt(3)–P(5)	2.240(4)	Re–C(4)	1.85(2)
Re–C(5)	1.86(2)	Re–O(2)	2.135(10)
Re–O(1)	2.158(10)	Re–P(7)	2.264(5)
P(7)–O(7)	1.58(2)	P(7)–O(8)	1.60(2)
P(7)–O(6)	1.61(2)	As(1)–F(1)	1.567(7) ^a
O(4)–C(4)	1.18(2)	O(5)–C(5)	1.21(2)
O(6)–C(6)	1.41(3)	O(7)–C(7)	1.45(3)
O(8)–C(8)	1.42(3)		
O(1)–Pt(1)–P(1)	166.6(3)	O(1)–Pt(1)–P(6)	79.8(3)
P(1)–Pt(1)–P(6)	107.2(2)	O(1)–Pt(1)–Re	50.4(3)
P(1)–Pt(1)–Re	118.4(1)	P(6)–Pt(1)–Re	126.4(1)
O(1)–Pt(1)–Pt(2)	87.4(3)	P(1)–Pt(1)–Pt(2)	92.5(1)
P(6)–Pt(1)–Pt(2)	145.4(1)	Re–Pt(1)–Pt(2)	60.9(1)
O(2)–Pt(2)–P(3)	82.6(3)	O(2)–Pt(2)–P(2)	167.1(3)
O(2)–Pt(2)–Pt(1)	86.9(3)	P(2)–Pt(2)–P(3)	103.6(2)
P(3)–Pt(2)–Pt(1)	151.7(1)	P(2)–Pt(2)–Pt(1)	92.2(1)
P(2)–Pt(2)–Re	120.6(1)	O(2)–Pt(2)–Re	48.7(3)
Pt(1)–Pt(2)–Re	58.9(1)	P(3)–Pt(2)–Re	126.6(1)
O(2)–Pt(3)–O(1)	80.3(4)	O(2)–Pt(3)–P(4)	90.7(3)
O(1)–Pt(3)–P(4)	170.2(3)	O(2)–Pt(3)–P(5)	168.8(3)
O(1)–Pt(3)–P(5)	88.5(3)	P(4)–Pt(3)–P(5)	100.5(2)
C(4)–Re–O(2)	171.2(6)	C(4)–Re–C(5)	83.0(8)
C(4)–Re–O(1)	100.1(6)	C(5)–Re–O(2)	101.2(6)
O(2)–Re–O(1)	75.1(4)	C(5)–Re–O(1)	174.3(6)
C(5)–Re–P(7)	85.3(6)	C(4)–Re–P(7)	87.7(6)
O(1)–Re–P(7)	99.5(3)	O(2)–Re–P(7)	100.3(3)
C(5)–Re–Pt(1)	129.4(5)	C(4)–Re–Pt(1)	85.5(6)
O(1)–Re–Pt(1)	46.8(3)	O(2)–Re–Pt(1)	85.9(3)
C(4)–Re–Pt(2)	127.4(6)	P(7)–Re–Pt(1)	143.3(1)
O(2)–Re–Pt(2)	45.6(3)	C(5)–Re–Pt(2)	89.6(5)
P(7)–Re–Pt(2)	143.6(1)	O(1)–Re–Pt(2)	84.7(3)
Pt(1)–O(1)–Pt(1)	100.6(4)	Pt(1)–Re–Pt(2)	60.2(1)
Pt(1)–O(1)–Re	82.8(4)	Pt(3)–O(1)–Re	101.8(4)
Pt(3)–O(2)–Re	102.8(4)	Pt(3)–O(2)–Pt(2)	98.9(4)
Pt(2)–O(2)–Re	85.7(4)		

^a The $[AsF_6]^-$ anion was treated as a variable metric rigid group with idealised octahedral geometry.

