[16] A. K. Rahimi, A. I. Popov, *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 703.
[17] M. Möhlen, B. Neumüller, K. Harms, H. Krautscheid, D. Fenske, M. Diedenhofen, G. Frenking, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1105.
[18] P. van der Sluis, A. L.Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194.
[19] A. L. Spek, PLATON 94, Crystallographic Program System, University of Utrecht **1994**.
[20] R. G. Solomon, J. K. Kochi, *J. Chem. Soc. Chem. Commun.* **1972**, 599.
[21] H. Schmidbaur, W. Wolfsberger, *Chem. Ber.* **1967**, *100*, 1000.

New Ni–Pt Carbonyl Clusters with a Tetrahedron of Platinum Atoms Encapsulated in an Incomplete Tetrahedron of Nickel Atoms: $[Ni_{36}Pt_4(CO)_{45}]^{6-}$ and $[Ni_{37}Pt_4(CO)_{46}]^{6-}$ **

Francesco Demartin, Cristina Femoni,
M. Carmela Iapalucci, Giuliano Longoni,* and
Piero Macchi

Only a limited number of structurally characterized carbonyl or carbonyl-substituted metal clusters containing more than 30 metal atoms is known.[1–3] Metal clusters of high nuclearity provide useful models for experimental[4] and theoretical[5] studies of the metallization process. For instance, we have recently ascertained that carbonyl clusters containing highly connected (coordination number 12 and 13) metal atoms behave as electron sinks; thus, $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ ($n = 5, 6$)[3b] and $[Ni_{32}C_6(CO)_{36}]^{6-}$ [3d] display an unusually rich redox chemistry[6] that encompasses up to six oxidation states.[7] Furthermore, the almost constant separation of about 0.3 V between the formal potentials of their electrochemically reversible consecutive redox couples indicates the absence of a well defined HOMO–LUMO gap.[7] This finding led us to pursue the synthesis of other carbonyl metal clusters with several interstitial metal atoms to gain a better understanding of the metallization process.

Here we report the synthesis and structural characterization of the complex hexaanions **1** and **2**, which are chemically and structurally related to the previously reported clusters $[H_{6-n}Ni_{38}Pt_6(CO)_{48}]^{n-}$ ($n = 4, 5, 6$).[5a] The latter have a cherry structure in which a Pt_6 octahedron is fully encapsulated in a ν_3[8] Ni_{38} octahedron; the present clusters may be considered as being derived by encapsulation of a Pt_4 tetrahedron in an incomplete ν_5 tetrahedron of nickel atoms.

$[Ni_{36}Pt_4(CO)_{45}]^{6-}$ **1**

$[Ni_{37}Pt_4(CO)_{46}]^{6-}$ **2**

The cluster anions **1** and **2** were obtained by reaction of $[NMe_4]_2[Ni_6(CO)_{12}]$ with $K_2[PtCl_4]$ in the molar ratio 2.5:1 in acetonitrile under nitrogen. The final brown mixture of products was separated by extraction with THF ($[Ni_9(CO)_{18}]^{2-}$, $[HNi_9Pt_3(CO)_{21}]^{3-}$),[9, 10] acetone ($[H_2Ni_{38}Pt_6(CO)_{48}]^{4-}$), propionitrile ($[Ni_9Pt_3(CO)_{21}]^{4-}$, $[HNi_{38}Pt_6(CO)_{48}]^{5-}$), and acetonitrile ($[Ni_{36}Pt_4(CO)_{45}]^{6-}$, $[Ni_{37}Pt_4(CO)_{46}]^{6-}$). The hexaanions **1** and **2** are indistinguishable by IR spectroscopy, and their $[NMe_4]^+$ salts cocrystallize when a solution in acetonitrile is layered with diisopropyl ether. The tetramethylammonium salts were converted to other quaternary ammonium and phosphonium salts by metathesis with the corresponding halides in DMSO, precipitation with water, and crystallization from acetonitrile/diisopropyl ether. The **1**/**2** mixture as the $[NMe_3CH_2Ph]^+$ salts shows strong carbonyl absorption bands in acetonitrile at 2003 and 1856 cm^{-1}. The ^1H NMR spectrum ($[D_3]$acetonitrile, 25 °C) only shows signals for the trimethylbenzylammonium cation and organic solvents over the range $\delta = -50$ to $+50$.

