

A Supramolecular Heteropolyoxopalladate {Pd₁₅} Cluster Host Encapsulating a {Pd₂} Dinuclear Guest: [Pd^{II}₂{H_{16-n}Pd^{II}₁₅O₁₀(PO₄)₁₀}]ⁿ⁻

Feng Xu, Rachel Scullion, Jun Yan, Haralampos N. Miras, Christoph Busche, Antonino Scandurra,² Bruno Pignataro,³ De-Liang Long, Leroy Cronin*

WestCHEM, School of Chemistry, The University of Glasgow, Glasgow, G12 8QQ, U.K,
<http://www.croninlab.com>

Superlab-Consorzio Catania Ricerche, Stradale Primosole 50, 95121, Catania – Italy

Dipartimento di Chimica Fisica, Università di Palermo, V.le delle Scienze ed. 17 - 90128
Palermo – Italy

Supporting Information

- (1) General experimental section and synthesis methods
- (2) IR Spectrum of {Pd₁₅}, {Pd_{15.4}} and {Pd₁₇} (**Figure S1**)
- (3) UV, TGA and ³¹P-NMR Spectra of {Pd₁₇} and {Pd₁₅} (**Figure S2-5**)
- (4) Preliminary ³¹P-NMR Job's Plot by mixing the stock solutions of the Guest, Pd(II) nitrate, and the Host, {Pd₁₅}, at different ratios(**Figure S6**)
- (5) Crystal data and structure refinement for {Pd₁₇} and {Pd₁₅} (**Table S1**)
- (6) XPS high resolution spectrum in the Pd3d spectral region (**Figure S7**).

(1) General Experimental Section

All chemicals and solvents were of analytical grade purchased from Sigma Aldrich and used as supplied, without further purification. We acknowledge Prof. D. P. Kögerler, Institut für Anorganische Chemie, Aachen for ICP-OES analysis.

Single crystal X-Ray diffraction: Single crystal datasets were collected at 150(2) K on an Oxford Diffraction Gemini Ultra S λ (Cu K $_{\alpha}$ = 1.5418 Å).

Flame Atomic Absorption Spectroscopy Analysis: FAAS analysis was performed at the Environmental Chemistry Section, Department of Chemistry, The University of Glasgow on a Perkin-Elmer 1100B Atomic Absorption Spectrophotometer.

Thermogravimetric Analysis: TGA was performed on a TA Q500 instrument under a nitrogen atmosphere.

Infrared: All IR experiments were carried out with a Shimadzu FTIR 8400S.

UV/Vis: A JASCO V/670 was used for UV measurements.

Mass spectrometry: Measurements were made using a Bruker micro ToFQ in negative ion mode.

³¹P NMR: Experiments were performed using a Bruker DPX 400. All δ values are given in ppm.

XPS analysis: XPS analysis has been performed using the AXIS-HS spectrometer Kratos.

MgK α radiation of 1253.6 eV has been used at the condition of 10 mA and 15 keV. The energy analyzer was set with a pass energy of 40 eV. The sample has been dispensed as powder and then pressed onto an Indium foil. The binding energy scale was referred to the C1s component at 284.5 eV that originates from adventitious carbon contamination. During the analysis the residual pressure in the chamber was about 10⁻⁷ Pa. Electron flood was used to compensate the surface charging up. Quantitative data have been obtained by using experimental atomic sensitivity factors after linear spectral background subtraction.

