

Bimetallic Organoplatinum(II)-Ag(I) Cluster Cations with Ag-Pt Interactions Unsupported by Conventional Bridging Ligands

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Dedication ((optional))

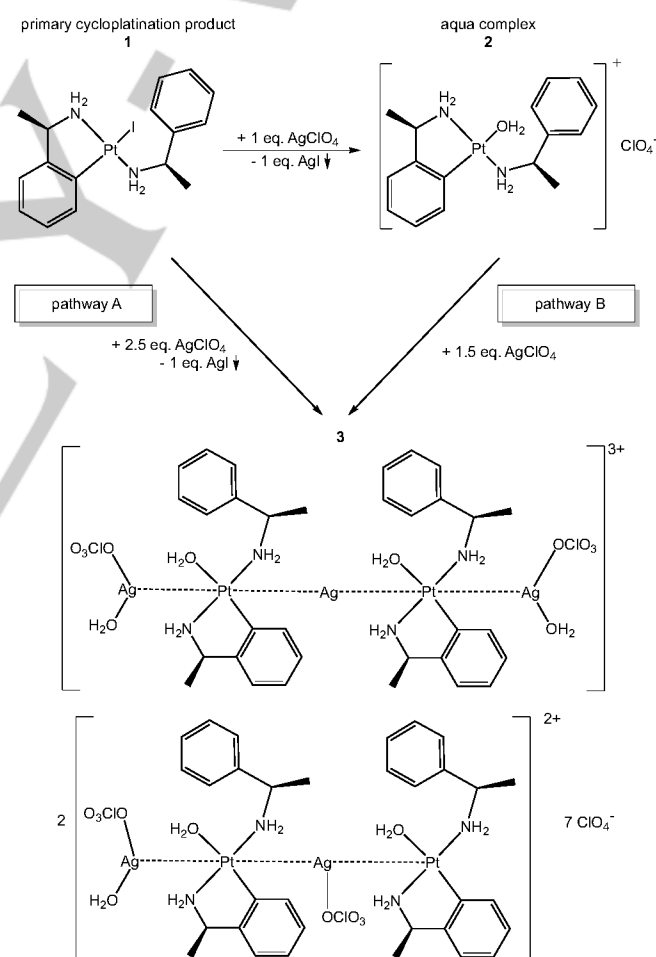
Abstract: The organoplatinum complex of a primary amine and AgClO_4 aggregate in methanol to oligonuclear mixed-metal species. A perchlorate salt **3** with the empirical formula $\text{C}_{96}\text{H}_{146}\text{Ag}_7\text{Cl}_{13}\text{N}_{12}\text{O}_{62}\text{Pt}_6$ could be isolated and structurally characterized with the help of X-ray diffraction at the DESY synchrotron. The product contains both a penta- and a tetra-nuclear complex cation in which Ag(I) and Pt(II) alternate, held together without any conventional bridge. The cationic species feature short $\text{Ag}\cdots\text{Pt}$ distances between 2.7 and 2.9 Å and contacts longer than 2.4 Å between Ag and C atoms in aromatic rings. In addition to the interactions with Ag(I) cations, Pt(II) is in a square-planar arrangement, coordinated by a chelating and a terminal amine and an aqua ligand. The central Ag(I) in the pentanuclear cation is located on a twofold crystallographic axis and not involved in any obvious coordinative bond; it exclusively shows short contacts to the neighboring Pt(II) ions and the Pt-bonded, formally anionic carbon atoms of the cyclometallated organic ligand. Powder diffraction shows that **3** melts and re-solidifies without decomposition.

Introduction

Orthometallation of activated benzyl amines with palladium and platinum was discovered by Cope and Friedrich in 1968 [1]. The reaction with palladium was soon expanded to a wider range of substrates [2-7]. Our group focused on the structural characterization of intermediates along the reaction pathway [8,9] and reported the first *trans* configured cyclopalladated amine [10]. Cyclopalladated primary amines with different substitution patterns proved suitable building blocks for the construction of quasiracemic solids [11,12].

