$\label{eq:crystallographic identification of an unusual homoleptic palladium citrate $$ [Na(OH_2)_6] \cdot {[Na_3(OH_2)_8]_3[NaPd_3(C_6H_4O_7)_3]_2} \cdot (H_2O)$ stabilised by intermetallic aggregation with sodium and heavy hydration $$ the second seco$

Parag Gunari,^a Suresh s/o Krishnasamy,^a Shi-Qiang Bai^a and T. S. Andy Hor^{*a,b}

Received 7th April 2010, Accepted 11th August 2010 DOI: 10.1039/c0dt00273a

A rare precious metal binary citrate represented by palladium in the form of a water-rich Na–Pd intermetallic aggregate has been isolated and crystallographically characterised. It shows a penta-anionic $[NaPd_3(citrate)_3]^{5-}$ core balanced by $[Na_3]^{3+}$ and Na⁺ hydrates in a 3-D coordination network stabilised exclusively by citrate bridges and fortified by extensive Hbonding.

Citric acid ($C_6H_8O_7$) is a natural and abundant α -hydroxy tricarboxylic acid. It binds to a range of metals,¹ notably those that are biologically active.² Its coordination behavior towards the precious metals is much less developed, probably because the complexes formed are mostly unstable.³ For example, pure gold citrates are difficult to be isolated. Ironically, the ready decomposition of these precious metal citrates enables them to be widely used as molecular precursor to nano-metal or its composites.⁴ Much of the attention in the citrates of platinum metals is focused on their nano applications⁵ whereas very little is known on the coordination behavior and structural chemistry. We are interested in structurally defined metal citrates of metals⁶ that are normally considered "incompatible" with citrates, such as gold and palladium. The stabilisation, isolation and structural understanding of their molecular networks enable better design of molecular substrates as precursors to materials.⁷ The use of binary citrate complexes also provides an avenue for water-based catalysis8 in lieu of the water amenability of citrate. Its presence in the core of a catalytically active metal such as palladium provides an ideal opportunity for such investigation. In this communication, we highlight the self-assembly of an intermetallic three-dimensional (3-D) supramolecular Na/Pd citrate of high symmetry that is water soluble and catalytically active. Amidst a large variety of structurally established metal citrates,9 this is one of the rare examples of precious metal citrates that are crystallographically identified. It offers a structural insight on citrate serving as a "capping agent"10 in the conversion of Pd2+ to palladium nanocrystals.11 We reveal herein how citrate can bring to proximity two inherently different metals (Na⁺ and Pd²⁺) within a molecular network from which one could explain the stabilisation of a normally unstable precious metal binary citrate.

PdCl₂ slowly dissolves in an aqueous mixture of citric acid and NaHCO₃ in a 1:2:6 molar ratio to give near-quantitative yield of a water-rich intermetallic ionic complex $[Na_2Pd(citrate)]_n$ 1 (Scheme S1, ESI[†]) which is sufficiently stable to be isolated as a solid at r.t. and remains stable for about 5 days. Its single-crystal X-ray crystallographic analysis revealed a 3-D ionic intermetallic complex network heavily fortified by hydrate *viz*. $[Na(OH_2)_6] \cdot \{[Na_3(OH_2)_8]_3[NaPd_3(C_6H_4O_7)_3]_2\} \cdot (H_2O).$ [‡] Its asymmetric unit (formula PdNa₂C₆H_{43/3}O_{73/6}) comprises one Pd, one citrate, four Na moieties (with occupancies 1/3, 1/2, 1 and 1/6 for Na1, Na2, Na3 and Na4, respectively), five coordinated hydrate, and one lattice hydrate with 1/6 occupancy.

