

Aprotic Synthesis and Structural Determination of the Nanosized Nonprotonated ν_3 -Octahedral $[\text{Pt}_6\text{Ni}_{38}(\text{CO})_{48}]^{6-}$ Hexaanion Stabilized as a Cubic Solvated $[\text{NMe}_4]^+$ Salt

Namal de Silva and Lawrence F. Dahl*

Department of Chemistry, University of Wisconsin—Madison, 1101 University Avenue, Madison, Wisconsin 53706

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The nonprotonated member, **1** ($n = 6$), of the previously established nanosized ν_3 -octahedral $[\text{H}_{6-n}\text{Pt}_6\text{Ni}_{38}(\text{CO})_{48}]^{n-}$ series ($n = 3-6$) has been isolated from an aprotic synthetic route and stabilized as the crystal-ordered cyclohexane/acetonitrile-solvated $[\text{NMe}_4]^+$ salt. A highly precise X-ray determination (cubic; $P2_3$; $Z = 4$ with **1** possessing -3 site symmetry) has allowed a comparative analysis of the nonprotonated pseudo- D_{3d} structure of **1** with the monoprotinated structure of **2** ($n = 5$), which constitutes the only previously reported complete geometry of any member of this extraordinary Pt_6 -encapsulated ν_3 -octahedral $\text{Pt}_6\text{Ni}_{38}$ cluster series.

As part of an extensive investigation to obtain nanosized Pt–Au carbonyl clusters,¹ we present herein the isolation and complete X-ray crystallographic determination of the nonprotonated $[\text{Pt}_6\text{Ni}_{38}(\text{CO})_{48}]^{6-}$ hexaanion (**1**) as the crystal-ordered acetonitrile/cyclohexane-solvated $[\text{NMe}_4]^+$ salt, which was initially obtained as a byproduct from the room-temperature reaction of $\text{Pt}(\text{COD})\text{Cl}_2$ and AuPPh_3Cl with $[\text{NMe}_4]_2[\text{Ni}_6(\text{CO})_{12}]$ (both reductant and carbonyl source) in dimethyl sulfoxide (DMSO).²

This nonprotonated 44-metal-atom cluster is a prime member of the extraordinary $[\text{H}_{6-n}\text{Pt}_6\text{Ni}_{38}(\text{CO})_{48}]^{n-}$ family

($n = 3-6$), which was initially reported in 1985 by Longoni and co-workers;³ they obtained variable mixtures of the monoprotinated **2** ($n = 5$) and diprotinated **3** ($n = 4$) by reaction of the $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ dianion in acetonitrile with either PtCl_2 or K_2PtCl_4 in a ca. 1:1 molar ratio. They found that interconversions among members of this family could be readily achieved by controlled addition of an acid or a base due to the occurrence in an acetonitrile solution of rapid protonation–deprotonation equilibria; the nonprotonated **1** ($n = 6$) was obtained from **2** by use of hydroxide ion and, reversibly, **2** from protonation of **1** by use of H_2O . Crystalline samples of **1–3** were isolated for X-ray crystallographic studies; however, a complete structural determination was obtained only for the monoprotinated $[\text{HPt}_6\text{Ni}_{38}(\text{CO})_{48}]^{5-}$ pentaanion (**2**) as the mixed $[\text{AsPh}_4]^+_2[\text{NBu}_4]^+_3$ salt. Partial structural determinations disclosed only analogous $\text{Pt}_6\text{Ni}_{38}$ frameworks in **1** and in the diprotinated **3** ($n = 4$); they mentioned that salts of **1** and **3** gave poor X-ray diffraction data due to the crystals undergoing rapid decay, probably resulting from the loss of clathrated solvent molecules.

A comprehensive investigation reported by Longoni, Zanello, and co-workers⁴ in 1999 of the electrochemical (cyclic voltammetry) and chemical redox behavior of this remarkable cluster series revealed that both **1** and **2** display unusually rich electron-sink features in dimethylformamide (DMF) involving each undergoing five one-electron redox processes: namely, one oxidation and four reductions for **1** versus two oxidations and three reductions for **2**. Particularly noteworthy is that the redox potential of the $6-/5-$ couple in **1**, which generates the oxidized $[\text{Pt}_6\text{Ni}_{38}(\text{CO})_{48}]^{5-}$ pentaanion (**4**), was observed to correspond to that of the isoelectronic $5-/4-$ couple in **2**.

