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New high-nuclearity Ni–Pt carbonyl clusters: synthesis and X-ray structure of the ordered $[Ni_{24}Pt_{14}(CO)_{44}]^{4-}$ and the substitutionally Ni/Pt disordered $[Ni_{10}(Ni_{6-x}Pt_x)Pt_8(CO)_{30}]^{4-}$ (x = 1.92) tetraanions

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The reaction of $[N^nBu_4]_2[Ni_6(CO)_{12}]$ in THF solution with 1.5–2 equivalents of K_2PtCl_4 leads to formation of the $[Ni_{24}Pt_{14}(CO)_{44}]^{4-}$ and $[Ni_{10}(Ni_{6-x}Pt_x)Pt_8(CO)_{30}]^{4-}$ ($x \approx 2$) tetraanions, the latter presents a localised substitutional Ni/Pt disorder and an unprecedented close-packed metal structure.

Most high-nuclearity metal carbonyl clusters containing interstitial Ni or Pt atoms, *e.g.* $[Ni_{11}E_2(CO)_{18}]^{n-}$ (E = Sb, Bi),[1,2] $[H_{6-n}Ni_{38}Pt_6(CO)_{48}]^{n-}$,[3] $[H_{6-n}Ni_{36}Pt_4(CO)_{45}]^{n-}$,[4] $[Pt_{19}(CO)_{22}]^{4-}$[5] and $[Pt_{24}(CO)_{30}]^{2-}$,[6,7] display multivalence encompassing several redox changes.[5,8,9] Previously reported Ni–Pd carbonyl clusters, *viz.* $[Ni_{16}Pd_{16}(CO)_{40}]^{4-}$ and $[Ni_{26}Pd_{20}(CO)_{54}]^{6-}$,[10] contain interstitial Pd atoms and are an exception to the above rule. This probably happens because of the weakness of all bonds involving palladium atoms, which may favour fragmentation–condensation processes under redox conditions. On the other hand, it is possible that the above weakness could favour crowding of almost degenerate energy levels in the frontier region and anticipate the size-induced metal–insulator transition,[11] which for metal carbonyl clusters is expected to occur for nuclearities beyond 70.[3] In partial agreement, preliminary magnetic measurements indicate that the even-electron $[Ni_{16}Pd_{16}(CO)_{40}]^{4-}$ displays magnetic behaviour arising from the presence of four unpaired electrons.[12]

The above considerations stirred interest in platinum-rich Ni–Pt carbonyl clusters. As a result, we now report the synthesis and structure of the first examples of such compounds consisting of the substitutionally Ni/Pt crystal disordered $[Ni_{10}(Ni_{6-x}Pt_x)Pt_8(CO)_{30}]^{4-}$ ($x \approx 2$) and the ordered $[Ni_{24}Pt_{14}(CO)_{44}]^{4-}$ tetraanions.

Both compounds were obtained by reaction of $[N^nBu_4]_2[Ni_6(CO)_{12}]$ in THF with 1.5–2 equivalents of K_2PtCl_4 and from the residue obtained by evaporation of the reaction solution were separated by differential solubility of their salts. Thus, treatment of the above residue with THF gave a dark-green solution containing a mixture of $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 3, 4)[13,14] and $[Ni_{24}Pt_{14}(CO)_{44}]^{4-}$, and an insoluble dark precipitate. Extraction of the latter with acetone and precipitation with hexane afforded $[N^nBu_4]_4[Ni_{10}(Ni_{6-x}Pt_x)Pt_8(CO)_{30}]\cdot Me_2CO$ (x = 1.92) (ν_{CO} in MeCN at 2003 s, 1990 sh, 1821 m (br) cm^{-1}) as black prisms. $[N^nBu_4]_4[Ni_{24}Pt_{14}(CO)_{44}]\cdot 6THF$ (ν_{CO} in MeCN at 2008 s, 1877 mw, 1854 m and 1835 mw cm^{-1}) separated out as hexagonal black crystals from the above dark-green THF solution upon concentration. Both compounds have been characterised by elemental analysis and X-ray diffraction studies.†

