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Note

Synthesis and X-ray structure of an octahedral platinum–silver cluster $[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Pt}_2\text{Ag}_4\text{Cl}_2(\text{C}_2\text{Ph})_8]$ with disordered silver atoms

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ABSTRACT

Variable-temperature X-ray structural study of the complex $[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Pt}_2\text{Ag}_4\text{Cl}_2(\text{C}_2\text{Ph})_8]$ prepared by the reaction of *cis*- $[\text{PtCl}_2(\text{AsPh}_3)_2]$ and $[(\text{Ph}_3\text{P})_2\text{N}][\text{Ag}(\text{C}_2\text{Ph})_2]$ in 1:2 M ratio, revealed isolated (non-polymerised) $[\text{Pt}_2\text{Ag}_4\text{Cl}_2(\text{C}\equiv\text{CPh})_8]^{2-}$ anions with a pseudo-octahedral arrangement of metal atoms. The Pt atoms (in mutually *trans* vertices) are each σ -bonded to four alkynyl ligands in a square planar arrangement; these moieties are bridged by four Ag atoms; each silver atom being η^2 -bonded to two alkynyl groups. Chloride ligands are asymmetrically bridging two opposite Ag–Ag edges. Silver atoms show strong and unusual temperature-dependent disorder.

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1. Introduction

The chemistry of metal acetylides has attracted enormous attention, in particular, with the emerging interest in their potential applications in the field of materials science. The linear geometry of the acetylide unit and its π -unsaturated nature have made metal acetylides attractive building blocks for molecular wires and organometallic oligomeric and polymeric materials which may possess important properties such as optical nonlinearity, electrical conductivity, and liquid crystallinity [1].

Although organometallic complexes of Group 11 metals with alkynyl ligands have been known for nearly 40 years [2], this field can still produce novel results. The alkynyl ligand has proved to be remarkably versatile in its coordinating abilities [3]. Many alkynyl-containing platinum complexes with coinage metals have been reported and several reviews discussing their structure and reactivity have appeared [4–10]. Here we describe the synthesis and structure of a new anionic bimetallic complex $[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Pt}_2\text{Ag}_4\text{Cl}_2(\text{C}_2\text{Ph})_8]$ (1).

2. Experimental

2.1. General

Melting points were determined using an electrothermal IA 9000 digital capillary melting point apparatus. IR spectra were re-

corded in KBr pellets on a 1000-Perin Elmer FT-IR spectrophotometer. ^1H NMR spectra were obtained on JEOL ECP-400 NMR spectrometer in CDCl_3 using TMS as an internal standard. Chemical shifts are given in δ . The ESI mass spectrometry experiments were performed on a Q-ToF Premier (Waters) mass spectrometer. Mass spectra were acquired in the negative mode using methanol as the mobile phase, with the sample injection rate of 5 $\mu\text{l}/\text{min}$ and the ESI ion spray source voltage of 3.0 kV.

2.2. Complex preparations

2.2.1. Synthesis of *cis*- $[\text{PtCl}_2(\text{AsPh}_3)_2]$ (2)

The compound was prepared by the same method as had been using for the preparation of $[\text{PtCl}_2(\text{PPh}_3)_2]$ [11]. A solution of chloroplatinic acid (3 g of $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, 39.9% Pt, 6.12 mmol) in ethanol (100 cm^3) was refluxed with triphenylarsine (5.62 g, 18.36 mmol). After 1 h, the reaction mixture was filtered and the off-white precipitate washed with ethanol, yielding **2** (5.35 g, 99.63%).