The only observed perturbation effect caused by neutralization of one of the negative charges in **1** with one proton in **2** consisted of **1** undergoing one additional reduction process and **2** undergoing one additional oxidation process.

* To whom correspondence should be addressed. E-mail: dahl@chem.wisc.edu.

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- (2) Initial isolation of $[\text{NMe}_4]_6[\text{Pt}_6\text{Ni}_{38}(\text{CO})_{48}] \cdot \text{cyclo-C}_6\text{H}_{12} \cdot 2\text{MeCN}$: $\text{PtCl}_2\text{-COD}$ (0.28 g, 0.75 mmol), AuPPh_3Cl (0.37 g, 0.75 mmol), and PPh_3 (0.39 g, 1.50 mmol) were dissolved in 30 mL of DMSO. $[\text{NMe}_4]_2\text{-}[\text{Ni}_6(\text{CO})_{12}]$ (1.36 g, 1.50 mmol) in 30 mL of DMSO was added quickly, and the mixture was stirred for 3 days under a N_2 purge. The addition of water (at 0 °C) to the reaction mixture produced a suspension, which was filtered. The resulting brown solid was extracted with MeOH followed by THF and acetonitrile. The acetonitrile extract was layered with cyclohexane. Large octahedral-shaped crystals of $[\text{NMe}_4]_6[\text{Pt}_6\text{Ni}_{38}(\text{CO})_{48}] \cdot \text{cyclo-C}_6\text{H}_{12} \cdot 2\text{MeCN}$ formed after several weeks.

(3) Ceriotti, A.; Demartin, F.; Longoni, G.; Manassero, M.; Marchionna, M.; Piva, G.; Sansoni, M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 697.

(4) Fabrizi de Biani, F.; Femoni, C.; Iapalucci, M. C.; Longoni, G.; Zanello, P.; Ceriotti, A. *Inorg. Chem.* **1999**, *38*, 3721.

On the basis of the nearly uniform changes in the formal potentials of consecutive redox couples in both **1** and **2**, Longoni, Zanello, and co-workers^{4,5} hypothesized that **1** and **2** “should still have semiconductor rather than metallic character” because of the indicated absence of well-defined highest occupied molecular orbital–lowest unoccupied molecular orbital gaps in both clusters.

This first example of a nanosized 44-atom cubic-close-packed metal framework of pseudo- O_h symmetry with the inner octahedral Pt₆ kernel encapsulated by an outer ν_3 Ni₃₈ octahedron (i.e., where ν_3 designates $3 + 1 = 4$ atoms equally spaced along each of the octahedral edges) has attracted much attention as a small ligated metal nanoparticle.⁶ Theoretical calculations (linear combination of Gaussian-type orbitals, local density functional, LCGTO-LDF) by Pacchioni, Rösch, and co-workers⁷ of a corresponding [Ni₄₄(CO)₄₈]^{n−} model system ($n = 0, 2, 4, 6$) led to the premise of developing metallic character involving primarily the interstitial metal atoms in proposed agreement with the initial experimental magnetic measurements⁸ of [HPt₆Ni₃₈(CO)₄₈]^{5−} (**2**), which indicated a residual magnetic moment due to incomplete spin pairing.^{8,9}

The well-determined crystal structure^{10,11} of [N(CH₃)₄]₆−[Pt₆Ni₃₈(CO)₄₈]·cyclo-C₆H₁₂·2CH₃CN is readily attributed to

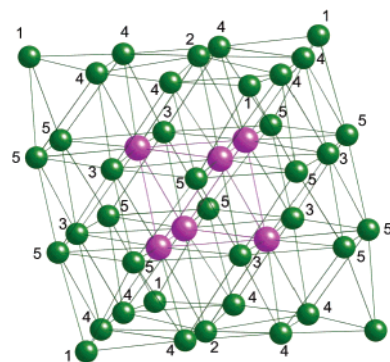


Figure 1. Geometry in **1** (and likewise in **2**) of the Pt₆Ni₃₈ core labeled under pseudo- D_{3d} site symmetry. The vertically oriented principal -3 (S_6) axis passes through the hexagon-centered Ni₂ atoms of the centrosymmetrically related top–bottom (opposite) triangular ν_3 octahedral faces and the center of the equilateral Pt₃ triangle within each of the two centrosymmetrically equivalent middle Pt₃Ni₉ layers. The other six symmetry-equivalent side triangular ν_3 octahedral faces are related to one another by the three horizontal 2-fold axes and three vertical σ_d mirror planes.

