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Supplementary Information

A Route to Small Clusters: A Twisted Half-Hexagram-Shaped $M_4(OH)_4$ Cluster and Its Capacity for Hosting Closed-Shell Metals

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Experimental Section

General Procedures and Starting Materials. The compound $(NBu_4)_2[\{Pt(C_6Cl_5)_2\}_2(\mu\text{-}OH)_2]$ was synthesized according to previously reported methods.[1] All other reagents and solvents were obtained from commercial suppliers and used as received. Elemental analysis was performed on a Perkin Elmer 2400 CHNS/O analyzer. The IR spectrum was measured on a Perkin-Elmer Spectrum 100 FT-IR Spectrophotometer with ATR accessory in the 4000 - 250 cm^{-1} range.

Preparative Procedures for New Compounds. Preparation of $(NBu_4)_2[Pt_4(\mu\text{-}OH)_2(\mu_3\text{-}OH)_2(C_6Cl_5)_8]$ (1). Solid $AgNO_3$ (0.018 g, 0.105 mmol) was added to a solution of $(NBu_4)_2[\{Pt(C_6Cl_5)_2\}_2(\mu\text{-}OH)_2]$ (0.200 g, 0.105 mmol) in acetone (10 mL), and the mixture was stirred at room temperature under exclusion of light for 3 h. I_2 (0.013 g, 0.053 mmol) was then added to the yellowish solution obtained, which immediately turned a deep orange color. After 1 h. of stirring, the mixture was filtered in order to eliminate the solid formed, and the filtrate was evaporated to dryness to give an orange oil. This residue was successively washed with H_2O (3 x 10 ml) and cold ^iPrOH (3 × 5 ml) and finally crystallized from an acetone-petroleum ether mixture at room temperature to give compound **1** as a bright yellow crystalline solid (0.101 g, 58%). Crystals of **1** suitable for X-ray diffraction analysis were obtained by slow diffusion of a layer of petroleum ether into an acetone solution of **1** at room temperature. Anal. Calcd for $C_{80}H_{76}Cl_{40}N_2O_4Pt_4\cdot 2(CH_3)_2CO$ (%): C 29.99, H 2.58, N 0.81. Found: C 30.43, H 2.76, N 1.05. IR (cm^{-1}): 3553 (w), 3507 (w), 2963 (m), 2934 (w, sh), 2875 (w), 1478 (m), 1470 (m), 1459 (vw,sh), 1378 (w), 1328 (m), 1315 (s), 1289 (vs), 1214 (m), 1149 (w), 1104 (w), 1072 (w), 1003 (w), 931 (vw), 872 (w), 843 (w), 778 (w), 736 (w), 672 (vs), 626 (s), 574 (w), 616 (w), 431 (m).

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[1] López, G.; Ruiz, J.; García, G.; Vicente, C.; Martí, J. M.; Hermoso, J. A.; Vegas, A.; Martínez-Ripoll, M. *J. Chem. Soc., Dalton Trans.*, **1992**, 53-58.