In contrast to the flourishing field of cyclopalladation, progress in cycloplatination was modest until 2007 [13]. In 2008, we reported the first convenient route to cycloplatination of primary amines via a mixed-valent platinum iodide precursor [14]. This reaction paved the way to a new class of compounds: The σ

donor and iodo ligands in the primary cycloplatination product **1** (Scheme 1) may be substituted [14,15], a chelating ligand may replace these two monodentate substituents [16], and Pt(IV) complexes are accessible via oxidative addition [17]. Dehalogenation of **1** with the Ag(I) salt of a weakly coordinated anion affords the aqua complex **2** [15]. We here report the surprising results of the reaction between **1** or **2** with AgClO_4 : reaction in methanol leads to a perchlorate salt with mixed-metal oligonuclear cluster cations, **3** (Scheme 1).



Scheme 1. Organoplatinum complexes involved in the synthesis and oligonuclear cations in the target compound **3**.

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Results and Discussion

The title compound **3** was first obtained as a by-product: it forms when an excess of silver perchlorate is used in the dehalogenation of **1** to the aqua complex **2**. After its discovery, we have then been able to obtain **3** as the main product of two alternative rational synthetic procedures: It is either available via dehalogenation of the primary cycloplatination product **1** (pathway A in Scheme 1) or via aggregation of AgClO₄ with the organoplatinum complex **2** (pathway B). In either case, a slight excess to the stoichiometrically required amount of AgClO₄ is advisable. The combination of small crystals with a relatively large unit cell, heavy atoms and slight disorder (see Experimental) precluded collection of satisfactory intensity data at the home laboratory and required access to a more brilliant radiation source. **3** is derived of enantiopure starting materials and hence necessarily crystallizes in a Sohncke group. The asymmetric unit contains a pentanuclear cation with the central Ag(I) and a disordered perchlorate counter anion on twofold axes and a tetranuclear cation and three perchlorate anions in general position of the chiral space group C₂; these residues have been assigned different colours in the packing diagram in Fig. 1.

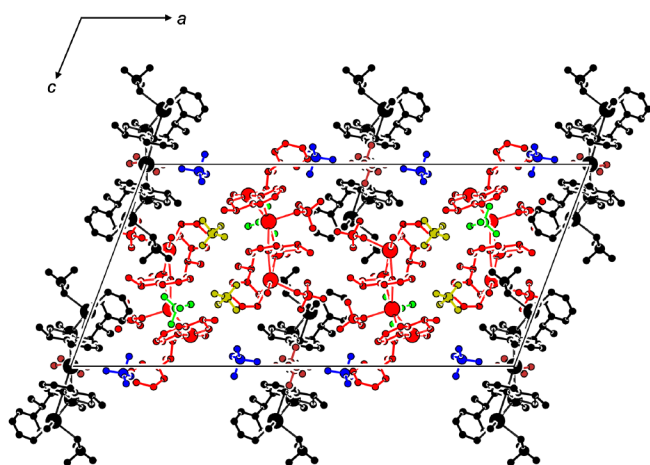


Figure 1. Packing in **3** along [0 1 0]; the pentanuclear cationic residue has been depicted in black, the tetranuclear residue in red, perchlorate counteranions in other colours.

At least three features of crystalline **3** are highly uncommon: The first exciting aspect are the ligand-unsupported contacts between metal cations. Fig. 2 shows that the silver ions "sandwiched" between two Pt neighbors, *i.e.* Ag1 in the tetranuclear and Ag3 in the pentanuclear cluster, subtend the shortest Ag-Pt bonds (Pt-Ag < 2.8 Å). In contrast, the intermetal distances to the peripheral silver cations Ag2 and Ag4 are longer than 2.9 Å. Contacts to their Ag neighbors apart, all Pt ions are in square-planar coordination and the peripheral silver ions bind to an aqua ligand and a perchlorate. A perchlorate anion is the only conventional coordination partner for Ag1 in the tetranuclear cluster, whereas the central Ag3 in the pentanuclear residue only interacts with its Pt neighbors and the formally anionic C33 of the cyclometallated

ligand. The distance to two perchlorate oxygen atoms, O22 and its symmetry equivalent (dashed lines in Fig. 2), is longer than 3 Å and corresponds to a favourable electrostatic interaction rather than a coordinative bond. We have previously addressed such ambiguities in coordination compounds [18]. **3** features 22 hydrogen atoms attached to nitrogen or oxygen and hence suitable for classical hydrogen bonds; all find at least one oxygen acceptor in an appropriate distance. A summary of all hydrogen bonds is available in the supporting information. These interactions link the ionic residues in **3** to a three-dimensional hydrogen-bonded network.