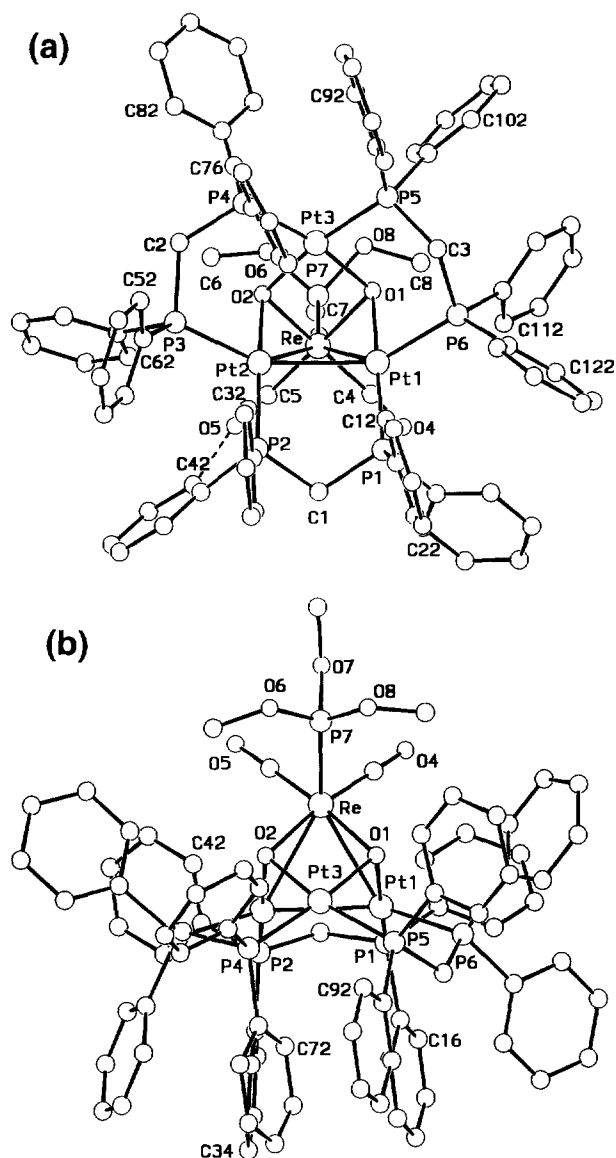
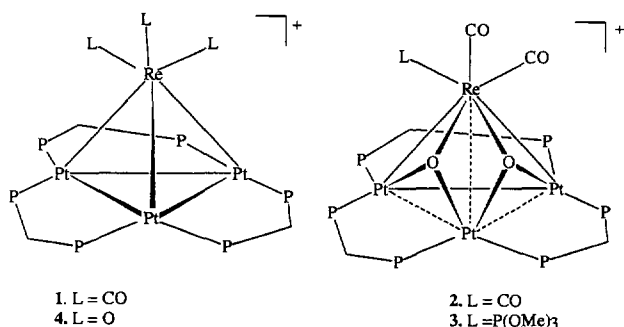


Fig. 1. (a) The structure of **3** with atoms represented by spheres of arbitrary size. In the 12 phenyl rings carbon atoms are numbered in sequence $Cn1-Cn6$, where $Cn1$ is bonded to phosphorus and n is the ring number (1–12). For clarity only the label of $Cn2$ (or $Cn6$) is shown and hydrogen atoms are omitted. (b) Another view of the cation, showing the conformation of the $Pt_3(\mu-dppm)_3$ fragment and the arrangement of the phenyl rings around the Pt_3P_6 skeleton.

Pt(2) centres can be described as highly distorted square pyramidal, while that around the Pt(3) centre approximates to square planar. In the $Re(CO)_2P(OMe)_3(\mu_3-O)_2$ unit a distorted octahedral geometry around the Re centre is completed by the midpoint of the Pt(1)–Pt(2) bond (Fig. 1, Table 1). The $Pt_3\{Re(CO)_2P(OMe)_3\}(\mu_3-O)_2$ skeleton shows approximate C_s symmetry, the plane of symmetry passing through the P(7), Re, Pt(3) and C(1) atoms and bisecting the Pt(1)–Pt(2) bond. Thus the structure of **3** gives credence to that proposed on the basis of IR and NMR spectra of the $[PF_6]^-$ salts of the $[Pt_3\{Re(CO)_2L\}(\mu_3-O)_2(\mu-dppm)_3]^+$ cations, L

= P(OPh)₃ and P(OMe)₃ [10]. It resembles closely the structure of the parent complex [Pt₃{Re(CO)₃}(μ₃-O)₂(μ-dppm)₃]⁺ (**2**), from which it can be derived by substituting a carbonyl ligand by phosphite. This contrasts with reactions of the less electron-rich complexes [Pt₃{Re(CO)₃}(μ-dppm)₃]⁺ (**1**) and [Pt₃{ReO₃}(μ-dppm)₃]⁺ (**4**), which add phosphite selectively (at the rhenium centre in **1** [7] and at a platinum centre in **4** [12]) without loss of other ligands.



In **3** the Pt(1)–Pt(2), Pt(1)–Re and Pt(2)–Re distances [2.815(1), 2.779(1) and 2.835(1) Å] are within the ranges accepted for Pt–Pt and Pt–Re single bonds (2.6–2.8 and 2.7–2.9 Å) [3–12, 14–16]. The Pt(1)–Pt(3), Pt(2)–Pt(3) and Pt(3)–Re distances [3.134(1), 3.082(1) and 3.252(1) Å] are too long to be considered indicative of normal covalent bonding. As is evident from Table 2, all metal–metal distances in **3** are essentially the same as the corresponding ones in **2**, but substantially longer than those in **1**. They suggest that substitution of one carbonyl ligand by phosphite at the rhenium centre has little or no effect on the metal–metal bonding, and reinforce our earlier observation [10] that oxidative addition of two μ₃-oxo ligands, associated with an increase in the valence electron count from 54 in **1** to 62 in **2** and **3**, can cause lengthening, and even cleavage, of metal–metal bonds. In contrast to **1**, where all metal atoms are held by M–M bonds coinciding with the edges of the Pt₃Re tetrahedron, in **2** and **3** they are held by normal covalent bonding in the Pt(1)Pt(2)Re triangle only.