2.2.2. Synthesis of $(\text{PPN})[\text{Ag}(\text{C}_2\text{Ph})_2]$ (3)

This compound was prepared by the literature method [12]. Triphenylphosphine, PPh_3 , (3.93 g, 15 mmol) was added to a stirred suspension of silver phenylacetylide (2.09 g, 10 mmol) in acetone (100 cm^3), a heavy precipitate of $[\text{Ag}(\text{C}_2\text{Ph})(\text{PPh}_3)]$ forming immediately. After stirring for 30 min, $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ (2.87 g, 5 mmol) was added with stirring and a white grey precipitate formed. After stirring for another 30 min, the precipitate was filtered off and identified as $[\text{ClAg}(\text{PPh}_3)_3]$ (4). The filtrate was evaporated to

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Table 1
Crystal data of **1**.

T (K)	100	120	200	293 ^c
<i>a</i> (Å)	12.6033(4)	12.6171(6)	12.6673(4)	12.7427(6)
<i>b</i> (Å)	14.5535(5)	14.5520(6)	14.5568(4)	14.5589(8)
<i>c</i> (Å)	30.4508(11)	30.4985(13)	30.6991(10)	30.9514(17)
β (°)	101.424(13)	101.513(6)	101.708(14)	102.125(6)
<i>V</i> (Å ³)	5474.7(3)	5487.0(4)	5543.0(3)	5614.1(5)
Number of reflections, total	54457	90454	68260	91473
Number of reflections, unique	15848	15995	16088	16325
<i>R</i> _{int}	0.062	0.054	0.049	0.033
ρ_{calcd} (g cm ⁻³)	1.686	1.682	1.665	1.644
μ (mm ⁻¹)	3.41	3.40	3.37	3.32
Transmission, minimum/maximum	0.441, 0.694	0.522, 0.733	0.460, 0.691	0.551, 0.746
<i>R</i> ₁ ^a	0.030	0.028	0.031	0.024
<i>wR</i> ₂ ^b	0.070	0.061	0.070	0.054

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, reflections with $I \geq 2\sigma(I)$.^b $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$, all data.^c The unit cell setting is chosen for compatibility with low-temperature data; the reduced cell corresponds to the space group $P2_1/c$, $a = 12.7427(6)$, $b = 14.5589(8)$, $c = 30.898(2)$ Å, $\beta = 101.65(1)^\circ$.

dryness, the residue was washed with toluene (100 cm³) to remove any remaining **4** and then re-dissolved in acetone (40 cm³). Addition of hexane to the filtrate gave white woolly crystals of **3** (3.85 g, 91%), m.p. 130 °C, $\nu(\text{C}\equiv\text{C})$ 2085 cm⁻¹.

2.2.3. Synthesis of (PPN)₂[Pt₂Ag₄(C₂Ph)₈Cl₂] (**1**)

To a colourless solution of **2** (0.060 g, 0.068 mmol) in 20 ml of CH₂Cl₂, 0.116 g (0.137 mmol) of **3** was added. The solution was stirred in the dark for 24 h, acquiring yellow colour, was then evaporated to dryness and re-dissolved in CHCl₃. Adding hexane precipitated yellow crystals of **1** (0.045 g, 47%), m.p. 180 °C. *Anal.* Calc. for C₁₃₆H₁₀₀N₂P₄Cl₂Ag₄Pt₂: C, 58.79; H, 3.63; Ag, 15.53; Pt, 14.04. Found: C, 58.67; H, 3.59; Cl, 2.64; Ag, 14.50; Pt, 13.9%. IR (cm⁻¹): $\nu(\text{C}\equiv\text{C})$ 2055. ¹H NMR (δ , ppm, CDCl₃): 7.1–7.21 (m, Ph of [Pt₂Ag₄(C₂Ph)₈Cl₂]²⁻), 7.63–7.67 (m, Ph of PPN). ESI-MS (*m/z*): molecular peak of the anion not observed, *m/z* 1666 [Pt₂Ag₄(C₂Ph)₈Cl]⁻ (27%); *m/z* 1523 [Pt₂Ag₃(C₂Ph)₈]⁻ (100%); *m/z* 179 [AgCl₂]⁻ (100%).