Synthesis of Na₉[Pd₂{H₇Pd^{II}₁₅O₁₀(PO₄)₁₀}]: *Procedure 1*: Pd(OAc)₂ (0.139 g, 0.620 mmol) and NaH₂PO₄ (0.074 g, 0.620 mmol) were added into 5.5 mL of a 0.5 M NaOAc solution at a pH of 5.8 (prepared from adding ca. 0.27g HOAc to 100ml 0.5 M solution of NaOAc), while stirring and heating to 85 °C for 90 min. Then, the dark brown solution was cooled to room temperature and filtered to remove a small amount of Pd precipitate. Slow evaporation at room temperature led to some needle black crystals after 2 weeks. The crystals were collected by filtration and air-dried; *Procedure 2*: 22 mL of NaH₂PO₄-Na₂HPO₄ solution at a pH of 6.5 (prepared from adding 1M NaOH to 0.15 M solution of NaH₂PO₄) was added to Pd(OAc)₂ (0.56 g, 2.5mmol). The suspension was left stirring rigorously and heating to 85 °C for 90 min. After the heating, the dark black solution was cooled to room temperature (pH=4.0) and filtered to remove a small amount of black solids. Slow evaporation at room temperature led to some black needle crystals after 2 weeks. The crystals were collected by filtration and air-dried. Yield: ca. 5% (based on Pd); ³¹P-NMR (400MHz, D₂O) δ 18.13 (s); IR: 3350, 2350, 1600, 950, 875 cm⁻¹; Elemental analysis, Calc. for H₈₇Na₉O₉₀P₁₀Pd₁₇, Na 5.4%, P 8.0%, Pd 46.9%; Found Na 5.5%, P 7.9%, Pd 46.2%.

Synthesis of Na₁₃[H₇Pd^{II}₁₅O₁₀(PO₄)₁₀]: 20 mL of NaH₂PO₄-Na₂HPO₄ solution at a pH of 6.9 (prepared from adding 1M NaOH to 0.5 M solution of NaH₂PO₄) was added to Pd(OAc)₂ (0.56 g, 2.5mmol). The suspension was left stirring rigorously and heating to 80 °C for 90 min. After the heating, the dark red solution was cooled to room temperature and filtered to remove a small amount of black solids. The crystals, with reported formula Na₁₂[Pd_{0.4}Na_{0.6}Pd₁₅P₁₀O₅₀H_{6.6}], were checked by x-ray machine and filtered in two days. Slow evaporation at room temperature led to block crystals in a few days from the red-brown filtrate solution. (Multi-filtering should be applied until the crystallographically pure {Pd₁₅} is obtained, which checked for purity by ³¹P NMR.) The crystals were collected by filtration and air-dried. Yield: ca. 30% (based on Pd); ³¹P-NMR (400MHz, D₂O) δ 17.02 (s); IR: 3350, 2350, 1600, 950 cm⁻¹; Elemental analysis, Calc. for H₈₇Na₁₃O₉₀P₁₀Pd₁₅, Na 8.0%, P 8.3%, Pd 42.8%; Found Na 8.2%, P 8.0%, Pd 42.3%.

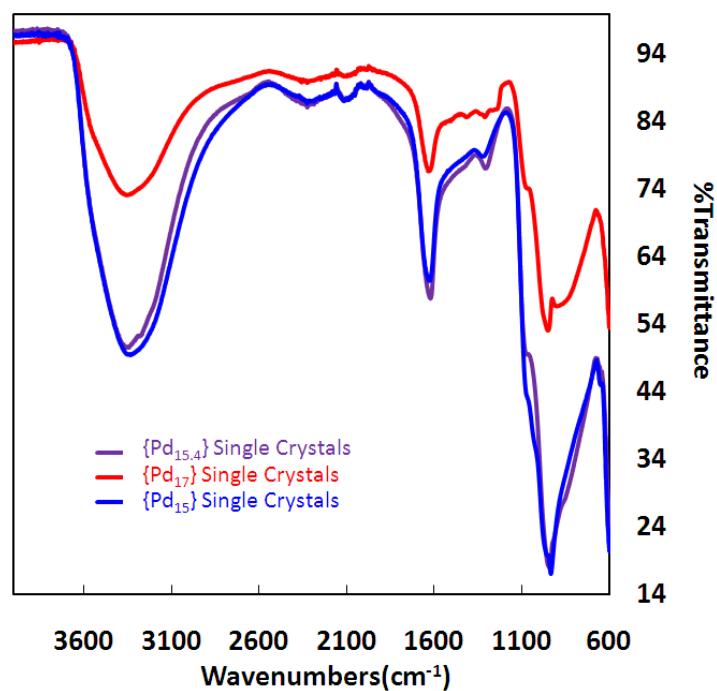


Figure S1. IR spectrum of {Pd₁₅}, {Pd_{15.4}} and {Pd₁₇} single crystals.