In addition to the obvious metal-metal bonds, we explicitly mention the shortest contacts between Ag(I) cations and C atoms of the Pt-bonded organic ligands of 2.4 - 2.5 Å. They are substantially longer than the Pt-C bonds (< 2.0 Å) but still fall into the range of previously reported distances between silver cations and aromatic π systems [19]. These contacts have been included as dashed lines in Figs. 2 and 3, and a compilation of all relevant interatomic distances and angles is provided in the Supporting Information.

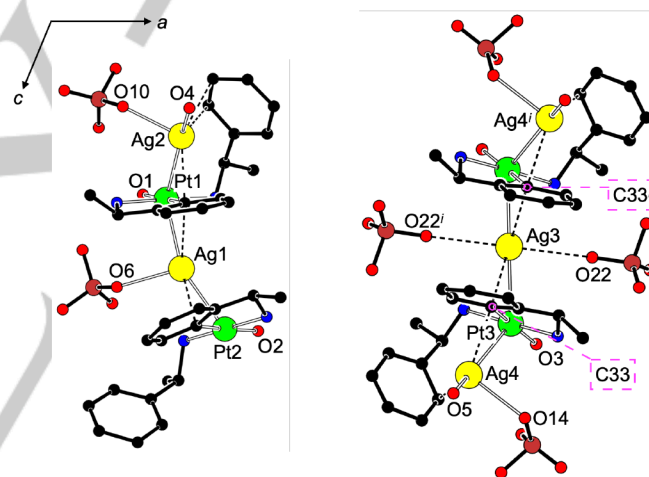


Figure 2. Tetranuclear (left) and pentanuclear (right) cationic mixed-metal clusters in **3** along [0 1 0]; symmetry operator: $i = -x, y, -z$. Selected interatomic distances and angles: Ag1-Pt1 2.7213(17), Ag1-Pt2 2.7839(18), Ag2-Pt1 2.908(18), Ag3-Pt3 2.776(16), Ag4-Pt3 2.9138(19), Ag3-C33 2.448(10) Å, Ag1-Pt1-Ag2 121.45(4), Pt1-Ag1-Pt2 141.98(5), Ag3-Pt3-Ag4 116.18(4), Pt3-Ag3-Pt3' 151.41(9)°.

Although the short Ag-Pt contacts unsupported by conventional bridging ligands are unexpected, they are not entirely unprecedented: we are aware of a closely related pentanuclear cationic Ag-Pt cluster reported by Yamaguchi *et al.* [20]. Intermetal distances are similar to the situation in **3**, but in contrast to our pentanuclear Ag₃Pt₂ cluster, the metal cation sequence is Pt-Ag-Pt-Ag-Pt and thus corresponds to a composition Ag₂Pt₃. The authors of this earlier communication interpreted the metal...metal interactions as strong dative Pt(II) → Ag(I) bonds. An extended structure with overall neutral heterometallic chains of alternating Pt(II) and Ag(I) cations [21] shows similar geometry as the cationic clusters in **3**, in particular with respect to Pt-Ag

distances and angles subtended by the noble metal cations. In contrast to the interpretation given above, these authors emphasize the secondary $\text{Ag}\cdots\text{C}$ contacts in the distance range 2.4–2.5 Å as relevant for intrachain bonding. In our compound **3**, both interactions, metal \cdots metal bonds and $\text{Ag}\cdots\text{C}\cdots\text{Pt}$ contacts, stabilize the oligonuclear cluster cations. Fig. 3 shows the short contacts between Ag1 and the neighbouring π systems in the tetranuclear cluster; the environments for the other Ag(I) cations in **3** are similar.