The geometry of the Pt₃Re(μ₃-O)₂ core is essentially the same in **2** and **3**, and therefore the metal–metal interactions in **3** can be rationalised as previously proposed for **2** [4, 10]. It is assumed that an oxygen atom inserted into a Pt–Pt bond to form a Pt–O–Pt linkage donates two electrons to the ReL₃ fragment. Hence, addition of two μ₃-O ligands to **1** results in cleavage of one Pt–Re and two Pt–Pt bonds, leaving the electron count of the platinum and rhenium atoms unchanged at 16 and 18 electrons, but oxidising the platinum triangle from [Pt₃]⁰ to [Pt₃]⁴⁺. Thus, in the dioxo clusters **2** and

Table 2

A comparison of metal–metal distances (Å) in complexes **1**, **2** and **3**

	1	2	3
Pt(1)–Pt(2)	2.611(1)	2.826(1)	2.815(1)
Pt(1)–Pt(3)	2.593(1)	3.094(1)	3.134(1)
Pt(2)–Pt(3)	2.608(1)	3.081(1)	3.082(1)
Pt(1)–Re	2.684(1)	2.843(1)	2.779(1)
Pt(2)–Re	2.649(1)	2.854(1)	2.835(1)
Pt(3)–Re	2.685(1)	3.228(1)	3.252(1)

3 the metal atoms can be ascribed formal oxidation states +1 for Re, Pt(1) and Pt(2) and +2 for Pt(3), and the metal–metal bonding in the Pt₂Re triangle can be considered in terms of donation of charge from the Pt(1)–Pt(2) bond to a vacant acceptor orbital of the Re(CO)₂L⁺ fragment [L = CO or P(OMe)₃].

In the Pt₃Re(μ₃-O)₂ core the oxo ligands bridge the Pt₂Re faces in a nearly symmetrical manner. The Pt–O distances [2.03(1)–2.04(1) Å] are only slightly shorter than the Re–O distances [2.14(1) and 2.16(1) Å], and both are in good agreement with those observed in **2** and other complexes [10, 17]. The Re–P and Re–C distances in the Re(CO)₂P(OMe)₃ unit (Table 1) are unexceptional. The four Pt–P bonds roughly *trans* to μ₃-oxo ligands [2.204(4)–2.240(4) Å] are shorter than the two *trans* to Pt [2.293(4), 2.306(4) Å], presumably reflecting the relative *trans* influence of oxygen and platinum atoms.

In the Pt₃(μ-dppm)₃ fragment the five-membered Pt(1), Pt(2), P(2), C(1), P(1) ring adopts an envelope conformation, with the methylene carbon atom at the flap. The Pt₃P₆ skeleton is severely distorted from latitudinal geometry (Fig. 1), all six Pt–P bonds bending out of the Pt₃ plane and away from the Re(CO)₂P(OMe)₃(μ₃-O)₂ unit. The out-of-plane displacements of the phosphorus atoms range from 0.600(4) to 1.101(4) Å. Each face of the Pt₃P₆ skeleton is encircled by six phenyl rings (Fig. 1). On one side they form a cavity large enough to accommodate the Re(CO)₂P(OMe)₃(μ₃-O)₂ fragment, while on the other side they completely encase the Pt₃ triangle (Fig. 2). Two pairs of nearly parallel phenyl rings on adjacent phosphorus atoms (Fig. 1(b)) form aromatic stacking interactions which help to stabilise the conformation of the Pt₃(μ-dppm)₃ fragment. The shortest C...C contacts arising from these interactions are 3.30(1) Å for the rings containing atoms C(34) and C(16) and 3.31(1) Å for the rings containing atoms C(76) and C(92).

A carbonyl ligand of the Re(CO)₂P(OMe)₃ group interacts with a C–H dipole of a phenyl group at the cavity wall of the Pt₃(μ-dppm)₃ fragment. The C(42)...O(5) and H(42)...O(5) distances of 3.24 and 2.34 Å and the C(42)–H(42)...O(5) angle of 139°, which characterise this interaction, are typical of hydrogen bonding of the type C–H...O [18].

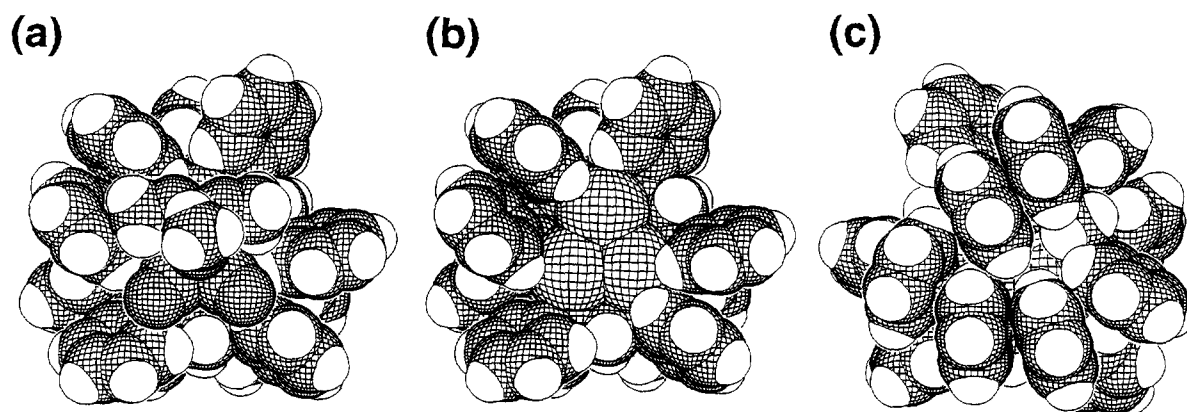


Fig. 2. Views of the van der Waals surface of **3** along the normal to the Pt_3 triangle: (a) from the side of the $\text{Re}(\text{CO})_2\text{P}(\text{OMe})_3$ fragment, (b) the same view but with the $\text{Re}(\text{CO})_2\text{P}(\text{OMe})_3$ fragment removed, and (c) from the opposite side of the triangle.