Complete deprotonation of tetra-basic citric acid gives a citrate with maximum coordinative functions in the form of tricarboxylates and alkoxide. They bring together three discrete entities, namely, C_3 symmetric NaPd₃ cubane, linear Na₃ cation aggregate, and mononuclear hydrated Na cation ([Na(OH₂)₆]⁺) (Fig. 1 and S1, ESI[†]). The entire intermetallic network is supported by oxygen donors from the citrate and water. The



Fig. 1 (*a*) Na-capped trinuclear palladium core of **1** omitting lattice H_2O and $[Na(OH_2)_6]^+$ for clarity. (*b*) Linear $[Na]_3^{3+}$ chain connecting the NaPd₃ nodes in the 3-D network of **1**. (Pd: green, Na: blue, O: red, H: cyan)

^aDepartment of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543. E-mail: andyhor@nus.edu.sg; Fax: (+)65-6873-1324 ^bInstitute of Materials Research and Engineering, Agency for Science, Technology and Research, 3 Research Link, Singapore 117602

[†] Electronic supplementary information (ESI) available: Fig. S1, experimental and X-ray crystallography. CCDC reference number 692934. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00273a



Fig. 2 XPS spectrum of a mixture of Pd and PdO formed from decomposition of 1.

heterometals (Na/Pd) are bridged exclusively by the citrate. The two bridging alkoxo (O7) and two carboxylate (O1 and O5) oxygen donors form the coordination sphere of square planar Pd(II) (Fig. 1). The [NaPd₃] core is held together by three capping alkoxo oxygen atoms (O7). The distorted octahedral Na⁺ (Na1) on the C_3 axis is supported by six O donors from citrates (three O3 and three O7). The $[NaPd_3O_3]$ frame thus constitutes a cubane with a missing vertex ("defective cubane"). The central symmetric Na₃ chain comprises a distorted octahedral Na2 sandwiched by two seven-coordinated Na3 with doubly-bridging aqua ligands and co-bridged by μ -O atom (O4) of the carboxylate. The external Na3 atoms are connected to the [NaPd₃(C₆H₄O₇)₃] cores via the carboxylate groups (O5–O6). Effectively, this Na₃ entity serves as a central unit to connect to all the four NaPd₃ aggregates. (Fig. 1(b)) Each nano-sized [NaPd₃] node is in turn linked to six different Na₃ blocks to give the present 3-D coordination network (Fig. 1 and Fig. S1, ESI[†]). In addition, the octahedral [Na(OH₂)₆]⁺ is sandwiched by two C_3 symmetric cavities in this network with six intermolecular H-bonding interactions (O1S-H···O5S 2.83 Å) between the bridging aqua (O1S) of $[Na_3]^{3+}$ and coordinated hydrate (O5S) of $[Na(OH_2)_6]^+$ (Fig. S1, ESI[†]). A related system is found in the malate (mal)-stabilised Na₃[Cu₃(mal)₃(H₂O)]·8H₂O^{12a} which is stabilised by malate. ESI-MS analysis reveals the palladium citrate species ($[Pd_2Na(citrate)(H_2O)_4]^+$ (m/z 495, 85%)) in water. A similar iron-citrate species has been reported.^{12b,c} Formation of this complex network illustrates the challenges in the assembly of C_3 symmetric molecules for supramolecular recognition, new materials, and asymmetric catalysis.13

The citrate ligand supplies the oxygen donors for both Na(I) and Pd(II) and the bridging framework to connect the inherently different metals. It also attracts hydration and provides the media for extensive H-bonding in the network. These enable the rare isolation of 1 among a large number of unstable precious metal citrates. The sodium ion provides a site for hydration and fortifies the network through inter-ionic H-bonding. It also plays a unique role to bridge, connect and stabilise the Pd₃ core intra- and intermolecularly. This unprecedented form of sodium ion arrangement within the palladium network offers a mechanism to stabilise the usually unstable precious metal homoleptic citrates. Accordingly, when Na⁺ is replaced by other alkaline metals (Li⁺, K⁺, Cs⁺) in the synthesis, the orange solids isolated are significantly less stable with rapid decomposition. Such decomposition in the solid state or in water is not apparent in 1. However, in ethanol or upon sonication, the Na/Pd aggregate readily decomposes to give a solid comprises mainly PdO and Pd, as verified by the XPS analysis (Fig. 2). This substantiates the important role of H-bonding in this hydrate-saturated aggregate. Further experiments are under way to examine the metallic palladium distributions under different solvent or cation conditions.