the high-quality low-temperature X-ray diffraction data resulting from the highly symmetrical close-packed cubic arrangement under $Pa\bar{3}$ symmetry, in which the [NMe₄]⁺ counterions and solvated cyclohexane and acetonitrile molecules are all crystal-ordered. The four hexaanions (**1**) and four solvated cyclohexane molecules of -3 site symmetry are located on inversion centers [i.e., $(0, 0, 0)$; $(0, 1/2, 1/2)$; $(1/2, 0, 1/2)$; $(1/2, 1/2, 0)$ + xyz] with centroid (x, y, z) coordinates $(0, 0, 0)$ and $(1/2, 0, 0)$, respectively (corresponding to the Na⁺ and Cl[−] sites in the face-centered cubic NaCl structure). Six of the 24 symmetry-equivalent [NMe₄]⁺ counterions lying in general positions are octahedrally disposed about each hexaanion (**1**). The eight acetonitrile molecules of 3-fold site symmetry are oriented along the four nonintersecting -3 axes.

A comparison of the corresponding bond-length connectivities of the Pt₆Ni₃₈ core geometry (Figure 1) under pseudo- D_{3d} symmetry for the analogous entire configurations of the nonprotonated **1** and monoprotonated **2** is given in Table 1s (Supporting Information). Particularly noteworthy is the close

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- (6) For example, see: (a) Mednikov, E. G.; Ivanov, S. A.; Slovokhotova, I. V.; Dahl, L. F. *Angew. Chem., Int. Ed.* **2005**, *44*, 6848. (b) Femoni, C.; Iapalucci, M. C.; Longoni, G.; Svensson, P. H.; Zanello, P.; Fabrizi de Biani, F. *Chem.—Eur. J.* **2004**, *10*, 2318. (c) Femoni, C.; Iapalucci, M. C.; Longoni, G.; Svensson, P. H. *J. Chem. Soc., Chem. Commun.* **2004**, 2274. (d) Femoni, C.; Iapalucci, M. C.; Longoni, G.; Svensson, P. H. *J. Chem. Soc., Chem. Commun.* **2001**, 1776. (e) Belyakova, O. A.; Slovokhotov, Yu. L. *Russ. Chem. Bull. (Engl. Transl.)* **2003**, *52*, 2209. (f) Alvarez, S. *Dalton Trans.* **2005**, 2209. (g) Adams, R. D.; Captain, B. *J. Organomet. Chem.* **2004**, *689*, 4521. (h) Demartin, F.; Fabrizi de Biani, F.; Femoni, C.; Iapalucci, M. C.; Longoni, G.; Macchi, P.; Zanello, P. *J. Cluster Sci.* **2001**, *12*, 61. Demartin, F.; Femoni, C.; Iapalucci, M. C.; Longoni, G.; Macchi, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 531. (i) Teo, B. K.; Zhang, H. *J. Cluster Sci.* **2001**, *12*, 349.
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- (8) (a) Pronk, B. J.; Brom, H. B.; de Jongh, L. J.; Longoni, G.; Ceriotti, A. *Solid State Commun.* **1986**, *59*, 349. (b) de Jongh, L. J.; Brom, H. B.; Longoni, G.; Pronk, B. J.; Schmid, G.; van Staveren, M. P. *J. Chem. Res.* **1987**, 150. (c) van Ruitenbeek, J. M.; van Leeuwen, D. A.; de Jongh, L. J. In *Physics and Chemistry of Metal Cluster Compounds*; de Jongh, L. J., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994; p 277. (d) van Leeuwen, D. A.; van Ruitenbeek, J. M.; de Jongh, L. J.; Ceriotti, A.; Pacchioni, G.; Häberlen, O. D.; Rösch, N. *Phys. Rev. Lett.* **1994**, *73*, 1432. (e) de Jongh, L. J. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH: New York, 1999; Vol. 3, p 1434.
- (9) Although initial temperature-dependent magnetic measurements^{8a–c} of powdered samples indicated a magnetic moment of 4–9 μ_B per Pt₆Ni₃₈ cluster, from a subsequent careful study^{8d} of a single-crystal sample (~18 mg) of the monoprotonated **2** (as the [AsPh₄]⁺[NBu₄][−] salt), it was concluded “that the intrinsic magnetic moment of this species is most probably zero” (i.e., the moments of the surface Ni atoms are completely quenched by the carbonyl ligands, while those of the encapsulated Pt atoms are presumably nonmagnetic).^{8e}