Preparation of [$Ag_2Pt_4(\mu$-$OH)_2(\mu_3$-$OH)_2(C_6Cl_5)_8$] (2). ***Method A (synthesis by crystallization procedure).*** Crystals of **2** suitable for X-ray diffraction analysis were obtained by the slow diffusion of a $AgSO_3CF_3$ benzene solution (0.007 g (0.024 mmol), 5mL) into a dichloromethane solution (2 mL) of complex **1** (0.020 g, 0.006 mmol) at room temperature under exclusion of light. ***Method B:*** The first step of the procedure is completely analogous to that described for **1** but using $(NBu_4)_2[\{Pt(C_6Cl_5)_2\}_2(\mu$-$OH)_2]$ (0.100 g, 0.053 mmol) in acetone (10 mL), I_2 (0.007 g, 0.027 mmol), and solid $AgSO_3CF_3$ (0.014 g, 0.054 mmol) instead of $AgNO_3$. The orange oil so obtained was redissolved in CH_2Cl_2 (10 mL) without further purification, and a benzene solution (10 mL) of $AgSO_3CF_3$ (0.034 g, 0.131 mmol) was added to give a yellow mixture, which was stirred at room temperature under exclusion of light for 2 h. After 20 h. without stirring, the suspension obtained was filtered in order to isolated the yellow solid formed, which was then treated with H_2O (3 x 10 ml) and cold ^{i}PrOH (3 × 5 ml) to give compound **2** as a yellow powder (0.031 g, 39%). Anal. Calcd for $C_{48}H_4Ag_2Cl_{40}O_4Pt_4\cdot 2C_6H_6$ (%): C 22.41, H 0.50. Found: C 22.68, H, 0.65. IR (cm^{-1}): 3506 (vw), 3479 (w), 3088 (vw), 3065 (vw), 3030 (vw), 1494 (vw), 1477 (w), 1332 (s), 1313 (s), 1288 (vs), 1210 (m), 1065 (vw), 1076 (vw), 1027 (w), 1003 (w), 933 (vw), 872 (vw), 860 (vw), 842 (m), 757 (m), 709 (w), 670 (vs), 630 (s), 597 (vw), 575 (vw), 436 (m), 317 (m).

Crystal Structure Analyses. Basic crystallographic data for both structures are given in Table 1. Full structural details, including the diffraction data and input files for the final refinements, are present in the CIF.

Crystal Structure Analysis of $(NBu_4)_2[Pt^{IV}Pt^{II}_3(\mu$-$OH)_2(\mu_3$-$OH)_2(C_6Cl_5)_8]$ (1). From preliminary measurements it was found that the primitive unit cell had a long axis of roughly 50 Å. It was estimated that rather than a typical crystal-to-detector distance of 50 mm, a longer distance of 63 mm would serve to avoid spot overlap in the diffraction pattern. When the structure had been solved and completed, symptoms of peak overlap, in the form of outliers in the refinement, were observed. The data were integrated again,[2] with a reduction of 25% in the calculated integration volume of each reflection as a means of alleviating the overlap. Because of the presence of the long axis, some 94 reflections fell within a software-imposed beamstop shadow, and were not integrated. This did not affect the completeness of the data in a noticeable way. Corrections for absorption and other systematic errors were made based on crystal morphology[3] with posterior application of the multi-scan method.[4] The structure was solved by direct methods,[5] which located nearly all of the non-H atoms correctly. The remainder were

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[2] CrysAlisPro, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01).

[3] Clark, R. C. & Reid, J. S. *Acta Cryst., Section A*, **1995**, *A51,* 887-897.

[4] (a) Blessing, R. H. *Acta Cryst., Section A*, **1995**, *A51*, 33-38. (b) Blessing, R. H. *J. Appl. Cryst.*, **1997**, *30*, 421-426.

[5] Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. *J. Appl. Cryst.* **1994**, *27,* 435.

found using the usual sequence of least-squares refinement[6] and difference Fourier maps. In the final refinement all non-H atoms were refined anisotropically. Hydroxy H atoms were not located. Methylene H atoms of the $^t\mathrm{Bu}_4\mathrm{N}^+$ cations were placed in calculated positions and refined as riding atoms with U_{iso} assigned as $1.2U_{eq}$ of their respective bonding partners. Methyl H atoms of the cations and the two acetone solvent molecules were located in local Fourier calculations and refined as riding atoms, with the CH_3 groups permitted to rotate but not to tilt. The U_{iso} values of the Me H atoms were set to $1.5U_{eq}$ of their respective bonding partners. Geometrical similarity restraints were used for the geometries of the two unique acetone molecules, with bonding pairs and 1,3-non-bonded distances being restrained.