The stability and isolability of the titled homoleptic intermetallic citrate is unusual but can be understood from the structural revelations. The absence of any β -hydride in a citrate is notable since Pd(II) alkoxyl complexes are prone to such elimination and decomposition.¹⁴

There is also evidence of weak anagostic interaction¹⁵ between the γ hydrogen of one of the CH₂ groups (H···Pd 2.80 Å; \angle C3–H3B····Pd 117° with downfield $\delta_{\rm H}$ shift of 0.72 ppm) with the metal (Fig. 1(a)). This sufficiently perturbs and distinguishes the CH₂ protons (¹H-NMR). Although β -hydride elimination is commonly found in transition metal alkyls in the hydrocarbon reforming process, nickel has shown a preference for α -hydride elimination whereas platinum also yields γ -hydride elimination.¹⁶ Such presence of anagostic γ -hydride interaction may explain our insofar futile attempts to prepare the stable Pt(II) analogue of 1. The presence of oxophilic Na⁺ provides an enthalpic drive for the aggregate formation, which is further assisted by the extensive Hbond formation within the network. Citrate, as a skeletally flexible multidendate oxygen donor and a ligand that is well suited for multidirectional H-bonding, is an ideal ligand as it meets all the structural and bonding demands. Without a formal $Pd \cdots Pd$ (3.23 Å) or Pd \cdots Na (3.40 Å) bond, this coordination network of **1** is best treated as a metal aggregate, not cluster, in which the major molecular entities are held together by citrates (in NaPd₃ nodes) or in conjunction with hydrate (in Na3 blocks). Taking advantage of the water-rich nature of the intermetallic complex and it being a ready source of active Pd2+, we have examined its Suzuki coupling activity of phenylboronic acid at r.t. with a selected range of aryl bromides and chlorides in aqueous-methanolic media [H₂O-MeOH, 5:1] and compare the alkali metal effect [M/Pd, M = Na (1a), K (1b), Cs (1c), Li (1d)] (Table 1). The catalyst is conveniently generated in situ from PdCl₂, citric acid and MHCO₃ or M₂CO₃. The yields for bromides (50-93%) are understandably higher than those of chloride (20-67%). The highest activities are observed for M = Na, which also gives the most stable intermetallic citrate. The poorest performance is found in M = Li when the complex is also the least stable. Other catalytic possibilities are currently being examined. Preliminary data suggest that 1 is active towards hydroamination of 1,3-cyclohexadiene with 4-nitroaniline in H₂O-THF (5:1) at 40 °C but with poor yield (27%).

This work offers a molecular level understanding of how citrate can bind to palladium and prevent it from oxidative etching

Entry	Ar-X (X = Br or Cl)	Catalyst	Isolated yield (%)
1	4-Bromotoluene	1a	93
2		1b	75
3		1c	75
4		1d	75
5	4-Bromobenzonitrile	1a	92
6		1b	87
7		1c	66
8		1d	51
9	4-Bromonitrobenzene	1a	80
10		1b	70
11		1c	63
12		1d	50
13	4-Bromoanisole	1a	88
14		1b	76
15		1c	67
16		1d	60
17	4-Chlorobenzonitrile	1a	67
18		1b	40
19		1c	34
20		1d	20

"Reaction conditions: phenylboronic acid (1.2 mmol); aryl halide (1 mmol); H₂O-MeOH 5:1 (6 mL); PdCl₂ (0.03 mmol), citric acid (0.06 mmol) and MHCO₃ or M₂CO₃ (7 mmol); r.t. for 24 h.

and eventually allow the formation of nano-materials such as palladium icosahedra.¹⁷ It demonstrates the potential of citrate to support water-based catalysis of Pd2+. The isolated anionic Pd²⁺ aggregate supported solely by carboxylate type donors is reminiscent of Pd(OAc)₂ which is among the most popular catalyst precursors, and also one that is known to lead to catalytically active anionic Pd(II) or Pd(0).¹⁸ The higher aqueous compatibility of citrate (compared to common mono- or di-carboxylates) and its higher denticity and donor flexibility would make citrate and related ligands good candidates for water-based reactions promoted by precious metal catalysts. Isolation of the titled aggregate has fuelled the optimism that such catalyst precursors can be easily prepared, and stable enough to be isolated and structurally characterised. The structural insights thus obtained would be key to future catalyst design.

