

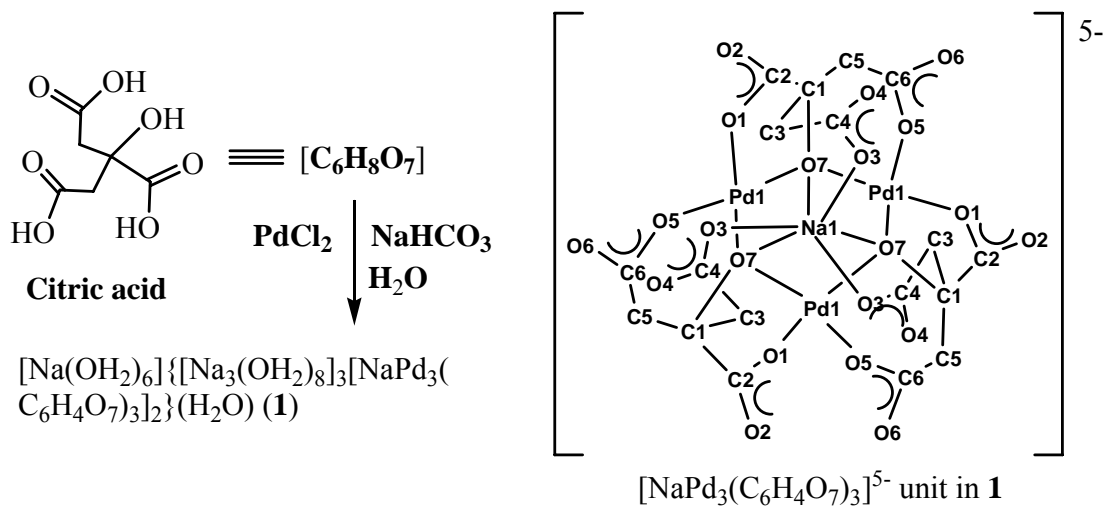
Electronic Supplementary Information

Crystallographic Identification of an Unusual Homoleptic Palladium Citrate [Na(OH₂)₆]{[Na₃(OH₂)₈]₃[NaPd₃(C₆H₄O₇)₃]₂}(H₂O) Stabilised by Intermetallic Aggregation with Sodium and Heavy Hydration

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Scheme S1. One-pot formation of intermetallic supramolecular network of **1** from $PdCl_2$ with citrate in aqueous solution (left) and the C_3 -symmetric $[NaPd_3(C_6H_4O_7)_3]^{5-}$ anion unit in **1** (right).

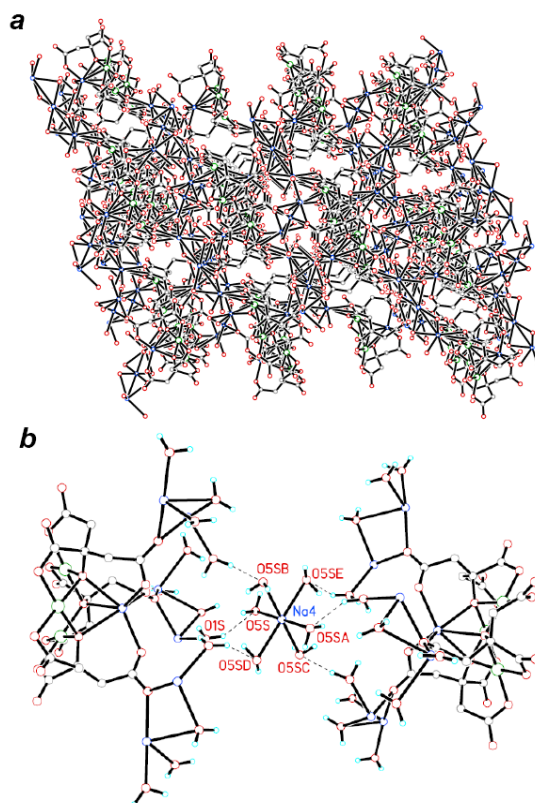


Figure S1. a) 3-D structure of **1**. b) $[\text{Na}(\text{OH}_2)_6]^+$ complex was stabilised among two C_3 -symmetry cavities by H-bond interactions in the network of **1**.

Experimental section

NaHCO_3 (0.5101 g, 6 mmol) was added to an aqueous solution of citric acid (0.39 g, 2 mmol) and the mixture was stirred for 10 min to give a colorless solution, into which PdCl_2 (0.1774g, 1 mmol) was added. The mixture was briefly swirled and then left standing overnight. It gradually turned to a clear orange solution. Ethanol was added to precipitate a yellow solid which was collected and redissolved in water and layered with ethanol to give orange crystals of **1**, yield 1.3 g (near-quantitative based on Pd). ^1H NMR (300 MHz, D_2O): δ = 3.3159, 3.2638, 2.5965, 2.5461, 2.4749, 2.4639, 2.4240, 2.4119, (m, 2H, J = 15.6 Hz, CH_2) 2.5965, 2.5461, 2.4749, and 2.4240, (m, 2H, J = 15.1 Hz, CH_2), 2.7 and 3.2 (d, 2H, H_2O) ^{13}C NMR: (75 MHz, D_2O): δ = 45.4, 48.6, 49.4, 50.6, 57.4 for CH_2 , 75.1, 83.7, 84.7, 85.3 for CO, 176.8, 179, 179.9, 180.3, 181.7, 185.5 for

CO₂. Anal. Calcd. for dried sample (PdNa₂C₆H_{43/3}O_{73/6} – H₂O, lose one H₂O per asymmetric unit): C, 17.34; H, 2.99 %. Found: C, 17.31; H, 2.46 %.

X-ray crystallography

The measurement for **1** was conducted at r.t. on a Bruker AXS SMART APEX diffractometer, equipped with a CCD area-detector using Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The collecting frames of date, indexing reflection and determination of lattice parameters and polarization effects were performed with the SMART suite programs.¹ The integration of intensity of reflections and scaling was carried out by SAINT.¹ The empirical absorption correction was performed by SADABS.² The space group determination, structure solution and least-squares refinements on $|F|^2$ were carried out with the SHELXS-97 and SHELXL-97.³ The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. O6S is situated at three fold axis, and the H atoms of O6S appeared to be disordered and were not located. H atoms were located from difference map, refined with thermal parameters following those of the atoms they were attached. OH distances were restrained. Pd is coordinated to four O's at about 2 Å and near to other Pd and Na at about 3.2–3.4 Å. O3 of the citrate is disordered (76 : 24 occupancy ratio).

References:

1. *SMART* (Version 5.631) & *SAINTE* (Version 6.63) *Software Reference Manuals*, Bruker AXS GmbH, Karlsruhe, Germany, **2000**.
2. G. M. Sheldrick, *SADABS: a Software for Empirical Absorption Correction*, University of Göttingen, Göttingen, Germany, **2001**.
3. (a) G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, **1997**; (b) G. M. Sheldrick, *SHELXL-97, Program for Crystal Structures Refinement*, University of Göttingen, Göttingen, Germany, **1997**.