2.3. X-ray crystallography

The X-ray diffraction experiment was repeated at four temperatures ($T = 100, 120, 200$ and 293 K) on a Bruker 3-circle diffractometer with a SMART 6000 CCD area detector, using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) and a Cryostream (Oxford Cryosystems) open-flow N₂ cryostat. Full

sphere of the reciprocal space was covered with narrow-frame (0.3°) ω scans. Reflection intensities were integrated using SAINT 6.45A software [13] and corrected for absorption by Gaussian integration based on crystal face-indexing [14]. Crystal data: [C₆₄H₄₀Ag₄Cl₂Pt₂]²⁻(C₃₆H₃₀NP₂)₂⁺, $M = 2778.62$, monoclinic, space group $P2_1/n$ (No. 14, non-standard setting), $Z = 2$, for other parameters see Table 1. The structure was solved by a combination of Patterson and direct methods and refined by full-matrix least squares against F^2 of all reflections, using OLEX2 [15] and SHELXTL 6.14 [16] software.

3. Results and discussion

The asymmetric unit of **1** comprises one Ph₃PNPPh₃⁺ cation in a general position and half of the [Pt₂Ag₄Cl₂(C≡CPh)₈]²⁻ anion located at a crystallographic inversion centre. The anion (Fig. 1) contains two square-planar Pt(C≡CPh)₄ units, bridged by four silver atoms, each of the latter coordinating in a η^2 fashion two acetylene moieties of different Pt(C≡CPh)₄ units. These units are almost eclipsed, if viewed down the Pt–Pt vector, with the C α –Pt–Pt–C α torsion angles of. The six metal atoms form a distorted octahedron with Pt atoms in the mutually *trans* disposition and four Ag atoms in the equatorial plane. Two opposite Ag–Ag edges bear asymmetric μ_2 chloro bridges, coplanar with the Ag₄ tetragon. Thus the anion can be described as the dichloro-derivative of the neutral [Pt₂Ag₄(C≡CPh)₈] complex (**5**), prepared earlier

Table 2
Selected bond distances (Å) in the anion of **1**.

T (K)	100	120	200	200 ^a	200 ^b	293	293 ^a	293 ^b
Pt–Pt'	4.2400(4)	4.2353(3)	4.2472(5)			4.2513(5)		
Pt–Ag(1)	3.2612(6)	3.2473(5)	3.341(3)	3.204(2)	3.017(2)	3.375(6)	3.176(2)	3.002(2)
Pt–Ag(2)	3.2097(16)	3.2082(8)	3.078(3)	3.281(3)	3.295(3)	3.076(9)	3.213(6)	3.329(3)
Pt–Ag(1')	3.2923(6)	3.2885(5)	3.417(3)	3.265(2)	3.055(2)	3.472(6)	3.275(3)	3.053(2)
Pt–Ag(2')	3.3635(16)	3.3750(8)	3.265(3)	3.489(3)	3.477(3)	3.331(9)	3.444(6)	3.547(3)
Ag(1)–Ag(2)	2.8398(13)	2.8388(7)	2.758(4)	2.935(4)	2.883(3)	2.80(1)	2.859(8)	2.908(4)
Ag(1)–Ag(2')	4.1289(15)	4.1286(9)	4.162(4)	4.149(4)	3.876(3)	4.26(1)	4.092(8)	3.934(4)
Pt–C(1)	1.996(3)	2.005(3)	2.002(3)			2.002(2)		
Pt–C(3)	2.000(3)	2.002(3)	2.010(3)			2.009(2)		
Pt–C(5')	1.994(3)	1.993(3)	1.997(3)			1.997(2)		
Pt–C(7')	2.010(3)	2.011(3)	2.015(3)			2.014(2)		
Ag(1)–Cl	2.675(1)	2.7227(8)	2.479(5)	2.904(5)	3.434(4)	2.481(5)	2.960(2)	3.529(2)
Ag(2)–Cl	2.929(1)	2.9335(9)	3.146(4)	2.839(4)	2.471(3)	3.18(1)	2.888(8)	2.420(2)
C≡C, av.	1.225(4)	1.223(4)	1.219(7)			1.213(3)		
(≡)C–C(Ph)	1.445(4)	1.444(3)	1.443(4)			1.442(3)		

^a For Ag(1) and Ag(2) read Ag(3) and Ag(4).^b For Ag(1) and Ag(2) read Ag(5) and Ag(6).