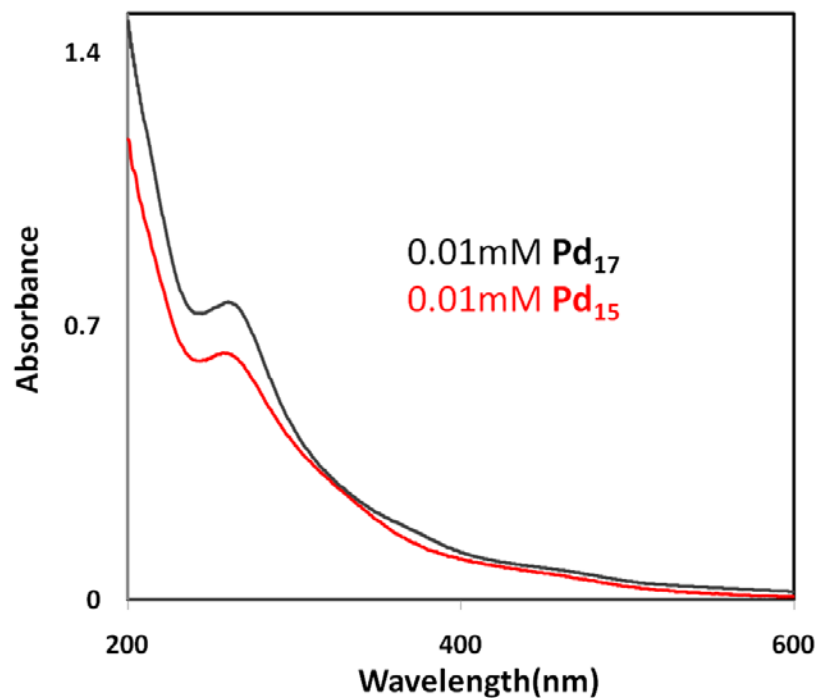


Figure S2. UV-Vis spectrum of dissolved single crystals of the {Pd₁₅} and {Pd₁₇} compounds in aqueous solution.