2.2. Aggregation of ions in the crystal structure of $3[\text{AsF}_6]$

In view of the rapidly emerging interest in the solid-state supramolecular chemistry of transition metal cluster complexes [19,20], we have investigated intermolec-

ular interactions and organisation of ions in crystalline $3[\text{AsF}_6]$.

The prominent packing mode in the crystal structure of this salt is the self-assembly of the large cluster cations into helical piles which coil around the 2_1 screw axes and extend throughout the crystal in the direction

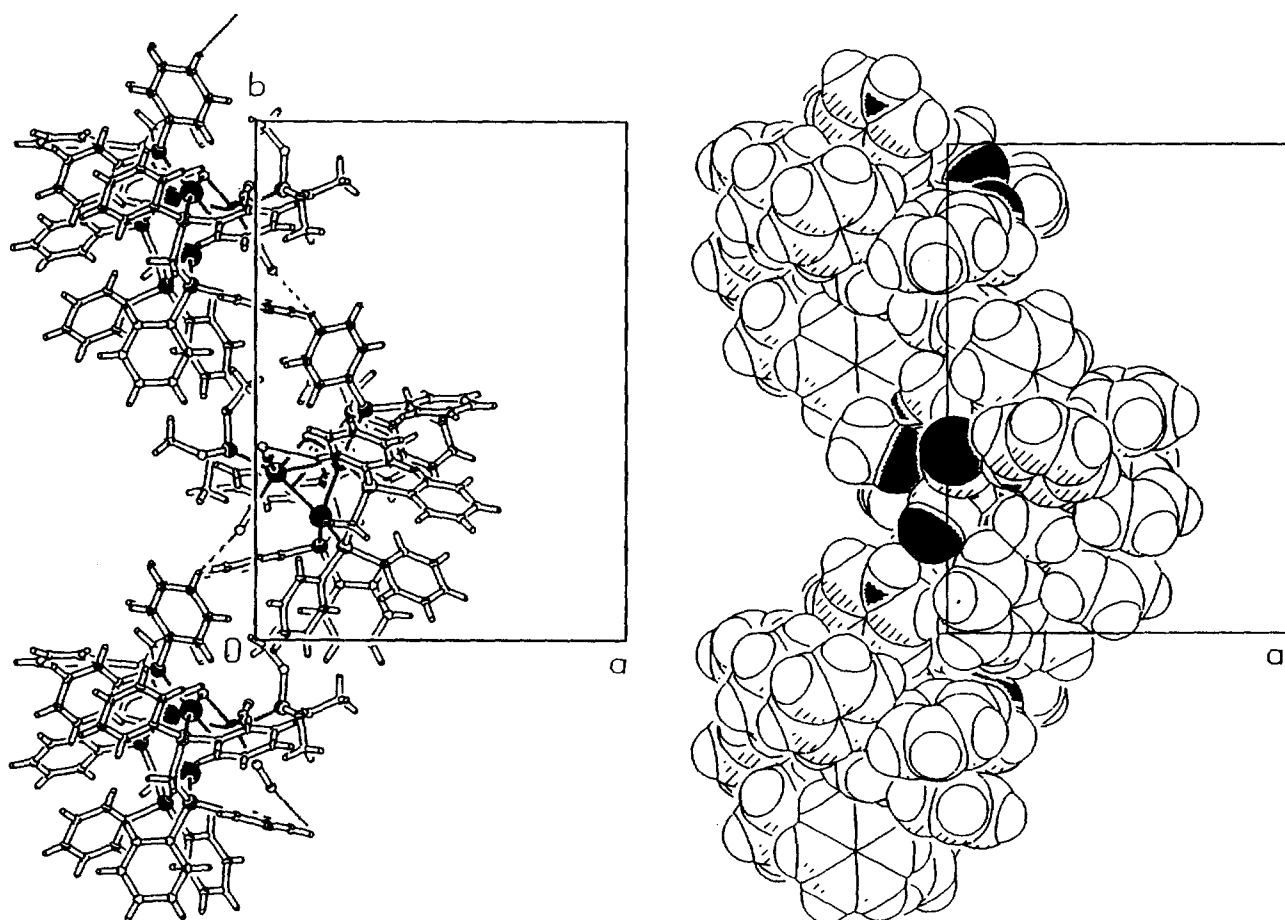


Fig. 3. One-dimensional aggregation of the cluster cations: the helical pile of cations is shown by a ball-and-stick model, with broken lines indicating hydrogen bonds, and by a space-filling model.