- (10) X-ray data of [N(CH₃)₄]₆[Pt₆Ni₃₈(CO)₄₈]·cyclo-C₆H₁₂·2CH₃CN were collected via ϕ -scan frames from an octahedral-shaped, dark-red crystal of $0.52 \times 0.50 \times 0.48$ mm³ size with a SMART CCD area detector diffractometry system from a standard Mo-sealed tube generator. The structural determination was obtained from direct methods followed by successive Fourier difference maps. Least-squares refinement (on F^2) was carried out with SHELXTL.¹¹ Supplementary crystallographic data in CIF for **1** have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K., and copies can be obtained free of charge upon request by quoting the publication citation and deposition number CCDC 604207. H atomic positions, initially determined from geometric considerations, were refined with a riding model. Empirical formula Pt₆Ni₃₈O₄₈C₈₂H₉₀; $M = 5357.1$ g mol^{−1}; $\lambda = 0.71073$ Å; $T = 173(2)$ K; cubic; $Pa\bar{3}$; $Z = 4$; $a = b = c = 23.019(2)$ Å; $V = 12197.7$ Å³; $d(\text{calc}) = 2.917$ g cm^{−3}; $F(000) = 10216$. A total of 54864 reflections obtained over $3.06 \leq 2\theta \leq 46.50^\circ$ were empirically corrected for absorption (SADABS); $\mu(\text{Mo K}\alpha) = 12.631$ mm^{−1}. Full-matrix least-squares anisotropic refinement (on F^2) with 279 parameters and 0 restraints on 2920 independent merged reflections [$R(\text{int}) = 0.0602$] converged at $R1(F) = 0.0363$ and $wR2(F^2) = 0.0756$ for all data; $R1(F) = 0.0301$ and $wR2(F^2) = 0.0730$ for $I > 2\sigma(I)$; $\text{GOF}(F^2) = 1.106$; max/min residual density, 1.13/−1.53 e Å^{−3}.
- (11) All crystallographic software and sources of the scattering factors are contained in: Sheldrick, G. SHELXTL, version 6.10; Bruker AXS Inc.: Madison, WI, 2000.

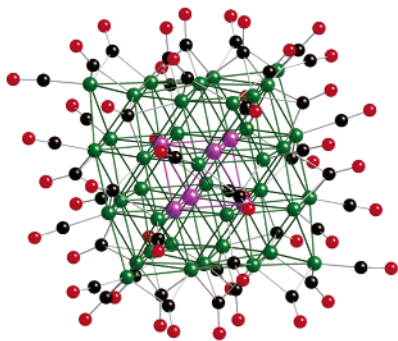


Figure 2. $\text{Pt}_6\text{Ni}_{38}(\text{CO})_{48}$ geometry in **1** (and likewise in monoprotonated **2**) showing the connectivities of the 18 terminal, 12 edge-bridging, and 18 face-bridging carbonyl ligands under pseudo- D_{3d} site symmetry. The top–bottom triangular v_3 octahedral faces have one terminal carbonyl ligand and two edge-bridging carbonyl ligands attached to each corner Ni1 atom, whereas each of the two hexagon-centered Ni2 atoms has three face-capping carbonyl ligands that are additionally coordinated to the two inner Ni4 atoms along the six Ni1–Ni4–Ni4–Ni1 edges. In contrast, the other six triangular Ni10 octahedral faces have one terminal carbonyl ligand located on each of the two inner Ni5 atoms along the six Ni1–Ni5–Ni5–Ni1 side edges, while each of the six hexagon-centered Ni3 atoms is connected to two face-capping carbonyl ligands, namely, with one carbonyl ligand additionally coordinated to the two inner Ni4 atoms of each top–bottom horizontal edge and the other carbonyl ligand additionally linked to the two inner Ni5 atoms on two adjacent side edges.

agreement of the corresponding means that are within 0.02 Å for both the Pt–Pt and Pt–Ni connectivities and within 0.05 Å for the Ni–Ni connectivities.

The virtually identical in-plane (IP) and out-of-plane (OP) Pt–Pt means of 2.705 Å in **1** and 2.722 Å in **2** compare favorably with the means of 2.71 and 2.70 Å for the 12 *radial* Pt(i)–Pt(cage) distances in the electronically equivalent and geometrically analogously centered Pt_{13} icosahedra (otherwise unknown) of $\text{Pt}_{13}[\text{Au}_2(\text{PPh}_3)_2]_2(\text{CO})_{10}(\text{PPh}_3)_4$ ^{1b} and $\text{Pt}_{13}-[(\text{PtPEt}_3)_2(\mu_2\text{-CO})]_2(\text{CO})_{10}(\text{PEt}_3)_4$,¹³ respectively; in contrast, the corresponding 30 *tangential* Pt(cage)–Pt(cage) distances of 2.85 and 2.84 Å respectively for the latter two icosahedral structures are 5% longer in exact accordance with the predicted value based upon a geometrically regular-centered icosahedron.

