ChemComm
www.rsc.org/chemcomm

New high-nuclearity Ni–Pt carbonyl clusters: synthesis and X-ray structure of the ordered $[HNi_{24}Pt_{17}(CO)_{46}]^{5-}$ and the substitutionally Ni/Pt disordered $[Ni_{32}Pt_{24}(CO)_{56}]^{6-}$ cluster anions

Cristina Femoni, M. Carmela Iapalucci, Giuliano Longoni* and Per H. Svensson†
Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, viale Risorgimento 4, 40136 Bologna, Italy. E-mail: longoni@ms.fci.unibo.it; Fax: +051 209 3690; Tel: +051 209 3711

Received (in Cambridge, UK) 24th June 2004, Accepted 5th August 2004
First published as an Advance Article on the web 7th September 2004

Condensation between preformed Ni–Pt and Pt carbonyl clusters leads to the new $[H_{6-n}Ni_{24}Pt_{17}(CO)_{46}]^{n-}$ (n = 5, 6) and the substitutionally Ni/Pt disordered $[Ni_{24}(Ni_{12-x}Pt_x)Pt_{20}(CO)_{56}]^{6-}$ (x = 4) carbonyl clusters, the latter of which represents the highest nuclearity homoleptic carbonyl cluster anion so far reported.

Several high-nuclearity Ni–Pt, Pd–Pt and Pt carbonyl clusters containing up to 6 interstitial Pt atoms are known, *e.g.* $[Ni_{14}Pt_{10}(CO)_{30}]^{4-}$,[1] $[H_2Ni_{24}Pt_{14}(CO)_{44}]^{4-}$,[1,2] $[H_{6-n}Ni_{38}Pt_6(CO)_{48}]^{n-}$,[3,4] $[H_{6-n}Ni_{36}Pt_4(CO)_{45}]^{n-}$,[5] $[H_{6-n}Ni_{35}Pt_9(CO)_{48}]^{n-}$,[6] $[H_{12}Pd_{28}Pt_{13}(CO)_{27}(PMe_3)(PPh_3)_{12}]$,[7] $[Pt_{19}(CO)_{22}]^{4-}$,[8] $[Pt_{24}(CO)_{30}]^{n-}$,[9,10] $[Pt_{26}(CO)_{32}]^{n-}$,[9,10] and $[Pt_{38}(CO)_{44}]^{n-}$.[9,11] Some of them are multivalent; most display behaviour of molecular capacitors and can accept up to 4–5 extra electrons.[12–14] The above features suggest metal clusters to be potential multilevel memory molecules capable of storing more than one bit of charge. This is a goal of *moletronics* (molecular electronics) which, for instance, would like to store information in the form of parcels of charges and overcome the on–off logic.[15]

The above considerations fuelled our interest in Pt atom-rich high-nuclearity Ni–Pt carbonyl clusters. As a result of our efforts, we now report the synthesis and structure of the ordered $[HNi_{24}Pt_{17}(CO)_{46}]^{5-}$ and the substitutionally Ni/Pt disordered $[Ni_{24}(Ni_{12-x}Pt_x)Pt_{20}(CO)_{56}]^{6-}$ (x = 4) anions. These clusters contain 7 and 8 interstitial Pt atoms. Besides, the latter represents the highest nuclearity homoleptic carbonyl cluster anion so far reported.

The $[HNi_{24}Pt_{17}(CO)_{46}]^{5-}$ pentaanion has been initially obtained in low yields during the optimization of the synthesis of $[H_2Ni_{24}Pt_{14}(CO)_{44}]^{4-}$,[1,2] by reaction of $[N\textit{n}\text{-}Bu_4]_2[Ni_6(CO)_{12}]$ in THF with 1.9 equivalents of $Pt(SEt_2)_2Cl_2$. Elucidation of its stoichiometry and structure prompted the tailored synthesis approximately represented by eqn. (1). Thus, treatment with THF of the residue obtained by evaporation of the reaction solution gave a dark-green solution containing a mixture of $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 4, 3)[16,17] species and a sparingly soluble precipitate of $[N\textit{n}\text{-}Bu_4]_5[HNi_{24}Pt_{17}(CO)_{46}]$. Extraction of the latter with acetone and precipitation with hexane afforded well-shaped crystals of $[N\textit{n}\text{-}Bu_4]_5[HNi_{24}Pt_{17}(CO)_{46}]$ (ν_{CO} at 2018 s, 1816 mw cm^{-1} in Me_2CO and 2021 s, 1818 mw cm^{-1} in MeCN). The presence of one hydride atom in $[HNi_{24}Pt_{17}(CO)_{46}]^{5-}$ could not be demonstrated by NMR; however, it is suggested by a slow deprotonation in MeCN to $[Ni_{24}Pt_{17}(CO)_{46}]^{6-}$ (ν_{CO} at 2011 s, 1811 mw cm^{-1} in MeCN), which may be reversed by addition of protic acids.