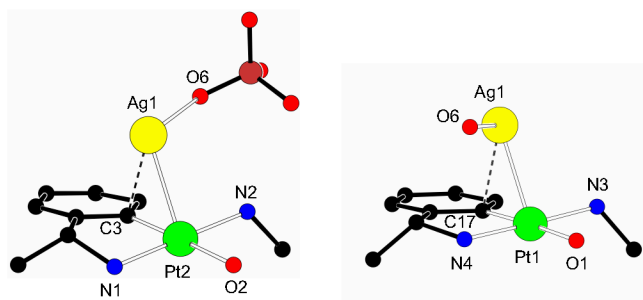


Figure 3. Left: Shortest $\text{Ag}\cdots\text{C}$ contact in **3**. Selected interatomic distances and angles: Ag1–Pt2 2.7839(18), Ag1–C3 2.421(11) Å, Ag1–Pt2–C3 58.2(3), Ag1–Pt2–N1 96.7(2), Ag1–Pt2–N2 83.9(3), Ag1–Pt2–O2 121.8(3)°. Right: A significantly longer $\text{Ag}\cdots\text{C}$ contact, also involving Ag1. Selected interatomic distances and angles: Ag1–Pt1 2.7213(15), Ag1–C17 2.602(10) Å, Ag1–Pt1–C17 65.0(3), Ag1–Pt1–N4 89.2(3), Ag1–Pt1–N3 89.8(3), Ag1–Pt1–O1 116.2(3)°.

Ag1 does not occupy an exactly apical position, neither on top of the coordination plane about Pt2 or Pt1 but is significantly shifted towards the metal-bonded carbon atoms C3 or C17. This shift is more pronounced for the Ag1 \cdots Pt2 bond (Fig. 3, left) in which the π interaction between Ag and the neighbouring aromatic system is stronger and the angle C–Pt–Ag more acute than for Ag1 \cdots Pt1 (Fig. 3, right). In view of the similar metal radii for Pt (1.385 Å) and Ag (1.442 Å) [22], it is tempting to compare the Pt–Ag distances in **3** with the ligand-unsupported Pt–Pt interactions in the Krogmann salts [23–27]. Partial oxidation of $\text{K}_2[\text{Pt}(\text{CN})_4]$ with chlorine or bromine leads to column of square-planar Pt complexes in which the incompletely filled dz^2 orbitals are engaged in metal-metal bonds. The Pt–Pt distances observed in $\text{K}_2[\text{Pt}(\text{CN})_4]\text{X}_{0.3}$ (X = Cl, Br) are slightly shorter than 2.9 Å [26], quite close to the Ag–Pt bonds in **3**.

We shortly address the remaining compounds with unbranched one-dimensional $\text{Ag}\cdots\text{Pt}$ sequence and intermetal distances shorter than 3 Å. They feature bridging ligands such as amidate [28–30] which link neighboring cations.

Short metal \cdots metal contacts apart, a second remarkable feature of **3** is its unusual composition. The concomitant presence of tetra- and pentanuclear mixed-metal cluster cations is easily reproducible but we cannot offer a simple explanation for this unexpected stoichiometry. Fortunately, the crystalline salt offers at least two obvious sites for minor chemical changes: the perchlorate anions may be replaced by alternative counteranions, and the organoplatinum building block may be prepared with a range of substituted phenylethylamine derivatives [14].

Systematic studies in this context will, however, be associated with extensive synthetic work in organometallic chemistry.

Our salt **3** had yet another surprise in store: crystalline material turns liquid at 115 °C, and we first expected decomposition. An X-ray powder pattern of a molten and re-solidified sample does, however, closely match the simulated pattern based on the structure model from single crystal diffraction (Fig. 4).

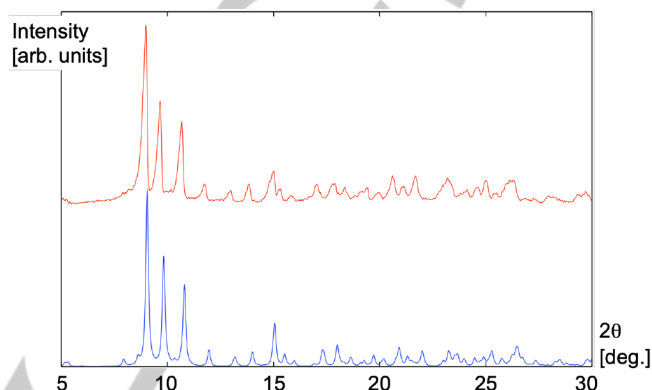


Figure 4. Powder pattern of a molten and re-solidified sample (red) of **3**, collected at ambient temperature, and simulated powder pattern (blue) based on the single crystal diffraction experiment conducted at 100 K.