Crystal Structure Analysis of $[\mathrm{Pt^{IV}Pt^{II}_3Ag^{I}_2(\mu\text{-}OH)_2(\mu_3\text{-}OH)_2(C_6Cl_5)_8}]\cdot2\mathrm{C_6H_6}\cdot0.4\mathrm{H_2O}$ (2). The crystal was twinned (the so-called non-merohedral twinning), with a ratio of principal to minor component estimated as 83:17 by the data reduction program. In addition, the scattering from this sample was very weak, to the extent that the intensity statistics from the second component were poor enough to obviate its use in refinement, either as a stand-alone component or as part of a joint refinement to the data from the two domains. Consequently, refinement was conducted using data from the principal component alone. This reduced the completeness to 90%, which along with poor resolution (effective resolution estimated to be 0.9 Å) limits the use of the results to establishing the connectivity, the layout of the structure, and the dimensions of the molecules to modest accuracy.

The twin law describes rotation of just over one degree about the orthorhombic *c*-axis of the principal component, to arrive at the second domain. Some half-dozen different data integration and correction strategies were explored,[2] and the structure was refined to all of the resulting data sets. (One of the strategies examined consisted of ignoring the twinning altogether.) The analysis reported here is based on an integration that takes into account the detrimental effects of the minor second component on the quality of the data derived from the principal component. The integration surface obtained for each reflection by the data reduction program was contracted uniformly to a volume of 75% of that calculated in the first instance. Following integration, absorption corrections were applied based on crystal morphology[3] (a reasonable approximation given the nature of the twin law), and further corrections for systematic errors, including residual uncorrected absorption if present, were applied using the multi-scan technique.[4] For this calculation, the 15 strongest reflections and their symmetry equivalents were excluded on the grounds that they may have been corrupted by the twinning. A spherical correction was not applied, since this correction is implicit in the morphology-based absorption calculations.

The structure was solved by direct phasing[7] and refined by full-matrix least squares.

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[6] Sheldrick, G. M. *Acta Cryst., Section C,* **2015**, *C71,* 3-8.

[7] Sheldrick, G. M. *Acta Cryst., Section A,* **2015**, *A71,* 3-8. http://dx.doi.org/10.1107/S2053273314026370

The crystallographic asymmetric unit consists of one half of the neutral complex $[Pt^{IV}Pt^{II}_3Ag^{I}_2(\mu\text{-}OH)_2(\mu_3\text{-}OH)_2(C_6Cl_5)_8]$, which sits astride a two-fold axis; one benzene molecule on a general position; and a number of disordered solvent molecules, treated as water, occupying large channels parallel to the crystallographic *a*-axis. The channels are centered at $y = 1/4$, $z = (1/8, 5/8)$ and $y = 3/4$, $z = (3/8, 7/8)$ -- four channels per cell. Platon[8] calculates a volume of 391 Å^3 per channel, giving a total channel volume of 1564 Å^3 per cell [16% of the cell volume of 9426.2 (10) Å^3].

The Pt_4Ag_2 complex possesses only four H atoms, which were not located. The six H atoms of the benzene molecule were placed in calculated positions and refined as riding atoms with displacement parameters *U(iso)* calculated as 1.2*U(eq)* of their respective bonding partners.

The electron density in the channels could be apportioned among ten sites that appeared in a difference map. These sites refined stably with isotropic displacement parameters of what we considered to be reasonable magnitude, if they were assigned as oxygen atoms with occupancies of 0.2 each. They describe geometry that would be chemically impossible if these sites were fully occupied, with too-short contacts all along the chain. We note that none of the sites lies within H-bonding geometry of its surroundings, other than along the channel itself. The lack of a chemical anchor is likely to be the cause of the severe disorder observed. Nevertheless, the fact that discrete sites could be identified indicates that the sites observed are energetically favored, at least weakly. In the final refinement, these O atoms were refined anisotropically, but with similarity restraints on the anisotropic displacement parameters of any pair of them that lay within 4 Å of each other, and with individual restraints to isotropic behavior applied to all of them. Hydrogen atoms were not located in this region of the structure.

The non-H atoms of the Pt_4Ag_2 cluster and of the benzene molecule were refined anisotropically, but with restraints to rigid bond behavior applied to the anisotropic displacement parameters of all bonding partners, including the bonds involving the metal atoms. In addition, one of the OH oxygen atoms, O2, was subjected to a restraint to isotropic behavior.