$$[HNi_{24}Pt_{14}(CO)_{44}]^{5-} + [Pt_{15}(CO)_{30}]^{2-} \rightarrow [HNi_{24}Pt_{17}(CO)_{46}]^{5-} + [Pt_{12}(CO)_{24}]^{2-} + 4CO \qquad (1)$$

The substitutionally Ni/Pt disordered $[N\textit{n}\text{-}Bu_4]_6[Ni_{24}(Ni_{12-x}Pt_x)Pt_{20}(CO)_{56}]$ (x = 4) (ν_{CO} in MeCN at 2023 s, 1860 mw, 1821 mw cm^{-1}) salt has been similarly obtained by reaction of $[Ni_{35}Pt_9(CO)_{48}]^{6-}$ with one equivalent of $[Pt_{30}(CO)_{60}]^{2-}$.[17] Both $[N\textit{n}\text{-}Bu_4]_5[HNi_{24}Pt_{17}(CO)_{46}]$ and $[N\textit{n}\text{-}Bu_4]_6[Ni_{32}Pt_{24}(CO)_{56}]$ salts have been characterised by elemental analysis and X-ray diffraction studies.‡

As shown in Fig. 1, the structure of $[HNi_{24}Pt_{17}(CO)_{46}]^{5-}$ is based on a ccp metal fragment and is closely related to that of $[H_2Ni_{24}Pt_{14}(CO)_{44}]^{4-}$.[1] The former formally derives from the latter by condensation of a Pt_3 triangle on top of one hexagonal face, followed by site exchange with three Ni atoms of the underlying hexagonal face. As a result, a $Ni_{21}Pt_{17}$ truncated ν_3-octahedron displaying alternating Ni and Pt atoms on the edges of the hexagonal face capped by the Ni_3 triangle, is generated. The ordered occupation is probably favoured by distinctive preferences in carbonyl and metal coordination of the two metals. Thus, 14 out of 17 Pt atoms choose sites featuring the highest metal coordination (*viz.* 7 interstitial and 7 centre-of-face positions). 21 out of 24 Ni atoms choose sites featuring the lowest metal coordination of 5 (3 atoms) and 6 (18 atoms). The sites with intermediate coordination of 7 are alternately occupied by the remaining 3 Ni and 3 Pt atoms. The carbonyl stereochemistry of $[HNi_{24}Pt_{17}(CO)_{25}(\mu\text{-}CO)_{21}]^{5-}$ is little influenced by the miscellaneous coordinations of the two metals. Thus, all Ni atoms bind one terminal and one edge-bridging carbonyl group. All but one of the surface Pt atoms bind two edge-bridging carbonyls. The surface Pt atom of the bottom hexagonal face is unique in binding only one terminal carbonyl group. Also the carbonyl stereochemistry of $[HNi_{24}Pt_{17}(CO)_{25}(\mu\text{-}CO)_{21}]^{5-}$ is closely related to that of the parent $[H_2Ni_{24}Pt_{14}(CO)_{26}(\mu\text{-}CO)_{18}]^{4-}$.[1]