The asymmetric unit of the cocrystallized mixture of $[NMe_3CH_2Ph]_6$-**1** and $[NMe_3CH_2Ph]_6$-**2** consists of one anion (**1** or **2**) located on a crystallographic C_3 axis with an average occupancy factor of 0.5, two $[NMe_3CH_2Ph]^+$ cations in general positions, and a disordered isopropanol molecule located on a crystallographic C_3 axis.[11] The idealized metal framework of **1** can be derived from a ν_5 Ni_{56} tetrahedron (Figure 1 top) by

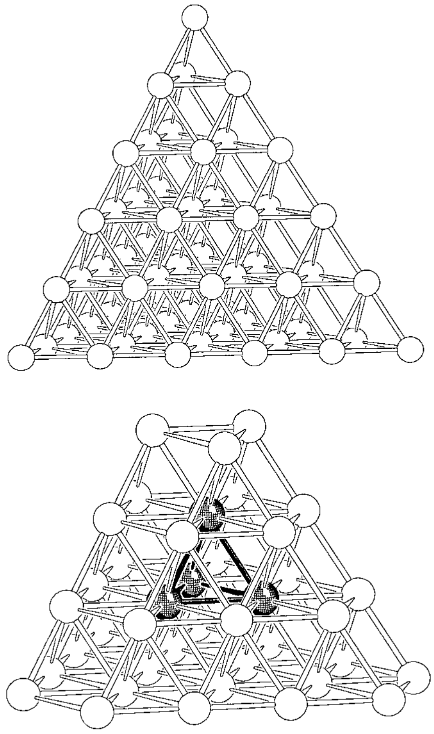

Figure 1. The ν_5 Ni_{56} tetrahedron (top) and the derived idealized $Ni_{36}Pt_4$ metal framework of **1** (bottom).

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[*] Prof. G. Longoni, Dr. C. Femoni, Dr. M. C. Iapalucci
Dipartimento di Chimica Fisica ed Inorganica
viale Risorgimento 4, I-40136 Bologna (Italy)
Fax: (+390) 51-6443690
E-mail: longoni@ms.fci.unibo.it

Prof. F. Demartin, Dr. P. Macchi
Dipartimento di Chimica Strutturale e Stereochimica Inorganica
via G. Venezian 21, I-20133 Milano (Italy)
Fax: (+390) 2-70635288
E-mail: demartin@csmtbo.mi.cnr.it

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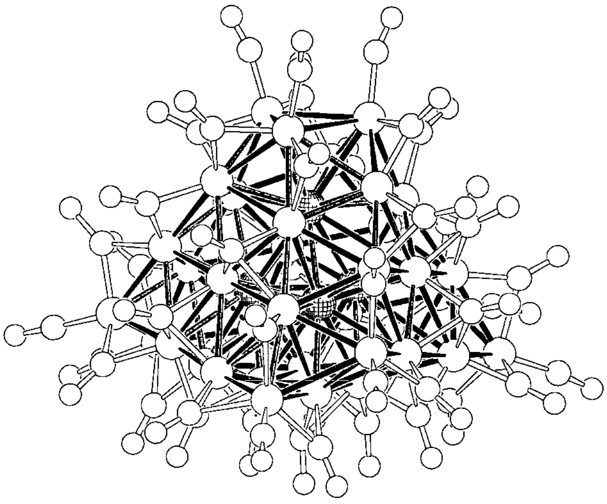
replacing the four interstitial nickel atoms by platinum atoms and by removing the 16 nickel atoms that belong to a set of three edges having a common vertex (Figure 1 bottom). The experimentally determined structure of the **1** is shown in Figure 2 top. The departures of the metal framework from the idealized model given in Figure 1 bottom consist of a helicoidal twist around the C_3 axis and enlargement of the bottom face of the outer Ni_{36} polyhedron. These distortions efficiently minimize the energy of the molecule by increasing the number of Ni–Ni interactions (105 Ni–Ni distances within the range given in Figure 2 versus 102 in the idealized structure), provide better accomodation for the bulkier encapsulated Pt_4 tetrahedron, and minimize nonbonding repulsions between the carbonyl ligands, which comprise nine terminal, 24 edge-bridging, and 12 face-bridging ligands.



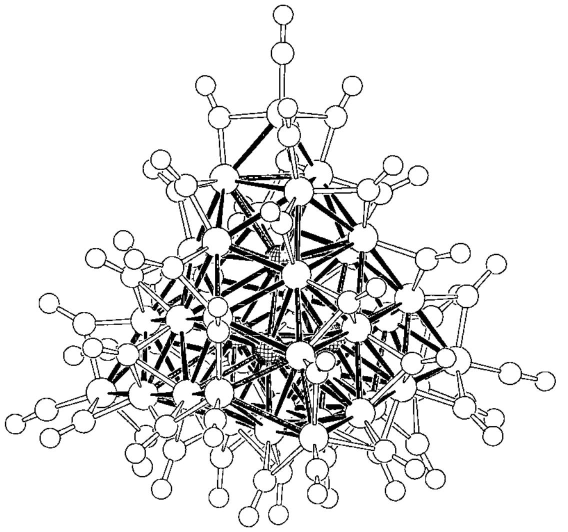


Figure 2. The structure of $[Ni_{36}Pt_4(CO)_9(\mu\text{-}CO)_{24}(\mu_3\text{-}CO)_{12}]^{6-}$ (top) and $[Ni_{37}Pt_4(CO)_7(\mu\text{-}CO)_{27}(\mu_3\text{-}CO)_{12}]^{6-}$ (bottom). Metal–metal distances [Å]: Pt–Pt 2.709(1)–2.733(1), Pt–Ni 2.536(2)–2.776(2), Ni–Ni 2.421(2)–2.782(2).