This unexpected result suggests to attempt a structural characterization of the melt; in particular, we wish to clarify whether **3** retains the oligonuclear building blocks in the liquid phase or whether the melt simply represents a mixture of organoplatinum and silver cations and perchlorate counter anions. Such a structural study of the liquid phase can obviously not rely on diffraction; we will come back to this aspect in the following section, Conclusions and future work.

Conclusions and future work

We have synthesized and structurally characterized oligonuclear Ag(I)/Pt(II) clusters in which the constituents are bonded through metal \cdots metal and $\text{Ag}(\text{I})\cdots\pi$ interactions, without any conventional bridging ligand. As such compounds are very rare, the question about a potentially more general approach arises. Mononuclear derivatives of the organoplatinum constituents with similar steric requirements can be synthesized [14] – can they act as alternative building blocks and, combined with Ag(I) cations from salts with weakly or non-coordinating anions, afford oligonuclear clusters as well? Substitution might lead to products with different nuclearity or to the formation of extended structures.

In future work we will attempt to characterize the Ag–Pt bonds with the help of an alternative toolbox: **3** melts without decomposition, and a structural characterization of the melt and of potentially related non-crystalline adducts might be achieved by edge spectroscopy. EXAFS can in principle identify short intermetal contacts in liquid phase, and XANES may give insight

into the spectroscopic oxidation state of formally monovalent Ag cations in **3** and suitable reference compounds. In this context proposals for beamtime at synchrotron facilities have been submitted.

Experimental Section

Synthesis and crystallization

Caution! Although we never encountered any problem in our syntheses with AgClO_4 , it should be noted that perchlorates represent a safety hazard when mixed with combustibles. We recommend not to upscale the reactions reported here.

a) 0.3 mmol (169 mg) of the primary cycloplatinated complex **1** were dissolved in 15 ml of MeOH at 40 °C. A solution of 0.75 mmol (155.5 mg) AgClO_4 in 2 ml of MeOH was added. Immediately, a substantial amount of AgI precipitated. The mixture was filtered, and the solvent was partially removed. The residual viscous solution with a volume of ca. 5 ml was transferred into a desiccator. After 2 d, a colourless and hygroscopic solid formed which should be kept in the desiccator. The product may be re-crystallized from methanol. Yield: 223.7 mg of **3** (92 % with respect to Pt).
b) 0.14 mmol (74.8 mg) of the aqua complex **2** were dissolved in 5 ml of MeOH at 40 °C. A solution of 0.20 mmol (42 mg) AgClO_4 in 1 ml of MeOH was added. The mixture was stirred for 5 minutes, and concentrated to 1 ml in a rotatory evaporator. Colourless crystals precipitated after one night; they were dried and kept in a desiccator. The product may be re-crystallized from methanol. Yield: 100.3 mg of **3** (86 % with respect to Pt). Microanalytical data for **3**: $\text{C}_{96}\text{H}_{146}\text{Ag}_7\text{Cl}_{13}\text{N}_{12}\text{O}_{62}\text{Pt}_6$ (4846.72); C 22.86 (calc. 23.79); H 2.78 (3.04); N 3.32 (3.47)%.

Fig. 5 shows that the crystalline powder of **3** as-synthesized essentially corresponds to the phase identified by single crystal diffraction.

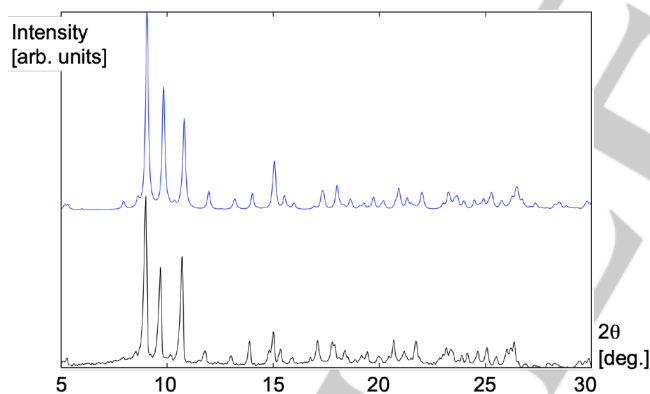


Figure 5. Experimental powder pattern (black) collected at ambient temperature, and simulated powder pattern (blue) based on the single crystal diffraction experiment conducted at 100 K.