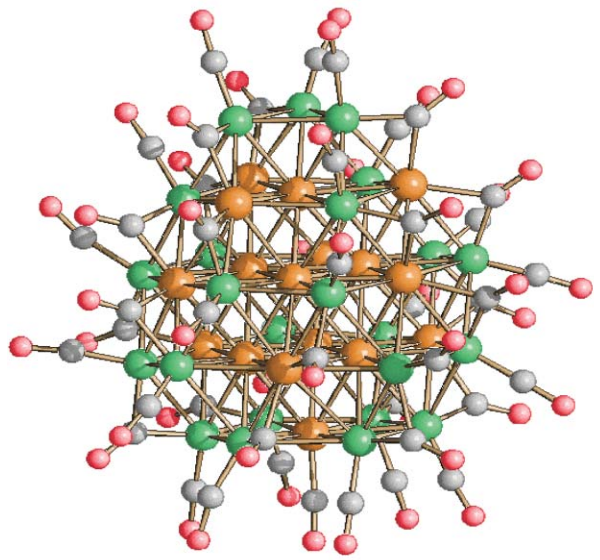

Fig. 1 The $[HNi_{24}Pt_{17}(CO)_{25}(\mu\text{-}CO)_{21}]^{5-}$ pentaanion. Pt and Ni atoms are shown as orange and green spheres, respectively. Range of M–M distances: Pt–Pt 2.685(2)–2.961(2), Ni–Pt 2.567(3)–2.913(2), Ni–Ni 2.540(5)–2.842(4) Å.

---

† Present address: AstraZeneca R&D Sodertalje Solid State Analysis, S-151 85 Sodertalje, Sweden.

DOI: 10.1039/b409522g

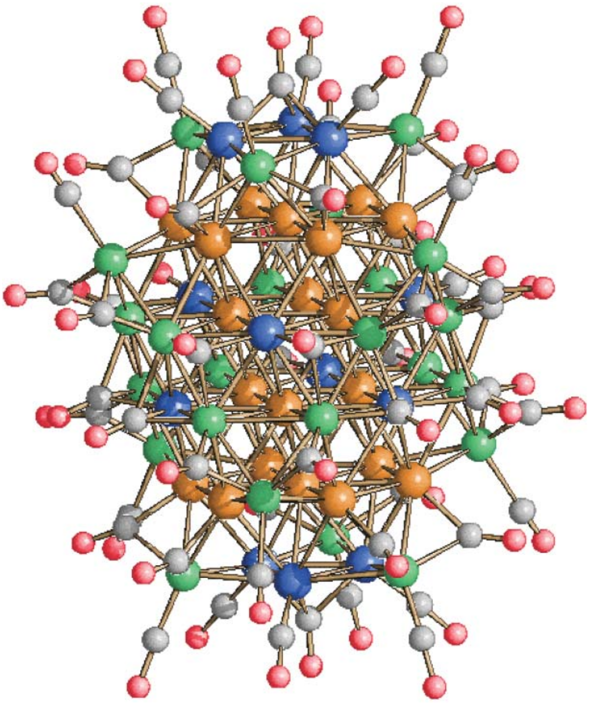

Fig. 2 The $[\mathrm{Ni}_{24}(\mathrm{Ni}_{12-x}\mathrm{Pt}_x)\mathrm{Pt}_{20}(\mathrm{CO})_{56}]^{6-}$ (x = 4) hexaanion. Pt, Ni and Ni/Pt (0.66/0.33) disordered atoms are shown as orange, green and blue spheres, respectively. Range of M–M distances: Pt–Pt 2.696(2)–2.795(2), Ni–Pt 2.538(5)–2.676(4), Ni–Ni 2.438(5)–2.816(4), Ni/Pt–Ni 2.569(4)–2.764(6), Ni/Pt–Pt 2.626(3)–2.792(2), Ni/Pt–Ni/Pt 2.653(4) Å.