of the *b*-axis (Fig. 3). Within these piles cations are linked to one another by hydrogen bonds of the type C–H···O; in each bond a phenyl C–H dipole acts as a donor to a carbonyl oxygen atom from an adjacent cation. The C(84)···O(4) and H(84)···O(4) distances (3.30 and 2.40 Å) and the C(84)–H(84)···O(4) angle (139°) are in agreement with those characterising the C–H···O(CO) bonding in other transition metal cluster complexes (C···O 3.0–3.7, H···O 2.2–2.8 Å and C–H···O 109–177°) [18,21]. It has been shown earlier that in crystalline molecular salts with large transition metal cluster anions and small cations, one- and two-dimensional aggregations of anions are produced [22]. We now find that in $3[\text{AsF}_6]$, where the cluster cations are much larger than the anions, the cations self-organise into one-dimensional aggregations (piles), leaving the anions to occupy the cavities left in the crystal structure (Fig. 4(a)). The cationic piles are packed into layers parallel to the (100) plane. Co-operative aromatic stacking interactions enhance the stability of the layer structure through partial overlap of centrosymmetrically-related phenyl rings from the successive layers (Fig. 4); they are revealed by the short C(55)···C(55^{IV}) contact of 3.16(1) Å (iv: 1 – *x*, 1 – *y*, 1 – *z*).

The $[\text{AsF}_6]^-$ ions contribute significantly to the cohesion of the crystals by interacting with the polar C–H groups lining the walls of the cavities in the cationic substructure. Each anion forms four C–H···F interactions with three cationic piles from two successive layers: C(82)–H(82)···F(1), C(96)–H(96)···F(2), C(13)–H(13)···F(3) and C(45)–H(45)···F(6) (Fig. 4(b)). In these interactions the C···F and H···F distances and C–H···F angles are within the respective ranges of 3.16–3.46, 2.34–2.45 Å and 128–176° (Table 3). Although they may be somewhat affected by constraints imposed on the geometry of the $[\text{AsF}_6]^-$ anion (see Section 3), they are in agreement with the H···F distances (2.32–2.45 Å) and C–H···F angles (116–177°) in $[\{\text{Ru}(\eta^6\text{-arene})_2(\mu\text{-Cl})_3\}][\text{BF}_4]$ salts (arene = C₆H₆, C₆H₅Me), where the C–H···F interactions are considered important in stabilising the crystal structures [19,23].

It is interesting to note that the crystals of $3[\text{AsF}_6]$ used in this analysis were obtained from a CH₂Cl₂ solution containing an excess of $[\text{PF}_6]^-$ anions, with $[\text{AsF}_6]^-$ present only as a contaminant [24]. The apparent preference of **3** for $[\text{AsF}_6]^-$ as counterion, rather than $[\text{PF}_6]^-$, established by this diffraction study, may be ascribed to the size of the anions: the packing radius and volume are 3.02 Å and 63 Å³ for $[\text{AsF}_6]^-$ and 2.88 Å and 54 Å³ for $[\text{PF}_6]^-$ [25]. Obviously, the larger $[\text{AsF}_6]^-$ ions use the cavities in the cationic substructure more effectively. However, even then the anions do not fully occupy the cavities, each of which has a volume of ca. 300 Å³; they dock at the cavity walls, apparently in

order to maximise the number of C–H···F interactions and thus optimise their contribution to stabilisation of the crystal structure.