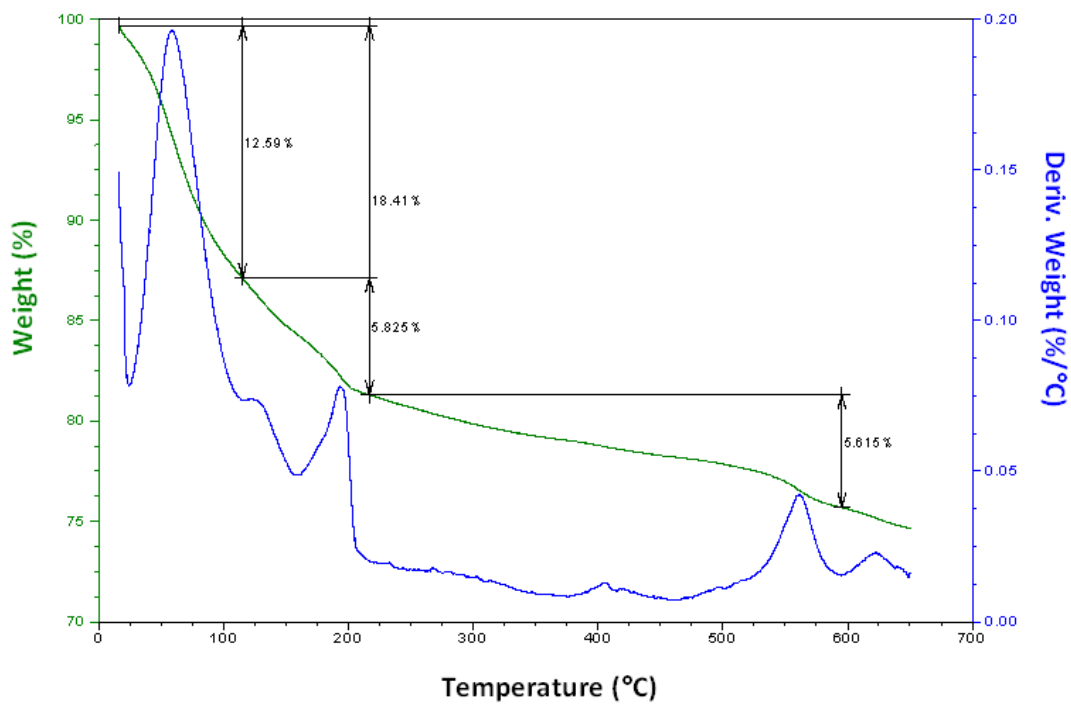


Figure S3. TGA Plot of {Pd₁₇} single crystals.

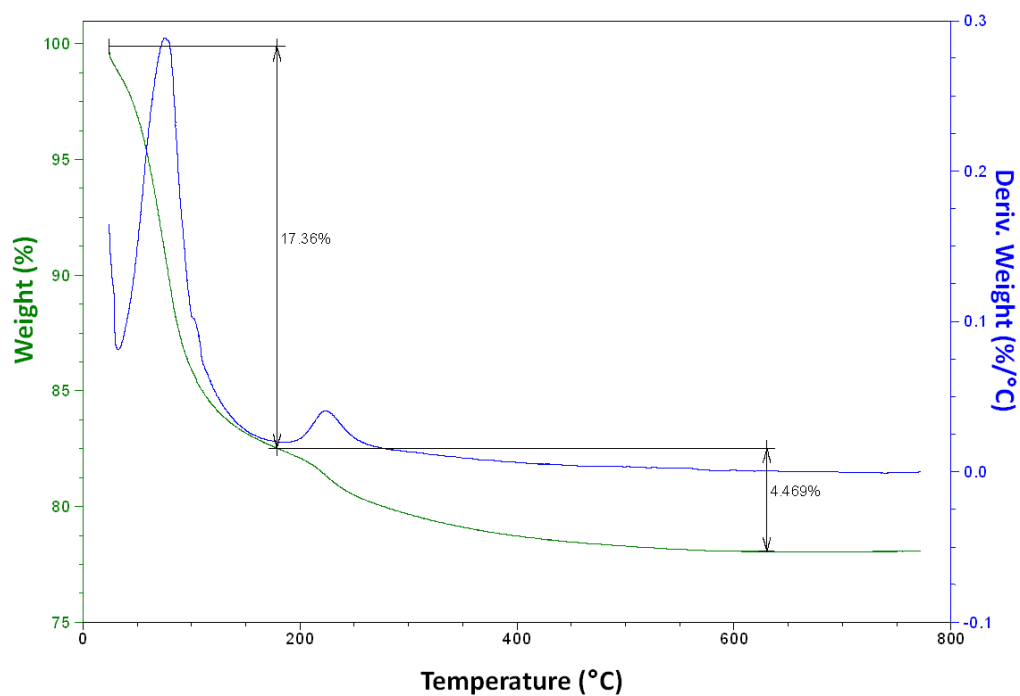


Figure S4. TGA Plot of {Pd₁₅} single crystals.