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the methanol mother liquor at ambient temperature after ca. 5 d.

Surprisingly, solid **3** does not decompose but melts at 115 °C. The identity of a molten and then re-solidified sample was controlled by powder diffraction (Fig. 4).

Powder diffraction

Powder patterns were recorded on flat samples at room temperature using a STOE STADI-P diffractometer with Guinier geometry (Cu-K α 1, λ = 1.54059 Å, Johann germanium monochromator, STOE image plate detector IP-PSD, 0.005° step width in 2θ).

Single crystal diffraction

$\text{C}_{96}\text{H}_{146}\text{Ag}_7\text{Cl}_{13}\text{N}_{12}\text{O}_{62}\text{Pt}_6$, unit cell a = 36.524(19), b = 11.758(5), c = 17.739(7) Å, β = 110.56(3)°, V = 7133(6) Å³, Z = 2, d_{calc} = 2.257 g cm⁻³, μ = 2.839 mm⁻¹, monoclinic space group C2. Synchrotron data were collected at the DESY Hamburg, beamline P24 for chemical crystallography at PETRA-III on the κ diffractometer (station EH1) at a photon energy of 24.8 keV (λ = 0.50014 Å) with a Dectris CdTe 1M area detector on a colourless rod with dimensions 0.06·0.03·0.03 mm at 100(2) K. Data were processed with XDS [31] and corrected for absorption according to the multi-scan approach with SADABS [32]. 130924 reflections with $\theta < 22.5^\circ$ were collected in ω scan mode in the index range $-55 \leq h \leq 55$, $-17 \leq k \leq 17$, $-27 \leq l \leq 27$, 26735 symmetry-independent reflections (R_{int} = 0.0551). The structure was solved by intrinsic phasing [33] and refined by full-matrix least-squares [34]. One of the uncoordinated perchlorate counter anions showed disorder about a twofold axis. Non-H atoms were refined anisotropically. H atoms attached to O were located in differences Fourier syntheses or placed to match obvious donor...acceptor geometries; H atoms attached to N and C were introduced in calculated positions. All H atoms were treated as riding, with $U_{\text{iso}}(\text{H})$ constrained to a multiple of the parent atom. Final refinement results: 757 refined parameters, $wR2$ = 0.1337, $R1$ = 0.0480, GOF = 1.091.

Crystal data, data collection parameters and convergence results are summarized in tabular form in the supporting information. Crystallographic data (including structure factors) for **3** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2142579. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) + 44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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Keywords: heterometallic cluster • oligonuclear cations • metal-metal bonds • synchrotron data collection • organoplatinum chemistry

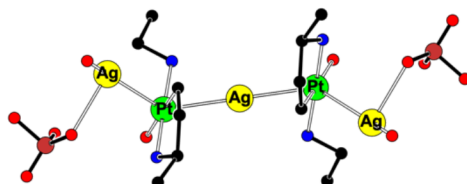
- [1] A. C. Cope, E. C. Friedrich, *J. Am. Chem. Soc.* **1968**, 90, 909-913.
- [2] B. N. Cockburn, D. V. Home, T. Keating, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Dalton Trans.* **1973**, 404-410.
- [3] V. V. Dunina, O. A. Zalevskaya, V. M. Potapov, *Russ. Chem. Rev.* **1988**, 57, 250-269.
- [4] A. Avshu, R. D. O'Sullivan, A. W. Parkins, N. W. Alcock, R. M. Countryman, *J. Chem. Soc. Dalton Trans.* **1983**, 1619-1624.
- [5] Y. Fuchita, H. Tsuchiya, *Inorg. Chim. Acta* **1993**, 209, 229-30.
- [6] Y. Fuchita, K. Yoshinaga, Y. Ikeda, J. Kinoshita-Kawashima, *J. Chem. Soc. Dalton Trans.* **1997**, 2495-2499.
- [7] J. Vicente, I. Saura-Llamas, P. G. Jones, *J. Chem. Soc. Dalton Trans.* **1993**, 3619-3624.
- [8] B. Calmuschi, U. Englert, *Acta Crystallogr. Sect C* **2002**, 58, m545-m548.
- [9] B. Calmuschi, A. E. Jonas, U. Englert, *Acta Crystallogr. Sect C* **2004**, 60, m320-m323.
- [10] B. Calmuschi-Cula, I. Kalf, R. Wang, U. Englert, *Organometallics* **2005**, 24, 5491-5493.
- [11] B. Calmuschi, M. Alesi, U. Englert, *Dalton Trans.* **2004**, 1852-1857.