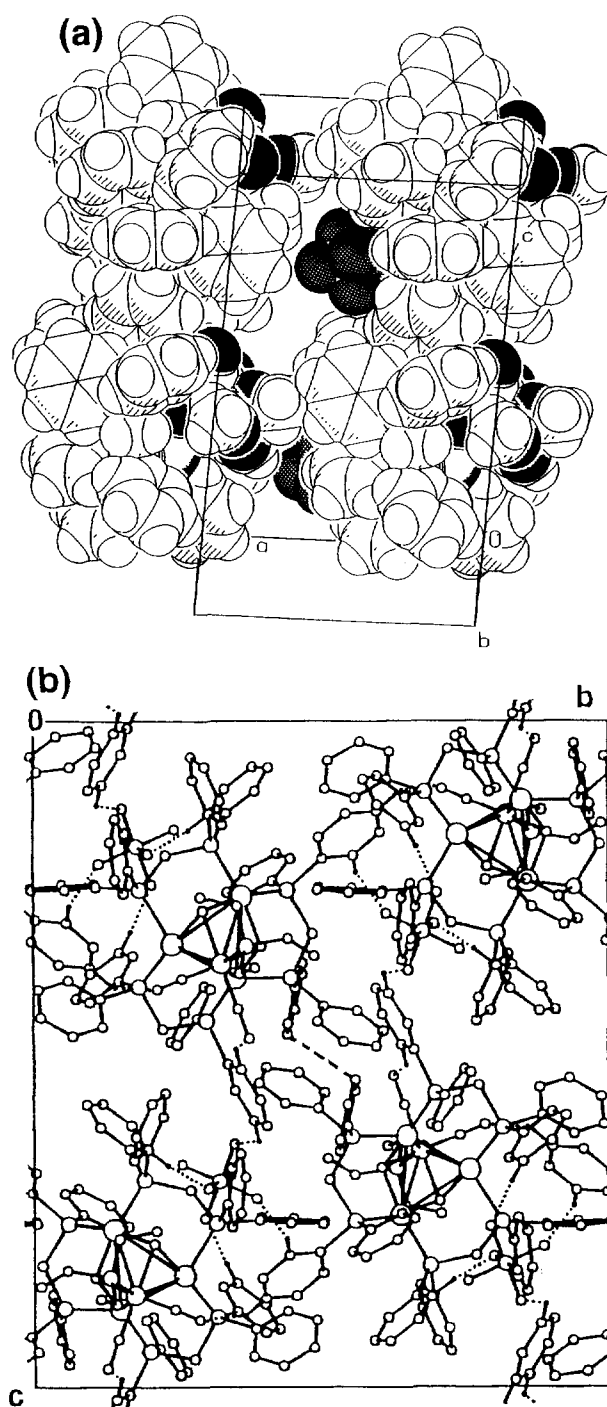


Fig. 4. (a) A space-filling drawing of the crystal structure, showing the anions docking at the walls of the cavities in the cationic substructure. (b) The hydrogen bonding network in the crystal structure viewed in projection down the *a*-axis. The C–H···O and C–H···F interactions are shown by broken lines, as is the short contact between phenyl rings related by the inversion centre at 1/2, 1/2, 1/2 [C55···C55 = 3.16(2) Å]. For clarity hydrogen atoms not involved in hydrogen bonding are omitted.

Table 3
Geometry (Å and °) of C–H⋯O(CO) and C–H⋯F interactions in the crystal structure of $3[\text{AsF}_6]^-$ ^a

D–H⋯A	D⋯A	H⋯A	∠D–H⋯A
C(42)–H(42)⋯O(5)	3.24(2)	2.34	139
C(84)–H(84)⋯O(4 ⁱ)	3.30(2)	2.40	139
C(82)–H(82)⋯F(1 ⁱⁱ)	3.46(2)	2.45	156
C(96)–H(96)⋯F(2)	3.36(2)	2.39	149
C(13)–H(13)⋯F(3)	3.42(2)	2.34	176
C(45)–H(45)⋯F(6 ⁱⁱⁱ)	3.16(2)	2.38	128

^a Based on normalised C–H distances of 1.08 Å.

Symmetry code: (i) $-x, 1/2+y, 1/2-z$; (ii) $1-x, 1/2+y, 1/2-z$; (iii) $x, 1/2-y, 1/2+z$.

In summary, the organisation of the ions in crystals of $3[\text{AsF}_6]^-$ is governed by the size of the cation, which is much larger than the anion, and by the need to use the space as efficiently as possible.

3. Experimental

The X-ray measurements were made at ambient temperature with graphite monochromated Mo K α radiation and an Enraf–Nonius CAD4 diffractometer. Crystals were orange prisms grown from CH_2Cl_2 solution. They were of relatively poor quality and decomposed in the X-ray beam. The analysis reported here is the most successful of three attempts performed on crystals from separately prepared batches of the compound.

Unit cell dimensions (Table 4) were determined by a least-squares treatment of the setting angles of 25 Bragg reflections with $17.5^\circ < \theta < 21.3^\circ$. The metric symmetry and Laue group were established from the diffraction pattern and the space group from the systematic absences.

The intensities were measured from $\omega/2\theta$ scans of width $(0.63 + 0.61 \tan \theta)^\circ$ in ω , counting for up to 60 s/reflection. Three standard reflections, monitored every 2 h, showed a linear decrease in mean intensity of 8.7%. The integrated intensities were corrected for crystal decomposition, Lp effects and absorption (DIFABS method embodied in PLATON [26,27]). Further details of the analysis are given in Table 4.

The structure was solved by the heavy atom method. The compound was initially believed to be a $[\text{PF}_6]^-$ salt. However, models based on this assumption gave negative U_{iso} values for the phosphorus atom of the anion for all three data sets measured. Many alternative refinement models were then considered, but the only satisfactory one was that presented here, which is based on the composition $3[\text{AsF}_6]^-$. We cannot however exclude the possibility that $[\text{PF}_6]^-$ replaces $[\text{AsF}_6]^-$ at a very small number of anion sites. The presence of arsenic in the bulk reagent used for sample preparations was eventually confirmed by chemical analysis [24].

The structure was refined by full-matrix least-squares, minimising the function $\sum w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2$, where $w = 1/[\sigma^2(F_{\text{obs}}^2) + a^2P^2 + bP]$, $P = [F_{\text{obs}}^2 + 2F_{\text{calc}}^2]/3$, $a = 0.079$ and $b = 88.3$ using SHELXL-93 [28]. Only the Pt, Re, As, P and F atoms were assigned anisotropic displacement parameters. The hydrogen atoms rode on their parent C atoms in calculated positions and with $U(\text{H}) = kU(\text{C})$, where k was 1.2–1.5 [28]. The orientations of the three methyl groups were determined from a difference synthesis. The 12 phenyl groups were refined as rigid hexagons of side 1.39 Å. The $[\text{AsF}_6]^-$ anion was treated as an idealized rigid octahedron, with pairs of *trans* F atoms constrained to have the same U_{ij} values.