The overall structures of the $[Ni_{10}(Ni_{6-x}Pt_x)Pt_8(CO)_{12}(\mu\text{-}CO)_{18}]^{4-}$ and $[Ni_{24}Pt_{14}(CO)_{26}(\mu\text{-}CO)_{18}]^{4-}$ tetraanions are shown in Fig. 1 and 2, respectively. The $[Ni_{10}(Ni_{6-x}Pt_x)Pt_8(CO)_{30}]^{4-}$ metal frame is based on an unprecedented *hcp* sequence of M_7, M_{10} and M_7 layers. Interestingly, the closely related homometallic $[Pt_{24}(CO)_{30}]^{2-}$[6,7] is based on a *ccp* fragment deriving from that of $[Pt_{38}(CO)_{44}]^{2-}$[15] by cutting two adjacent hexagonal Pt_7 faces. The metal sites (relative number of metal atoms in parentheses) of $[Ni_{10}(Ni_{6-x}Pt_x)Pt_8(CO)_{30}]^{4-}$ display rather spread metallic coordinations of 4 (4 Ni), 5 (2 Ni/Pt), 6 (1 Pt, 4 Ni/Pt), 7 (6 Ni, 4 Pt), 8 (1 Pt) and 12 (2 Pt). The Ni/Pt substitutional disorder is limited to the two middle-layer sites with metal connectivity of 5 and their adjacent atoms belonging to the top- and bottom-layer and displaying metal connectivity of 6. These were refined as a mixture of Ni and Pt atoms to obtain occupancy fractions of *ca.* 2/3 and 1/3, respectively. All other metal sites could be refined either as nickel or platinum atoms. Analysis of two other crystals, coming from different preparations of $[Ni_{10}(Ni_{6-x}Pt_x)Pt_8(CO)_{30}]^{4-}$, gave rise to slightly different Ni and Pt occupancy fractions in the same substitutionally disordered sites. However, an overall x value of *ca.* 2 was confirmed. This finding is in agreement with the presence of a stoichiometric $[Ni_{10}(Ni_4Pt_2)Pt_8(CO)_{30}]^{4-}$ species having localised substitutional Ni/Pt disorder (as, for instance, $[Fe_2Rh_4(CO)_{16}]^{2-}$).[16] A non-stoichiometric and substitutionally disordered mixture of $[Ni_{10}(Ni_{6-x}Pt_x)Pt_8(CO)_{30}]^{4-}$ species, as exemplified by the recently reported $[Au_6Pd_6(Pd_{6-x}Ni_x)Ni_{20}(CO)_{44}]^{6-}$,[17] seems less in keeping with the available data.

The metal framework of $[Ni_{24}Pt_{14}(CO)_{44}]^{4-}$ represents a fragment of *ccp* lattice identical to that displayed by the homometallic $[Pt_{38}(CO)_{44}]^{2-}$ dianion,[15] but different from that of other carbonyl clusters possessing the same metal nuclearity, *viz.* $[HNi_{38}C_6(CO)_{42}]^{5-}$,[18,19] $[Ni_{32}Au_6(CO)_{44}]^{6-}$,[17] $[Ni_{20}(Pd_{6-x}Ni_x)Pd_6Au_6(CO)_{44}]^{6-}$,[17] and $Pd_{38}(CO)_{28}$-