[17] and shown by X-ray diffraction study of **5** CHCl_3 [18] also to have crystallographic C_i symmetry and eclipsed conformation. On the contrary, its apparent analogue $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{CBu}^t)_8]$ (**6**) contains a similar Pt_2Ag_4 octahedron but has overall C_2 symmetry with staggered $\text{Pt}(\text{C}\equiv\text{CPh})_4$ units ($\text{C}_\alpha\text{--Pt--Pt--C}_\alpha$ torsion angles 37.1° and 32.8°) [17]. It is noteworthy that the anion of dichlorinated **6**, similar to **1** in composition, has been isolated as the $(\text{NBu}_4)_2[\text{Pt}_2\text{Ag}_4\text{Cl}_2(\text{C}\equiv\text{CBu}^t)_8]$ salt, although not characterised structurally [19]. Neutral $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{CR})_8]$ clusters in the solid state tend to oligomerise through Pt–Pt bonding [10], unless the axial sites of Pt atoms are masked by solvent of crystallisation [10,18]. No such oligomers are found in the crystal of **1**, the anions being effectively separated by the cations' phenyl groups.

The intramolecular Pt–Ag distances in **1** (see Table 2) are generally longer than in **5** (2.965(1) to 3.283(1) Å, mean 3.12(11) Å). The Cl-bridged Ag–Ag edges in **1** are much shorter than the unsupported ones, whereas in **5** all Ag–Ag distances are similar (3.169(1) to 3.232(1) Å, mean 3.19(3) Å). All these distances (except the longer Ag–Ag in **1**) are shorter than the sums of van der Waals radii, variously estimated as 2.10 Å [20,21] or 2.11 Å [21] for Ag, 2.05 Å [20], 2.09 Å [21] or 2.13 Å [22] for Pt, or 1.72 Å for both [23]. Thus, a degree of direct metal–metal bonding is possible. (See Fig. 1).

A prominent feature of **1**, not found in **5**, is the intense disorder of silver atoms. At 100 K it was approximated by two alternative positions for each silver atom; the occupancy factors were optimised (by trial and error) as 0.85 for the major positions [Ag(1) and Ag(2) with their inversion equivalents Ag(1') and Ag(2')], and 0.15 for the minor ones [Ag(3) and Ag(4) with their equivalents Ag(3') and Ag(4')]. Furthermore, the refinement of both major and minor positions gave large atomic displacement parameters: the equivalent isotropic U (U_{eq}) exceeded those of the bonded carbon atoms by a factor of 1.7 or more. The displacement ellipsoids of the silver atoms were strongly elongated in the direction tangential to the Ag_4 tetragon. Given the low temperature and large atomic mass, such displacement parameters can only indicate further static disorder, probably of the continuous kind (within a wide flat-bottomed potential well), rather than genuine thermal vibrations. The disorder can be described as libration of the entire Ag_4 tetragon within its own plane while the Cl ligands (as well as $\text{Pt}(\text{C}\equiv\text{CPh})_4$ units) stay put; thus the libration results in a switch in the chloro-bridge asymmetry, from $\text{Ag}(1)\text{--Cl}\cdots\text{Ag}(2)$ to $\text{Ag}(3)\cdots\text{Cl}\cdots\text{Ag}(4)$.