We are grateful to L. L. Koh and G. K. Tan for X-ray diffractometry measurement assistance. This work was supported by the National University of Singapore, the Ministry of Education (R-143-000-361-112) and the Agency for Science, Technology and Research (R-143-000-364-305). Several school students in the H3/SRP programs, notably J. Chen, L. Yeh, V. Lim, D. Lim and S. Lim have contributed in the form of experimental assistance.

Notes and references

‡ Crystal data of 1: empirical formula: C₆H_{43/3}Na₂O_{73/6}Pd, formula weight: 1300.66; crystal system: trigonal; space group: $R\overline{3}$; a = 15.8632(6), b =15.8632(6), c = 28.772(2) Å; $\alpha = 90$, $\beta = 90$, $\gamma = 120^{\circ}$; V = 6270.1(6)Å³; Z = 18; ρ (calcd) = 2.067 Mg m⁻³; F(000) = 3882; crystal size: 0.14 × $0.14 \times 0.08 \text{ mm}^3$; independent reflections: 2452 [$R_{int} = 0.0409$]; reflections collected: 11 706; GOF = 1.302; $R_1[I > 2\sigma(I)] = 0.0579$, w R_2 (all data) = 0.1123. CCDC number: 692934.

- 1 (a) P. Thuéry, CrystEngComm, 2007, 9, 358; (b) F.-Y. Li, L. Xu, G.-G. Gao, L.-H. Fan and B. Bi, Eur. J. Inorg. Chem., 2007, 3405; (c) W. Li, L. Jin, N. Zhu, X. Hou, F. Deng and H. Sun, J. Am. Chem. Soc., 2003, 125, 12408; (d) D. W. Hartley, G. Smith, D. S. Sagatys and C. H. L. Kennard, J. Chem. Soc., Dalton Trans., 1991, 2735; (e) R. C. Bott, G. Smith, D. S. Sagatys, D. E. Lynch and C. H. L. Kennard, Aust. J. Chem., 2000, 53, 917; (f) T. L. Feng, P. L. Gurian, M. D. Healy and A. R. Barron, Inorg. Chem., 1990, 29, 408; (g) A. Bodor, I. Bányai, L. Zékány and I. Tóth, Coord. Chem. Rev., 2002, 228, 163; (h) A. Bodor, I. Bányai and I. Tóth, Coord. Chem. Rev., 2002, 228, 175.
- 2 (a) A. Bino, I. Shweky, S. Cohen, E. R. Bauminger and S. J. Lippard, Inorg. Chem., 1998, 37, 5168; (b) M. Matzapetakis, N. Karligiano, A. Bino, M. Dakanali, C. P. Raptopoulou, V. Tangoulis, A. Terzis, J. Giapintzakis and A. Salifoglou, Inorg. Chem., 2000, 39, 4044; (c) F.-T. Xie, L.-M. Duan, X.-Y. Chen, P. Cheng, J.-Q. Xu, H. Ding and T.-G. Wang, Inorg. Chem. Commun., 2005, 8, 274; (d) T. A. Hudson, K. J. Berry, B. Moubaraki, K. S. Murray and R. Robson, Inorg. Chem., 2006, 45 3549