The 48 carbonyls (18 terminal, 12 edge-bridging, and 18 face-bridging) in **1** (Figure 2) are similarly disposed such that the hexaanion has the same pseudo- D_{3d} symmetry as the monoprotonated pentaanion found in **2**; this analogous carbonyl arrangement plays the dominant role in lowering the pseudosymmetry of the metal architecture from O_h to D_{3d} . The five means in **1** of the 48 Pt–Ni bonding connectivities range from 2.524 to 2.781 Å; the shortest Pt–Ni mean is observed (Figure 1) for the connections of each

(12) The significantly smaller observed individual bond-length uncertainties (estimated standard deviations) in **1** relative to those in **2** are readily attributed to the occurrence of one-sixth fewer independent atomic variables in **1** versus those in **2** (due to **1** possessing much higher crystallographic site symmetry) along with the X-ray data having been collected at low temperature (100 K) in **1** versus at room temperature in **2**.

(13) Kurasov, S. S.; Eremenko, N. K.; Slovokhotov, Yu. L.; Struchkov, Yu. T. *J. Organomet. Chem.* **1989**, *361*, 405.

Pt to two IP Ni5 atoms, while the longest Pt–Ni mean is found for the symmetrical capping of the OP Ni2 to the inner three triangular Pt atoms. The 11 different means in **1** of the 108 surface Ni–Ni bonding connectivities vary from 2.401 to 2.761 Å. Both of these shortest and longest Ni–Ni means involve the IP Ni4–Ni4 connectivities on the top–bottom octahedral faces (Figure 2); the six shortest equivalent edges are each spanned by two triply bridging carbonyls, while the six longest edges are each bridged by Ni1 atoms. We conclude that the close geometrical agreement between **1** and **2** (i.e., especially the same pseudo- D_{3d} distribution of the carbonyl ligands) is consistent with the suggestion by Longoni, Zanello, and co-workers⁴ based upon their electrochemical–IR studies that the hydrido-like proton in **2** interstitially occupies one of the octahedral-like metal cavities, as was previously ascertained for both the one/two hydrido-like protons in the $[\text{H}_n\text{Ni}_{12}(\text{CO})_{21}]^{n-4}$ series ($n = 1, 2$) from combined neutron–X-ray diffraction measurements.¹⁴

Upon determination of the crystal structure of **1**, we then decided to devise a direct aprotic route (without AuPPh_3Cl) to obtain selectively the nonprotonated **1**. Accordingly, we carried out reactions of $\text{Pt}(\text{COD})\text{Cl}_2$ with $[\text{NMe}_4]_2[\text{Ni}_6(\text{CO})_{12}]$ in DMSO, with OH^- added to eliminate the formation of protonated species. Details on the preparation and purification are similar to those already cited.² However, we found that an inert (nonoxidative) atmosphere is essential to the isolation of **1**. Whereas the IR carbonyl spectrum of **1** in DMF [1990 (s) and 1845 (ms) cm^{-1}] parallels that reported⁴ for the hexaanion (**1**), our experimental workup produced a product (from the acetonitrile extract) whose IR carbonyl spectrum in DMF [2000 (s) and 1860 (ms) cm^{-1}] corresponds to that reported⁴ for the oxidized **4**. Its spectral identity as **4** was then substantiated by the fact that it could easily be reduced by reaction with cobaltocene to give an IR spectrum corresponding to **1** (i.e., no spectral changes were observed when hydroxide ion was added to the product).

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Supporting Information Available: Crystallographic data for $[\text{N}(\text{CH}_3)_4]_6[\text{Pt}_6\text{Ni}_{38}(\text{CO})_{48}] \cdot \text{cyclo-C}_6\text{H}_{12} \cdot 2\text{CH}_3\text{CN}$ in CIF format and Table 1s comparing the mean connectivities and individual ranges under pseudo- D_{3d} symmetry for the $\text{Pt}_6\text{Ni}_{38}$ core geometries in the nonprotonated hexaanion (**1**) and previously reported monoprotonated pentaanion (**2**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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