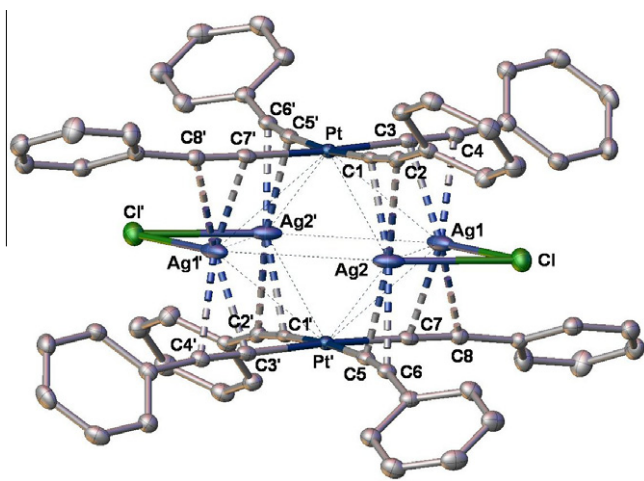


Fig. 1. Anion of **1** at 100 K. Minor positions of the disordered silver atoms and all hydrogen atoms are omitted for clarity. Here and below, atomic displacement ellipsoids are drawn at the 50% probability level, primed atoms have been generated by the inversion centre.

Essentially the same picture was observed at 120 K, except that the best-fit occupancies for the silver atoms were 0.83 and 0.17. At 200 K the disorder was of the same nature but much more intense; it was modelled by three sets of silver atom positions. Least squares refinement of the occupancies [with the anisotropic atomic displacement parameters constrained to equality for Ag(1), Ag(3), Ag(5) and for Ag(2), Ag(4), Ag(6)] converged at 0.282(4) for Ag(1) and Ag(2), 0.386(5) for Ag(3) and Ag(4), 0.324(3) for Ag(5) and Ag(6). At 293 K, a similar model of disorder was used, with occupancies optimised to 0.24 for Ag(1) and Ag(2), 0.34 for Ag(3) and Ag(4), 0.42 for Ag(5) and Ag(6).

The disorder at different temperatures is illustrated in Fig. 2. It is well known that X-ray diffraction gives the structure averaged both in time (thermal motion, dynamic disorder) and in space, i.e. over the whole crystal sample (static disorder). When a study is carried out at one temperature only, it is very difficult to distinguish between the two types of atomic displacements. However, a