- 3 (a) H. E. Bryndza and W. Tam, Chem. Rev., 1988, 88, 1163; (b) J. R. Fulton, A. W. Holland, D. J. Fox and R. G. Bergman, Acc. Chem. Res., 2002, 35, 44; (c) J.-E. Bäckvall, E. E. Björkman, L. Pettersson and P. Siegbahn, J. Am. Chem. Soc., 1984, 106, 4369; (d) J.-E. Bäckvall, E. E. Björkman, L. Pettersson and P. Siegbahn, J. Am. Chem. Soc., 1985, 107, 7265; (e) H. E. Bryndza, J. C. Calabrese, M. Marsi, D. C. Roe, W. Tam and J. E. Bercaw, J. Am. Chem. Soc., 1986, 108, 4805; (f) K. A. Bernard, W. M. Rees and J. D. Atwood, Organometallics, 1986, 5, 390; (g) A. S. Goldman and J. Halpern, J. Am. Chem. Soc., 1987, 109, 7537; (h) D. M. Hoffman, D. Lappas and D. A. Wierda, J. Am. Chem. Soc., 1993, 115, 10538; (i) G. M. Kapteijn, D. M. Grove, H. Kooijman, W. J. J. Smeets, A. L. Spek and G. van Koten, Inorg. Chem., 1996, 35, 526; (j) M. A. Jalil, T. Nagai, T. Murahashi and H. Kurosawa, Organometallics, 2002, **21**. 3317.
- 4 (a) B.-K. Pong, H. I. Elim, J.-X. Chong, W. Ji, B. L. Trout and J.-Y. Lee, J. Phys. Chem. C, 2007, 111, 6281; (b) R. Zhang and X. Wang, Chem. Mater., 2007, 19, 976; (c) S. H. Y. Lo, Y.-Y. Wang and C.-C. Wan, J. Colloid Interface Sci., 2007, 310, 190.
- 5 (a) O. M. Wilson, X. Hu, D. G. Cahill and P. V. Braun, Phys. Rev. B: Condens. Matter Mater. Phys., 2002, 66, 224301; (b) K. Niesz, M. M. Koebel and G. A. Somorjai, Inorg. Chim. Acta, 2006, 359, 2683; (c) X. Xiao and A. J. Bard, J. Am. Chem. Soc., 2007, 129, 9610.
- 6 C. R. K. Rao and D. C. Trivedi, Coord. Chem. Rev., 2005, 249, 613.
- 7 K. E. Neo, Y. Y. Ong, H. V. Huynh and T. S. A. Hor, J. Mater. Chem., 2007, 17, 1002.
- 8 (a) Z. Weng, L. L. Koh and T. S. A. Hor, J. Organomet. Chem., 2004, 689, 18; (b) Z. Weng, S. Teo and T. S. A. Hor, Acc. Chem. Res., 2007, 40, 676; (c) S.-Q. Bai and T. S. A. Hor, Chem. Commun., 2008, 3172. 9 P. Thuéry, CrystEngComm, 2008, 10, 79.
- 10 A. Henglein and M. Giersig, J. Phys. Chem. B, 1999, 103, 9533.
- 11 B. Lim, Y. Xiong and Y. Xia, Angew. Chem., Int. Ed., 2007, 46, 9279.
- 12 (a) I. Gautier-Luneau, D. Phanon, C. Duboc, D. Luneau and J.-L. Pierre, Dalton Trans., 2005, 3795; (b) I. Gautier-Luneau, C. Merle, D. Phanon, C. Lebrun, F. Biaso, G. Serratrice and J.-L. Pierre, Chem.-Eur. J., 2005, 11, 2207; (c) J. L. Pierre and I. Gautier-Luneau, BioMetals, 2000, 13, 91.
- 13 (a) J.-M. Lehn, Supramolecular Chemistry, Concepts and Perspectives; VCH: Weinheim, 1995; (b) L. R. MacGillivray and J. L. Atwood, Angew. Chem., Int. Ed., 1999, 38, 1018.
- 14 T. Yoshida, T. Okano and S. Otsuka, J. Chem. Soc., Dalton Trans., 1976, 993.
- 15 (a) M. Brookhart, M. L. H. Green and G. Parkin, Proc. Natl. Acad. Sci. U. S. A., 2007, 104, 6908; (b) J. J. Hu, F. Li and T. S. A. Hor, Organometallics, 2009, 28, 1212.
- 16 F. Zaera, Appl. Catal., A, 2002, 229, 75.
- 17 Y. Xiong, J. M. McLellan, Y. Yin and Y. Xia, Angew. Chem., Int. Ed., 2007. 46, 790.
- 18 C. Amatore and A. Jutand, Acc. Chem. Res., 2000, 33, 314.