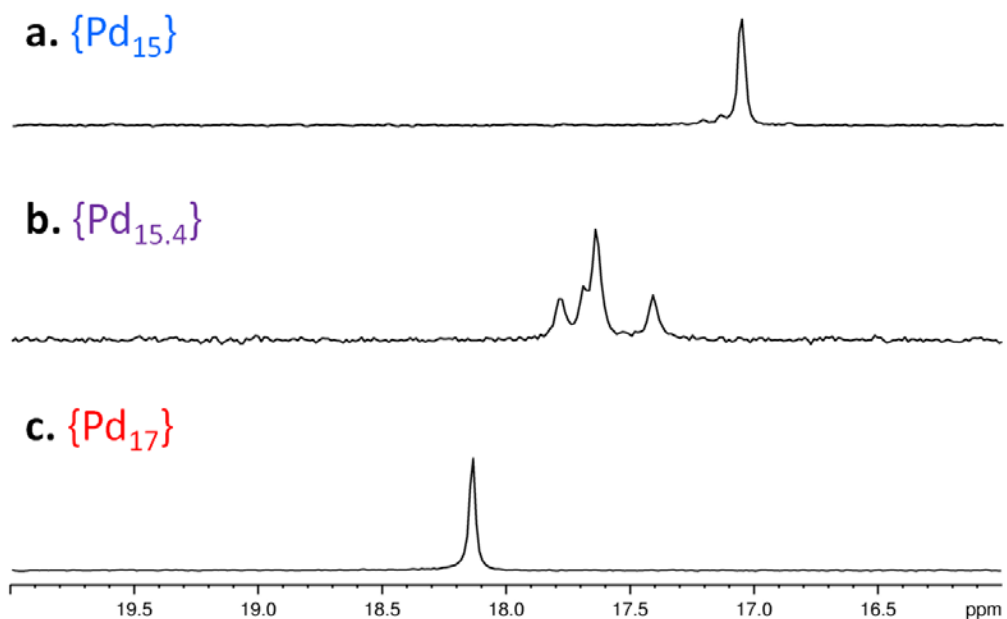


Figure S5. ^{31}P -NMR spectrum of (a) $\{Pd_{15}\}$, (b) $\{Pd_{15.4}\}$ and (c) $\{Pd_{17}\}$ single crystals in D_2O .

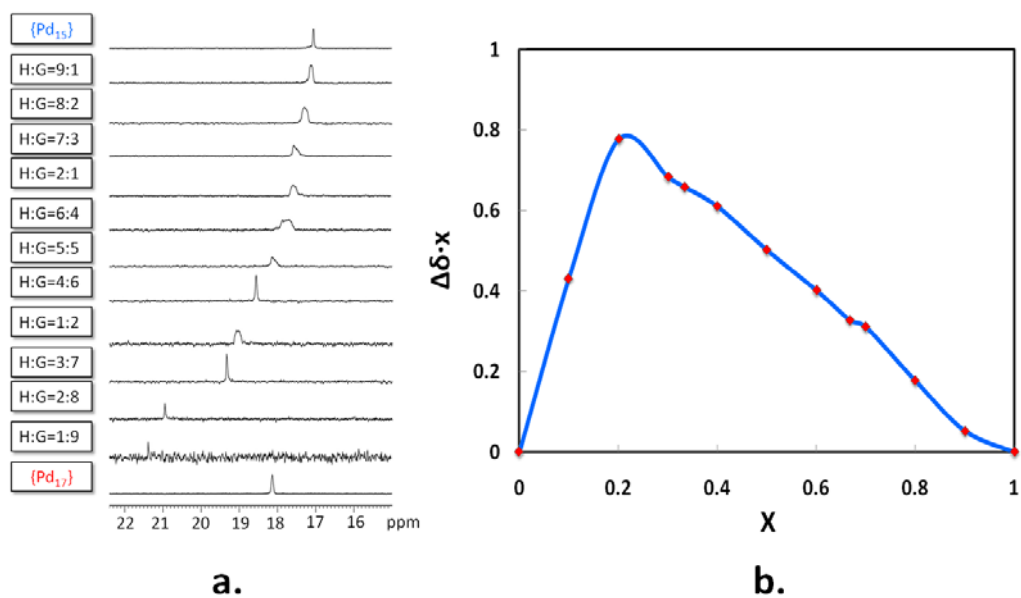


Figure S6. (a) Preliminary studies of ^{31}P -NMR Job's Plot by mixing the stock solutions of the Guest(G), Pd(II) nitrate, and the Host(H), $\{Pd_{15}\}$, at different ratios; (b) Job's plot derived from the chemical shift displacements($\Delta\delta$) as functions of the molar ratio.