- [12] B. Calmuschi, U. Englert, *CrystEngComm* **2005**, 7, 171-176.
- [13] A. C. Capapé, M. Crespo, J. Granell, M. Font-Bardia, X. Solans, *Dalton Trans.* **2007**, 2030-2039.
- [14] B. Calmuschi-Cula, U. Englert, *Organometallics* **2008**, 27, 3124-3130.
- [15] W. Raven, P. Hermes, I. Kalf, J. Schmaljohann, U. Englert, *J. Organomet. Chem.* **2014**, 766, 34-39.
- [16] W. Raven, I. Kalf, U. Englert, *Crystals* **2015**, 5, 244-251.
- [17] W. Raven, I. Kalf, U. Englert, *J. Organomet. Chem.* **2015**, 794, 146-152.
- [18] F. Pan, R. Wang, U. Englert, *Inorg. Chem.* **2012**, 51, 769-771.
- [19] G. L. Ning, L. P. Wu, K. Sugimoto, M. Munakata, T. Kurodasowa, M. Maekawa, *J. Chem. Soc. Dalton Trans.* **1999**, 2529-2536.
- [20] T. Yamaguchi, F. Yamazaki, T. Ito, *J. Am. Chem. Soc.* **2001**, 123, 743-744.
- [21] J. Forniés, S. Ibáñez, E. Lalinde, A. Martín, M. T. Moreno, A. C. Tsipis, *Dalton Trans.* **2012**, 41, 3439-3451.
- [22] L. Pauling, *J. Am. Chem. Soc.* **1947**, 69, 542-553.
- [23] K. Krogmann, H. D. Hausen, *Z. Anorg. Allg. Chem.* **1968**, 358, 67-81.
- [24] K. Krogmann, D. Stephan, *Z. Anorg. Allg. Chem.* **1968**, 362, 290-300.
- [25] K. Krogmann, G. Ringwald, *Z. Naturforsch. B* **1968**, 23, 1112-1112.
- [26] K. Krogmann, *Z. Anorg. Allg. Chem.* **1968**, 358, 97-110.
- [27] K. Krogmann, *Angew. Chem. Int. Ed. Engl.* **1969**, 8, 35-42.
- [28] A. Erxleben, B. Lippert, *J. Chem. Soc. - Dalton Trans.* **1996**, 2329-2333.
- [29] W. Chen, F. Liu, T. Nishioka, K. Matsumoto, *Eur. J. Inorg. Chem.* **2003**, 2, 4234-4243.
- [30] F. Liu, W. Chen, D. Wang, *Dalton Trans.* **2006**, 2, 3015-3024.
- [31] W. Kabsch, (2010). *Acta Crystallogr. Sect. D*, **2010**, 66, 125-132.
- [32] Bruker, SADABS-2014/4, Program for empirical absorption correction of area detector data, Madison, Wisconsin, USA, **2014**.
- [33] G. M. Sheldrick, *Acta Crystallogr. Sect. A*, **2015**, 71, 3-8.
- [34] G. M. Sheldrick, *Acta Crystallogr. Sect. C*, **2015**, 71, 3-8.

Entry for the Table of Contents

FULL PAPER

Ag-Pt = 2.8 - 2.9 Å



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unsupported Ag-Pt Interactions**

Direct metal-metal bonds represent the most intriguing aspect of the penta- and tetranuclear cationic clusters obtained from an organoplatinum complex in square-planar coordination and silver perchlorate.

ARTICLE

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