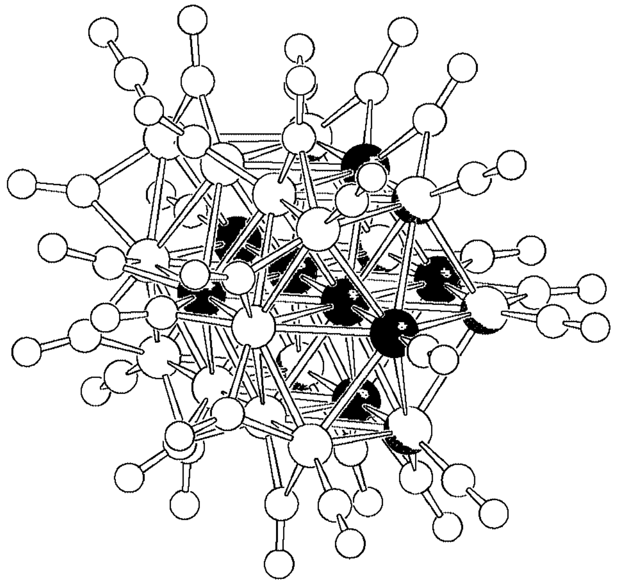

Fig. 1 The $[Ni_{10}(Ni_{6-x}Pt_x)Pt_8(CO)_{30}]^{4-}$ ($x \approx 2$) tetraanion. Pt and Ni atoms are shown as black and open spheres, respectively. Substitutional Ni–Pt disorder is limited to the sites shown as partially blackened spheres. Range of M–M distances: Pt–Pt 2.612(1)–2.817(1), Ni–Pt 2.673(2)–2.854(2), Ni–Ni 2.466(3)–2.815(3), Ni/Pt–Ni 2.705(3)–2.787(3), Ni/Pt–Pt 2.649(2)–2.796(2), Ni/Pt–Ni/Pt 2.732(3)–2.781(3) Å.

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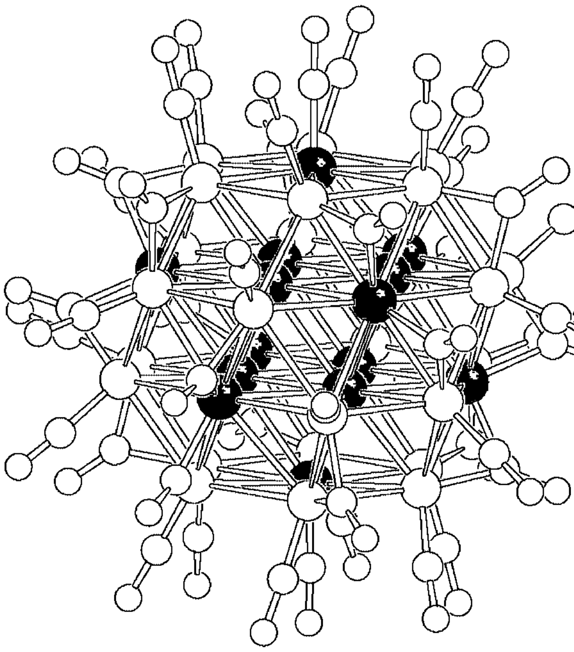

Fig. 2 The $[Ni_{24}Pt_{14}(CO)_{44}]^{4-}$ tetraanion (Pt atoms are shown as black spheres). Range of M–M and average M–C distances: Pt–Pt 2.725(1)–2.878(1), Ni–Pt 2.531(2)–2.861(2), Ni–Ni 2.524(3)–2.783(3) Å; Pt–C$_{terminal}$ 1.80(2), Pt–C$_{edge\text{-}bridging}$ 1.99, Ni–C$_{terminal}$ 1.71, Ni–C$_{edge\text{-}bridging}$ 1.85 Å.

$(PEt_3)_{12}$.[20] The 24 nickel atoms occupy the corner sites of the truncated-v_3-octahedron,[21] whereas the 14 platinum atoms occupy the six vertices of the interstitial octahedron and the centers of the eight hexagonal faces. Such an ordered occupation is probably favoured by the substantial difference in metal coordination (6, 9 and 12) of the three kinds of geometrically equivalent metal sites of $[Ni_{24}Pt_{14}(CO)_{44}]^{4-}$.