Table S1. Crystal data and structure refinement for {Pd₁₇} and {Pd₁₅}.

| | | |
|---|---|--|
| Empirical formula | H ₈₇ Na ₁₃ O ₉₀ P ₁₀ Pd ₁₅ | H ₈₇ Na ₉ O ₉₀ P ₁₀ Pd ₁₇ |
| F _w (g•mol ⁻¹) | 3732.27 | 3844.23 |
| Crystal system | Triclinic | Triclinic |
| Space group | <i>P</i> -1 | <i>P</i> -1 |
| <i>a</i> (Å) | 13.5833(5) | 14.9100(2) |
| <i>b</i> (Å) | 15.9930(5) | 14.9327(3) |
| <i>c</i> (Å) | 21.7485(8) | 23.0483(4) |
| <i>α</i> (°) | 88.083(3) | 87.270(2) |
| <i>β</i> (°) | 81.990(3) | 82.755(2) |
| <i>γ</i> (°) | 72.782(3) | 73.821(2) |
| <i>V</i> (Å ³) | 4468.7(3) | 4888.62(15) |
| <i>Z</i> | 2 | 2 |
| <i>ρ</i> _{calcd} (g•cm ⁻³) | 2.774 | 2.618 |
| <i>μ</i> (mm ⁻¹ , Cu K _α) | 27.258 | 27.610 |
| <i>T</i> /K | 150(2) | 150(2) |
| No. of reflections (measured) | 47938 | 84920 |
| No. of reflections (unique) | 14041 | 17546 |
| <i>R</i> _{int} | 0.0692 | 0.0350 |
| Residuals: <i>R</i> _{I(obs)} , <i>R</i> _{w2(all data)} | 0.0502, 0.1389 | 0.0319, 0.0916 |

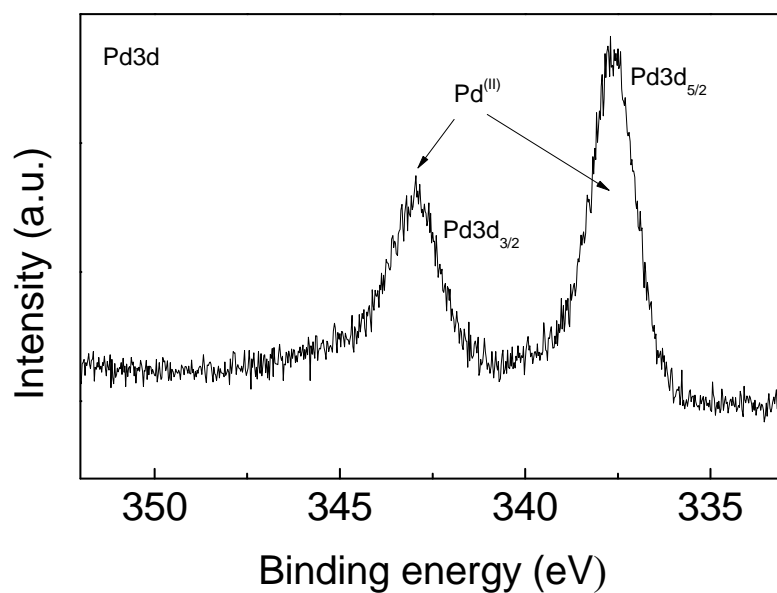


Figure S7. XPS high resolution spectrum in the Pd3d spectral region showing the Pd3d_{3/2} and Pd3d_{5/2} doublet. The presence of Pd⁰ and Pd^(I) can be ruled out being the corresponding Pd3d_{5/2} binding energies of 335.1 and 335.6-335.8 eV respectively. Also the presence of Pd^(IV) can be excluded since no significant signals have been revealed in the Pd^(IV) 3d_{5/2} BE region (about 2 eV higher than that of Pd^(II)).