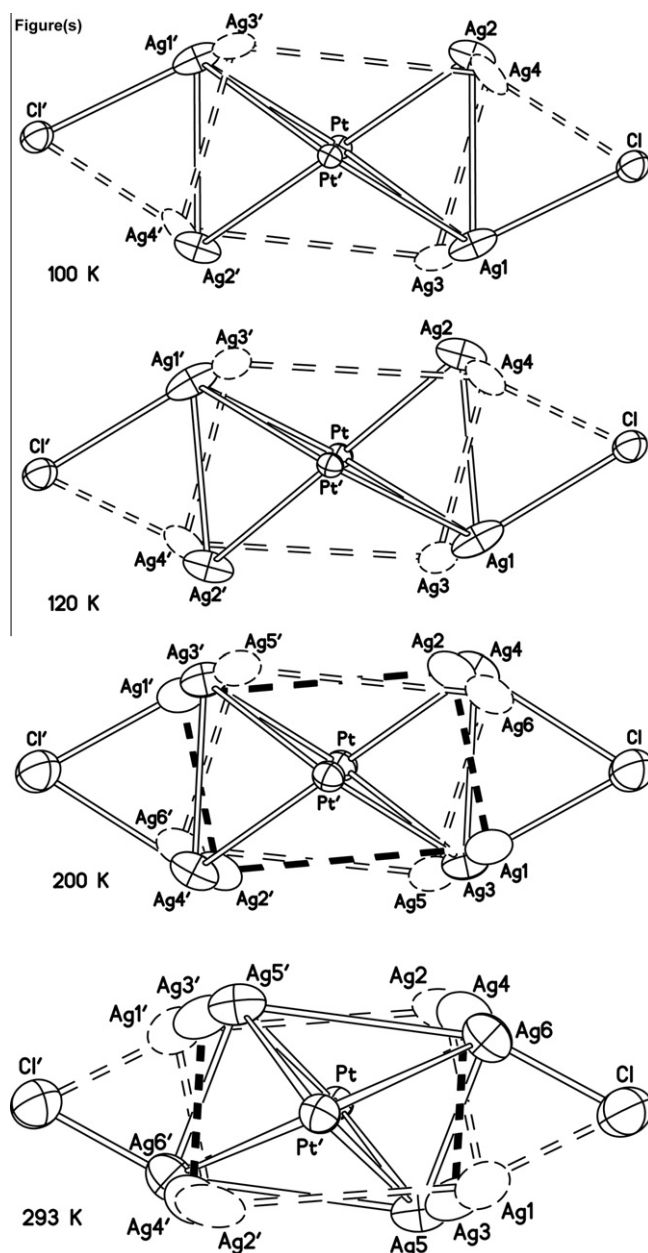


Fig. 2. Metal cluster of **1** at different temperatures, showing the disorder.

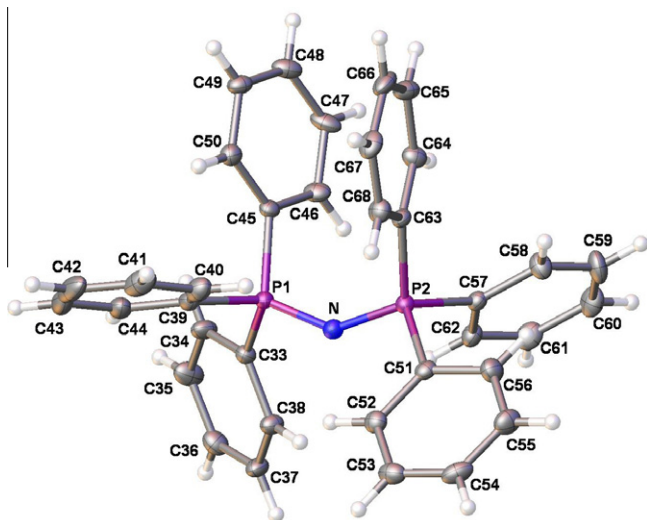


Fig. 3. Cation of **1** at 100 K.

variable-temperature study permits to resolve this problem, since thermal motion diminishes on cooling while static disorder does not. The present results show that the disorder clearly intensifies with the increase of temperature. However, even at low temperatures it remains much stronger than could be expected for the purely dynamic disorder. Thus, both types of disorder may be present simultaneously.

It is noteworthy that although no explicit disorder was observed in **5** (at 150 K), in **6** (at room temperature) one independent molecule has the silver atoms ordered and the other disordered (in the 0.92:0.08 ratio) between two sets of 'holes' which are widely separated but have essentially identical environment, due to staggered conformation of the $\text{Pt}(\text{C}\equiv\text{CPh})_4$ units.

The cation of **1** (Fig. 3) has usual geometry [24], identical in all three studies within experimental errors; N–P distances and P–N–P average 1.578(2) Å and 142.0(2)°, respectively.

4. Conclusions

The reaction of *cis*-[PtCl₂(AsPh₃)₂] with [(Ph₃P)₂N][Ag(C₂Ph)₂] yielded a new example of alkynyl- and chloride-bridged pseudo-octahedral Pt₇Ag₄ cluster complex. An unusual disorder of the

silver atoms deserves further investigation, probably by means of solid-state NMR, making use of the fact that both ^{107}Ag and ^{109}Ag isotopes have NMR-active nuclei.

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Appendix A. Supplementary material

CCDC 808939, 808940, 808941 and 808942 contain the supplementary crystallographic data for complex **1** at 100, 120, 200 and 293 K, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2011.08.046](https://doi.org/10.1016/j.ica.2011.08.046).

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