The refinement converged at $R_1 = 0.0501$ for 7403 reflections with $I \geq 2\sigma(I)$ and 0.0991 for all 10443 unique reflections, with a maximum shift/error ratio of 0.01. The final difference synthesis showed a residual peak of $3.2 \text{ e } \text{Å}^{-3}$ close to Re, but contained no features of chemical significance. Final atomic parameters are listed in Table 5.

Neutral atom scattering factors and anomalous dispersion corrections were taken from Ref. [29]. The C–H distances were normalised to 1.08 Å for the analysis of the organisation of the ions by PLATON [27]. Figures were prepared using the programs CAMERON and PLUTON

Table 4
Crystallographic data and refinement of the structure

Empirical formula	$\text{C}_{80}\text{H}_{75}\text{AsF}_6\text{O}_7\text{P}_7\text{Pt}_3\text{Re}$
Formula weight	2325.58
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å)	$a = 15.614(2)$ $b = 21.550(2)$ $c = 24.810(2)$ $\beta = 93.518(10)^\circ$
Volume (Å ³)	8332.5(13)
Z	4
Density (calc.) (Mg m^{-3})	1.854
Absorption coefficient (mm^{-1})	7.061
$F(000)$	4448
Crystal size (mm^3)	$0.30 \times 0.20 \times 0.13$
Range in θ for data collection	2.2 to 23.5°
Index ranges	$-17 \leq h \leq 16, -7 \leq k \leq 22,$ $-6 \leq l \leq 26$
Reflections collected	10739
Independent reflections	10443 [$R(\text{int}) = 0.0353$]
Absorption correction	Empirical (ΔF)
Transmission factor range	0.446 to 1.000
Refinement method	Full-matrix least-squares on F^2
Data (with $I > 0$)/parameters	8916/335
Goodness-of-fit on F^2	1.066
R indices [7403 data with $I > 2\sigma(I)$]	$R_1 = 0.0501, wR_2 = 0.1331$
R indices (all 10443 data)	$R_1 = 0.0991, wR_2 = 0.1719$
$\Delta\rho$, extreme values ($\text{e } \text{Å}^{-3}$)	3.20 and -1.83

Table 5

Atomic coordinates ($\times 10^4$) and displacement parameters ($\text{\AA}^2 \times 10^3$), U_{eq} for Pt, Re, P, As and F atoms, U_{iso} for O and C atoms

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/U_{\text{eq}}$
Pt(1)	1769(1)	2401(1)	3301(1)	34(1)
Pt(2)	2316(1)	3510(1)	3813(1)	33(1)
Pt(3)	1725(1)	3617(1)	2608(1)	33(1)
Re	547(1)	3253(1)	3597(1)	39(1)
P(1)	2417(3)	1824(2)	3936(2)	39(1)
P(2)	3074(3)	2999(2)	4459(2)	40(1)
P(3)	2963(3)	4471(2)	3805(2)	35(1)
P(4)	2623(3)	4411(2)	2518(2)	34(1)
P(5)	1924(3)	3092(2)	1846(2)	38(1)
P(6)	1734(3)	1837(2)	2516(2)	38(1)
P(7)	-731(3)	3686(2)	3330(2)	55(1)
As(1)	5726(2)	1787(1)	1874(1)	104(1)
F(1)	5569(8)	1137(4)	2132(5)	183(4)
F(2)	4786(6)	1984(6)	1983(5)	180(4)
F(3)	6047(8)	2046(5)	2441(4)	182(4)
F(4)	5883(8)	2437(4)	1615(5)	183(4)
F(5)	6666(6)	1590(6)	1765(5)	180(4)
F(6)	5405(8)	1528(5)	1307(4)	182(4)
O(1)	934(6)	2925(5)	2827(4)	39(3)
O(2)	1403(6)	3947(5)	3332(4)	37(3)
O(4)	-433(10)	2137(7)	3982(6)	83(4)
O(5)	186(9)	3747(6)	4719(5)	68(4)
O(6)	-778(10)	4421(7)	3223(6)	89(5)
O(7)	-1447(9)	3580(7)	3742(6)	78(4)
O(8)	-1199(9)	3529(7)	2752(6)	77(4)
C(1)	2614(11)	2235(7)	4577(7)	45(4)
C(2)	2725(10)	4856(7)	3151(5)	32(4)
C(3)	2245(10)	2291(7)	2005(6)	39(4)
C(4)	-56(12)	2568(9)	3818(8)	58(5)
C(5)	329(11)	3548(8)	4278(7)	51(5)
C(6)	-254(22)	4885(15)	3472(13)	145(12)
C(7)	-2294(16)	3852(12)	3661(10)	105(8)
C(8)	1340(17)	2895(12)	2629(11)	106(9)
C(11)	3469(6)	1475(5)	3853(5)	43(4)
C(12)	3993(8)	1725(5)	3475(5)	65(5)
C(13)	4808(8)	1483(7)	3421(5)	83(7)
C(14)	5100(7)	991(7)	3745(6)	97(8)
C(15)	4576(9)	741(6)	4123(6)	101(8)
C(16)	3761(8)	983(6)	4177(5)	70(6)
C(21)	1766(8)	1157(5)	4124(5)	39(4)
C(22)	1215(10)	1199(6)	4542(5)	101(8)
C(23)	737(10)	686(9)	4681(6)	134(11)
C(24)	809(10)	131(7)	4403(7)	106(9)
C(25)	1360(11)	88(5)	3985(7)	123(10)
C(26)	1838(9)	601(7)	3845(5)	82(7)
C(31)	4214(6)	2835(5)	4421(5)	48(4)
C(32)	4628(7)	3072(5)	3985(4)	41(4)
C(33)	5498(7)	2959(6)	3941(4)	58(5)
C(34)	5953(6)	2610(6)	4332(5)	84(7)
C(35)	5540(8)	2374(6)	4768(5)	82(7)
C(36)	4670(8)	2487(6)	4812(4)	72(6)
C(41)	2975(7)	3369(5)	5110(4)	41(4)
C(42)	2157(6)	3596(6)	5184(4)	65(5)
C(43)	2002(6)	3932(6)	5646(5)	79(6)
C(44)	2665(8)	4042(6)	6034(4)	62(5)
C(45)	3483(7)	3815(6)	5960(4)	82(7)
C(46)	3638(6)	3479(5)	5498(5)	53(5)
C(51)	4102(5)	4550(5)	3961(4)	40(4)
C(52)	4710(7)	4682(5)	3590(3)	47(4)
C(53)	5578(6)	4679(5)	3753(4)	58(5)