The structure of $[\mathrm{Ni}_{32}\mathrm{Pt}_{24}(\mathrm{CO})_{56}]^{6-}$ is shown in Fig. 2. Its metal frame represents a fragment of a ccp metal lattice comprising 8 interstitial Pt atoms. As shown in Fig. 3, it formally derives from condensation of two $\mathrm{Ni}_5\mathrm{Pt}$ ν_2-triangles onto two opposite faces of a $\mathrm{Ni}_{22}\mathrm{Pt}_{22}$ ν_3-octahedral fragment like that displayed by $[\mathrm{HNi}_{38}\mathrm{Pt}_6(\mathrm{CO})_{48}]^{5-}$ and $[\mathrm{Ni}_{35}\mathrm{Pt}_9(\mathrm{CO})_{48}]^{6-}$. Two Pt atoms (one per each $\mathrm{Ni}_5\mathrm{Pt}$ ν_2-triangle) are disordered over the three edge sites. The remaining two disordered Pt atoms are distributed over the three edge sites (Ni : Pt = 0.66 : 0.33) of the two inner truncated ν_4-triangular layers (Fig. 2). Significantly, the Ni/Pt disorder occurs on those sites displaying intermediate metal coordination of 7 and 9, and is roughly related to that found in the parent $[\mathrm{Ni}_{35}\mathrm{Pt}_9(\mathrm{CO})_{48}]^{6-}$ compound.[6] In rough agreement with the IR spectrum, the carbonyl stereochemistry of $[\mathrm{Ni}_{32}\mathrm{Pt}_{24}(\mathrm{CO})_{18}(\mu\text{-}\mathrm{CO})_{24}(\mu_3\text{-}\mathrm{CO})_{14}]^{6-}$ involves the presence of terminal, edge-bringing and face-bridging carbonyl groups. All Ni atoms are three-coordinated and bind one terminal and two edge-bridging carbonyl groups or two edge- and one face-bridging CO. Ni/Pt disordered sites are two-coordinated and bind one terminal and one face-bridging carbonyl or two edge-bridging COs. All surface Pt atoms are only bound to one edge-bridging CO.

Preliminary experiments suggest that both $[\mathrm{HNi}_{24}\mathrm{Pt}_{17}(\mathrm{CO})_{46}]^{5-}$ and $[\mathrm{Ni}_{32}\mathrm{Pt}_{24}(\mathrm{CO})_{56}]^{6-}$, as well as $[\mathrm{H}_{6-n}\mathrm{Ni}_{24}\mathrm{Pt}_{14}(\mathrm{CO})_{44}]^{n-}$ (n = 4, 5), undergo protonation–deprotonation equilibria in solution and redox changes. Studies devoted to elucidate their nanocapacitor properties are ongoing.

G. L. thanks MIUR (PRIN2003) for funding. P. H. S. acknowledges The Wenner-Gren Foundation, Stiftelsen BLANCEFLOR Boncompagni-Ludovisi, född Bildt and Svenska Institutet for a grant.

Notes and references

‡ Crystal data for $[\mathrm{N}n\text{-}\mathrm{Bu}_4]_5[\mathrm{HNi}_{24}\mathrm{Pt}_{17}(\mathrm{CO})_{46}]$: M = 7226.32, monoclinic, a = 18.206(1), b = 27.251(2), c = 18.653(1) Å, β = 98.417(2)°, U = 9154.8(10) Å^3, T = 273 K, space group Pn, Z = 2, μ(Mo-Kα) = 15.39 mm^{-1}, reflections measured 88419, unique 32230 (R_{int} = 0.0894) which were used in all calculations. The final $R1$ and $wR2$ were 0.0539 and 0.1218 [$I > 2\sigma(I)$]. CCDC 241936. Crystal data for $[\mathrm{N}n\text{-}\mathrm{Bu}_4]_6[\mathrm{Ni}_{24}(\mathrm{Ni}_{12-x}\mathrm{Pt}_x)\mathrm{Pt}_{20}(\mathrm{CO})_{56}]$ (x = 4): M = 9668.34, trigonal, a = 29.477(3), b = 29.477(3), c = 22.178(4) Å, U = 16689(3) Å^3, T = 293 K, space group $R\bar{3}$, Z = 3, μ(Mo-Kα) = 17.712 mm^{-1}, reflections collected 49691, unique 6528 (R_{int} = 0.2498) which were used in all calculations. The final $R1$ and $wR2$ were 0.0655 and 0.2363 [$I > 2\sigma(I)$]. CCDC 241935. In both structures distance and anisotropic displacement parameter restrains were applied to the cations and to a few carbonyl groups. See http://www.rsc.org/suppdata/cc/b4/b409522g/ for crystallographic data in .cif or other electronic format.