Despite the low effective resolution of the data, it was not considered necessary to use geometrical restraints for any part of the structure. The only geometrical constraints applied were the riding atom constraints for the H atoms of the benzene molecule.

In the course of working with data from all of our integration and correction strategies, we concluded that the deconvolution of overlapped reflections, while effective, left a number of data, especially the stronger low-angle data, with extra intensity. In an attempt to minimize the resulting pejorative effects on the refinement, the final refinement was conducted with a weak application of Dunitz-Seiler weights,[9] with the weight for each reflection calculated as

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[8] Spek, A. L. *Acta Cryst., Section D,* **2009**, *D65,* 148-155.

[9] Dunitz, J. D.; Seiler, P. *Acta Cryst., Section B,* **1973**, *B29,* 589-595.

$exp[3(sin\theta/\lambda)^2] / [\sigma^2(Fo^2) + (0.03*P)^2]$, in which P as usual is $1/3Fo^2 + 2/3Fc^2$ for positive Fo^2 or $2/3Fc^2$ if Fo^2 is non-positive.

$$w = \exp\left[3(sin\theta/\lambda)^2\right]/\,[\sigma^2(F_o^2) + (0.03P)^2]$$

The SQUEEZE algorithm can be applied to this structure, after refinement of a model excluding the ten sites that we assign as partially occupied oxygen atoms.[10] In this case, the results of SQUEEZE are not perceptibly better than the results of the refinement that we report (with the channel atomic sites present), in terms of the usual quality indicators -- least-squares residuals and neatness of the final difference map. The low resolution of the data, the twinning and resultant corruption of low-angle data all weigh against the use of SQUEEZE for this structure.

Thirteen strong outlying data, presumably affected by the twinning, were explicitly omitted from the final refinement.

FIGURES

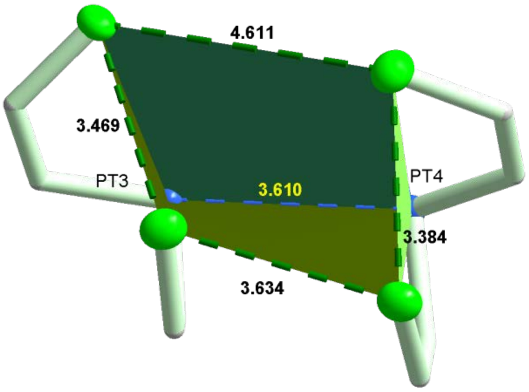


Fig. S1. “Cage-chair” formed by Pt3, Pt4, and four chlorine atoms (Cl46, Cl52, Cl66, Cl72) in compound **1**

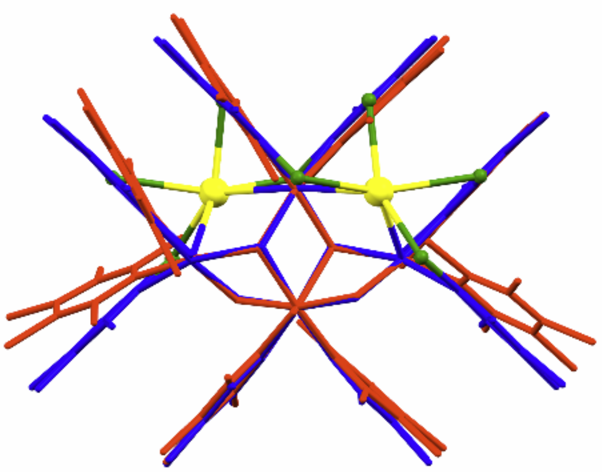
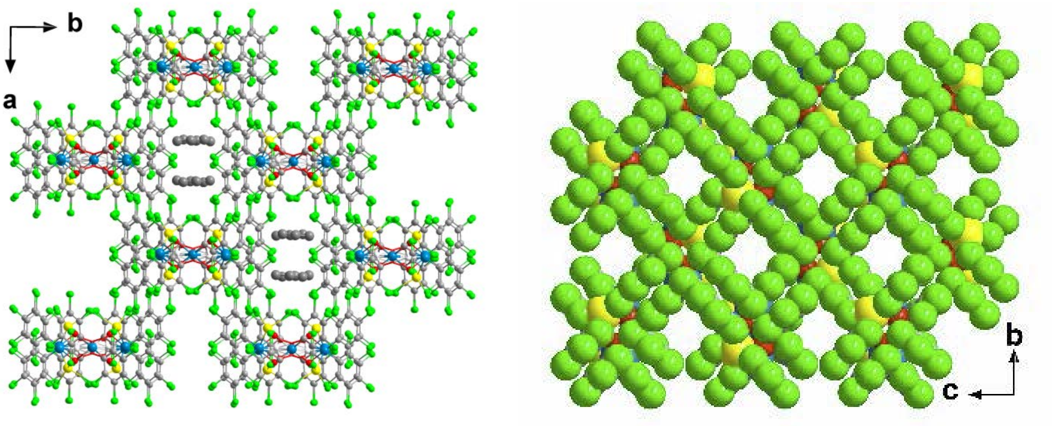