Table 5 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/U_{\text{eq}}$
C(54)	5838(5)	4544(6)	4286(4)	59(5)
C(55)	5230(7)	4413(5)	4656(3)	52(5)
C(56)	4362(6)	4416(5)	4494(4)	44(4)
C(61)	2501(7)	5058(4)	4233(4)	40(4)
C(62)	1731(7)	4940(4)	4467(5)	56(5)
C(63)	1358(6)	5396(6)	4772(5)	69(6)
C(64)	1756(8)	5970(5)	4844(5)	74(6)
C(65)	2526(7)	6087(4)	4610(5)	65(5)
C(66)	2899(6)	5632(5)	4305(4)	49(4)
C(71)	3684(5)	4152(4)	2384(4)	33(4)
C(72)	3950(6)	3600(4)	2632(4)	45(4)
C(73)	4763(7)	3366(4)	2554(4)	55(5)
C(74)	5309(5)	3683(5)	2228(5)	57(5)
C(75)	5043(6)	4234(5)	1980(4)	57(5)
C(76)	4230(6)	4469(4)	2058(4)	42(4)
C(81)	2304(8)	5031(5)	2047(5)	46(4)
C(82)	2790(7)	5567(6)	2008(5)	58(5)
C(83)	2507(9)	6040(5)	1660(6)	83(7)
C(84)	1738(10)	5977(6)	1352(5)	96(8)
C(85)	1252(8)	5441(7)	1392(6)	98(8)
C(86)	1534(7)	4968(5)	1739(5)	72(6)
C(91)	2728(6)	3343(5)	1385(4)	43(4)
C(92)	2506(6)	3845(5)	1053(5)	58(5)
C(93)	3093(8)	4079(5)	706(4)	70(6)
C(94)	3902(7)	3812(6)	691(5)	72(6)
C(95)	4123(6)	3310(5)	1023(5)	59(5)
C(96)	3536(7)	3076(4)	1370(4)	47(4)
C(101)	975(7)	3036(6)	1395(5)	47(4)
C(102)	1019(7)	2763(6)	890(5)	65(5)
C(103)	288(10)	2727(7)	541(4)	88(7)
C(104)	-486(8)	2964(8)	698(6)	107(9)
C(105)	-530(7)	3238(7)	1203(7)	111(9)
C(106)	201(9)	3274(6)	1551(5)	73(6)
C(111)	670(6)	1647(6)	2225(4)	43(4)
C(112)	10(8)	1567(6)	2570(4)	71(6)
C(113)	-808(7)	1410(6)	2362(5)	75(6)
C(114)	-967(6)	1334(6)	1809(5)	87(7)
C(115)	-307(8)	1414(6)	1464(4)	72(6)
C(116)	511(7)	1570(6)	1672(4)	59(5)
C(121)	2282(7)	1090(4)	2467(5)	39(4)
C(122)	1815(5)	545(5)	2512(5)	60(5)
C(123)	2232(8)	-25(4)	2520(5)	74(6)
C(124)	3116(8)	-50(4)	2484(6)	85(7)
C(125)	3584(6)	495(6)	2440(5)	73(6)
C(126)	3167(6)	1065(5)	2431(5)	53(5)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

[30]. A complete list of bond lengths and angles, and tables of hydrogen atom coordinates and anisotropic displacement parameters, have been deposited at the Cambridge Crystallographic Data Centre. Lists of observed and calculated structure amplitudes are available from the authors on request.

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