The carbonyl stereochemistry of $[Ni_{24}Pt_{14}(CO)_{26}(\mu\text{-}CO)_{18}]^{4-}$ represents a variant of that of the non-isoelectronic $[Pt_{38}(CO)_{32}(\mu\text{-}CO)_{12}]^{2-}$ dianion.[15] The tetraanion has 26 terminal ligands (one per each nickel atom and the two platinum atoms centering two opposite Ni_6 hexagonal rings) and 18 edge-bridges (12 onto the Ni–Pt–Ni diagonals of the other six Pt-centered Ni_6 hexagonal faces and six onto one Ni–Ni edge of each Ni_4 square face). Spanning of Ni–Pt bonds rather than a second opposite Ni–Ni edge of each Ni_4 square face reduces the number of short C···C non-bonding contacts and releases the steric pressure among the carbonyl groups. Moreover, an increased number of edge-bridging carbonyl groups with respect to $[Pt_{38}(CO)_{44}]^{2-}$ is in keeping with the increased negative charge of $[Ni_{24}Pt_{14}(CO)_{44}]^{4-}$. Regeneration of the carbonyl stereochemistry of the former would only require a concerted terminal–edge site exchange of the 12 edge-bridging carbonyls spanning the Ni–Pt–Ni diagonals of 6 out of 8 hexagonal faces and six terminal ligands bonded to one of the two nickel atoms of the above diagonals.

EHMO calculations with CACAO[22] show that the frontier regions of each of $[Ni_{24}Pt_{14}(CO)_{44}]^{4-}$ and $[Ni_{10}(Ni_{6-x}Pt_x)Pt_8(CO)_{30}]^{4-}$ do not feature a well-defined HOMO–LUMO gap. Therefore, it appears possible that both compounds could exhibit a wide range of redox states as their homometallic $[Pt_{24}(CO)_{30}]^{2-}$ and $[Pt_{38}(CO)_{44}]^{2-}$ congeners.[6,7] A further hint is given by the electron counts of both $[Ni_{24}Pt_{14}(CO)_{44}]^{4-}$ and $[Ni_{10}(Ni_{6-x}Pt_x)Pt_8(CO)_{30}]^{4-}$, which exceed by two valence electrons those of the related dianions, $[Pt_{38}(CO)_{44}]^{2-}$ [15] and $[Pt_{24}(CO)_{30}]$,$^{2-}$ respectively.[6,7] Studies devoted to elucidating their magnetic and electrochemical behaviour and the eventual structural changes occurring upon reduction or oxidation are ongoing.

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Notes and references

† *Crystal data* for $[N^nBu_4]_4[Ni_{24}Pt_{14}(CO)_{44}]\cdot 6THF$: M = 6775.2, orthorhombic, a = 29.464(1), b = 18.581(1), c = 31.648(1) Å, U = 17327.0(8) Å^3, T = 298 K, space group $Pbca$, Z = 4, μ(Mo-Kα) = 50.59 cm^{-1}, reflections measured 152459, unique 15233 (R_{int} = 0.1468) which were used in all calculations. The final $R1$ and $wR2$ were 0.0487 and 0.1141 [$I > 2\sigma(I)$].

Crystal data for $[N^nBu_4]_4[Ni_{10}(Ni_{6-x}Pt_x)Pt_8(CO)_{30}]\cdot Me_2CO$ (x = 1.92): M = 4630.48, monoclinic, a = 26.716(1), b = 15.276(1), c = 31.998(1) Å, β = 98.404(1),° U = 12918.3(8) Å^3, T = 193 K, space group $P2_1/n$, Z = 4, μ(Mo-Kα) = 50.59 cm^{-1}, reflections measured 111119, unique 21957 (R_{int} = 0.1347) which were used in all calculations. The final $R1$ and $wR2$ were 0.0458 and 0.0924 [$I > 2\sigma(I)$].

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See http://www.rsc.org/suppdata/cc/b1/b103610f/ for crystallographic data in CIF or other electronic format.

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