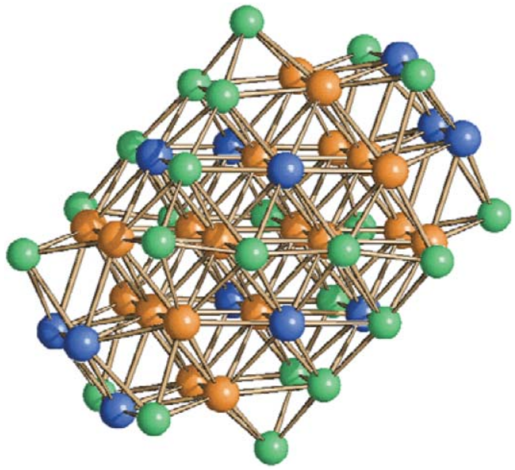

Fig. 3 A view of the $[\mathrm{Ni}_{24}(\mathrm{Ni}_{12-x}\mathrm{Pt}_x)\mathrm{Pt}_{20}(\mathrm{CO})_{56}]^{6-}$ (x = 4) metal framework pointing out its formal relationship with the ν_3-octahedral structure of $[\mathrm{H}_{6-n}\mathrm{Ni}_{44-x}\mathrm{Pt}_x(\mathrm{CO})_{48}]^{n-}$ (x = 6, 9; colours as in Fig. 2).

1 C. Femoni, M. C. Iapalucci, G. Longoni and P. H. Svensson, *Chem. Commun.*, 2001, 1776.

2 Circumstantial evidence suggests the presence of two hydride atoms in the cluster originally formulated as $[\mathrm{Ni}_{24}\mathrm{Pt}_{14}(\mathrm{CO})_{44}]^{4-}$.

3 A. Ceriotti, F. Demartin, G. Longoni, M. Manassero, M. Marchionna, G. Piva and M. Sansoni, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 696.

4 C. Femoni, M. C. Iapalucci, G. Longoni, P. H. Svensson and J. Wolowska, *Angew. Chem., Int. Ed.*, 2000, **39**, 1635.

5 F. Demartin, C. Femoni, M. C. Iapalucci, G. Longoni and P. Zanello, *J. Cluster Sci.*, 2001, **12**, 61.

6 C. Femoni, M. C. Iapalucci, G. Longoni and P. H. Svensson, *Chem. Eur. J.*, 2004, **10**, 2318.

7 J. M. Bemis and L. F. Dahl, *J. Am. Chem. Soc.*, 1997, **119**, 4545.

8 D. M. Washecheck, E. J. Wucherer, L. F. Dahl, A. Ceriotti, G. Longoni, M. Manassero, M. Sansoni and P. Chini, *J. Am. Chem. Soc.*, 1979, **101**, 6110.

9 G. J. Lewis, J. D. Roth, R. A. Montag, L. K. Safford, X. Gao, S-C. Chang, L. F. Dahl and M. J. Weaver, *J. Am. Chem. Soc.*, 1990, **112**, 2831.

10 J. D. Roth, G. J. Lewis, L. K. Safford, X. Jiang, L. F. Dahl and M. J. Weaver, *J. Am. Chem. Soc.*, 1992, **114**, 6159.

11 A. Ceriotti, N. Masciocchi, P. Macchi and G. Longoni, *Angew. Chem., Int. Ed.*, 1999, **38**, 3724.

12 (*a*) P. Zanello, in *Stereochemistry of Organometallic and Inorganic Compounds*, ed. P. Zanello, Elsevier, Amsterdam, 1994, **vol. 5**, p. 163; (*b*) P. Zanello, in *Structure and Bonding*, Spinger-Verlag, Berlin, 1992, **vol. 79**, p. 101.

13 C. Femoni, M. C. Iapalucci, G. Longoni, P. Zanello and A. Ceriotti, *Inorg. Chem.*, 1999, **38**, 3721.

14 D. Collini, C. Femoni, M. C. Iapalucci, G. Longoni and P. Zanello, *Perspectives in Organometallic Chemistry*, ed. C. G. Screttas and B. R. Steele, Royal Society of Chemistry, Cambridge, 2003, Special Publication 287, p. 183.

15 C. Li, W. Fan, B. Lei, D. Zhang, S. Han, T. Tang, X. Liu, Z. Liu, S. Asano, M. Meyyappan, J. Han and C. Zhou, *Appl. Phys. Lett.*, 2004, **84**, 1949.

16 J. C. Calabrese, L. F. Dahl, P. Chini, G. Longoni and S. Martinengo, *J. Am. Chem. Soc.*, 1974, **96**, 2614.

17 G. Longoni and P. Chini, *J. Am. Chem. Soc.*, 1976, **98**, 7225.