Fig. S2. Superposition of **1** (red) and **2** (blue)



(a) (b)

Fig. S3. Packing of 2 showing: (a) the clathrated benzene molecules and (b) the channels in the [100] direction.

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[10] Spek, A. L. *Acta Cryst., Section C*, **2015**, *C71*, 9-18.

Table 1. Crystal data and structure refinement for $(NBu_4)_2[Pt^{II}_3Pt^{IV}(\mu\text{-}OH)_2(\mu_3\text{-}OH)_2(C_6Cl_5)_8]$ (**1**) and $[Pt^{II}_3Pt^{IV}Ag^{I}_2(\mu\text{-}OH)_2(\mu_3\text{-}OH)_2(C_6Cl_5)_8]\cdot 2C_6H_6\cdot 0.4H_2O$ (**2**).

Identification code	**1**	**2**
CCDC deposition number	1461799	1461798
Empirical formula	C86 H88 Cl40 N2 O6 Pt4	C60 H24 Ag2 Cl40 O8 Pt4
Formula weight	3443.94	3286.89
Temperature	173(1) K	150(1) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	orthorhombic	orthorhombic
Space group	$Pna2_1$	*Pccn*
Unit cell dimensions	a = 50.3157(9) Å	a = 16.8782(5) Å
	b = 13.2707(2) Å	b = 17.9950(7) Å
	c = 17.5344(2) Å	c = 31.0107(8) Å
Volume	11708.1(3) Å^3	9418.7(5) Å^3
Z	4	4
Density (calculated)	1.954 Mg/m^3	2.318 Mg/m^3
Absorption coefficient	5.726 mm^{-1}	7.509 mm^{-1}
F(000)	6632	6136
Crystal size	0.424 x 0.077 x 0.065 mm^3	0.122 x 0.045 x 0.028 mm^3
Theta range for data collection	4.804 to 27.500°	4.169 to 27.499°
Index ranges	-61<=h<=65	-21<=h<=21
	-17<=k<=17	-23<=k<=23
	-22<=l<=22	-37<=l<=39
Reflections collected	76053	31555
Independent reflections	26376 [R(int) = 0.0387]	9533 [R(int) = 0.1394]
Completeness to theta = 27.500°	99.3 %	90.7 %
Absorption correction	analytical, multi-scan	analytical, multi-scan
Max. and min. transmission	0.703, 0.247	0.817, 0.470
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	26376 / 15 / 1255	9533 / 846 / 587
Goodness-of-fit on F^2	1.035	1.094
Final R indices [I>2sigma(I)]	R1 = 0.0280, wR2 = 0.0556	R1 = 0.0575, wR2 = 0.0975
R indices (all data)	R1 = 0.0305, wR2 = 0.0567	R1 = 0.1795, wR2 = 0.1213
Absolute structure parameter	-0.0132(16)	-
Largest diff. peak and hole	1.840 and -0.635 e.Å^{-3}	1.702 and -1.113 e.Å^{-3}