Figure 2 bottom shows the structure of $[Ni_{37}Pt_4(CO)_7(\mu\text{-}CO)_{27}(\mu_3\text{-}CO)_{12}]^{6-}$ (**2**), which is derived by capping the unique triangular face that constitutes the truncated vertex of the polyhedron of Figure 2 top with a Ni(CO) moiety and by tilting three formerly terminal carbonyl ligands into edge-bridging positions. The addition of Ni(CO) fragments to clusters does not alter the number of skeletal electron pairs, and often subsequent additions (or subtractions) of this moiety can be carried out.[3b–d, 15] The recently reported cluster $[H_{12}Pd_{28}Pt_{13}(CO)_{27}(PMe_3)(PPh_3)_{12}]$[3h] has the same nuclearity as **2** and analogously contains a fully interstitial Pd_4 tetrahedron. However, the two are neither isoelectronic nor isostructural.

The mixture of **1** and **2** is readily degraded by carbon monoxide at atmospheric pressure to $[Ni_9Pt_3(CO)_{21}]^{4-}$, whereas oxidation with K_2PtCl_4 yields $[H_{6-n}Ni_{38}Pt_6(CO)_{48}]^{n-}$ derivatives. These reactions are probably the origin of most the side products in the synthesis of **1** and **2**. In contrast, preliminary experiments indicate that the cluster anions of **1** and **2** can remain intact over several reduction steps. Indeed, as shown by IR monitoring, they are reduced by sodium naphthalene in DMF in at least three distinct steps and can be quantitatively reoxidized with tropylium tetrafluoroborate. Electrochemical studies to evaluate the electron-sink behavior and the separation between the one-electron energy levels in the frontier region of **1/2** and $[H_{6-n}Ni_{38}Pt_6(CO)_{48}]^{n-}$ are in progress.

Experimental Section

1/2: K_2PtCl_4 (0.80 g, 1.96 mmol) was added in portions over 6 h to a solution of $[NMe_4]_6[Ni_6(CO)_{12}]$ (4.03 g, 4.82 mmol) in acetonitrile (60 mL) under a continuously renewed nitrogen atmosphere with stirring. The mixture was stirred for 48 h. The resulting dark brown suspension was filtered, and the filtrate evaporated to dryness. The residue was thoroughly washed in sequence with water (40 mL), THF (60 mL), acetone (40 mL), and propionitrile (60 mL). The brown residue was extracted with acetonitrile (40 mL) and precipitated by layering with diisopropyl ether (40 mL) to give black plates of cocrystallized $[NMe_4]_6$-**1** and $[NMe_4]_6$-**2** (610 mg, 0.13 mmol, 26.5 % based on Pt). The salts are soluble in acetonitrile, dimethylformamide, DMSO, and *N*-methylpirrolidinone, sparingly soluble in acetone, and insoluble in THF, alcohols, and nonpolar solvents. Elemental analysis for $[NMe_4]_6[Ni_{36}Pt_4(CO)_{45}]$ and $[NMe_4]_6[Ni_{37}Pt_4(CO)_{46}]$: calcd (1:1 mixture) (%): Ni 46.16, Pt 16.81, C 17.97, H 1.55, N 1.81; found: Ni 45.87, Pt 16.52, C 18.08, H 1.63, N 1.70.

The corresponding cocrystallized mixture of $[NMe_3CH_2Ph]_6$-**1** and $[NMe_3CH_2Ph]_6$-**2** was obtained by metathesis of the tetramethylammonium salts in DMSO solution with an aqueous solution of trimethylbenzylammonium chloride. The salt was precipitated with water, washed with isopropanol, and crystallized from acetonitrile/diisopropyl ether. IR (CH_3CN): $\tilde{\nu}_{CO} = 2002$ (s) and 1854 cm^{-1} (s); elemental analysis: calcd (1:1 mixture) (%): Ni 42.03, Pt 15.31, C 24.84, H 1.88, N 1.65; found: Ni 41.87, Pt 15.12, C 24.94, H 1.93, N 1.56.

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[1] G. Longoni, M. C. Iapalucci in *Clusters and Colloids: From Theory to Applications* (Ed.: G. Schmid), VCH, Weinheim, **1994**, p. 91.

[2] A. Ceriotti, R. Della Pergola, L. Garlaschelli in *Physics and Chemistry of Metal Cluster Compounds, Vol. 18* (Ed.: L. J. de Jongh), Kluwer Academic, Dordrecht, **1994**, p. 41.

[3] a) $[HNi_{38}Pt_6(CO)_{48}]^{5-}$: A. Ceriotti, F. Demartin, G. Longoni, M. Manassero, M. Marchionna, G. Piva, M. Sansoni, *Angew. Chem.* **1985**, *97*, 708; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 697; b) $[H_{6-n}Ni_{38}C_6$-

$(CO)_{42}]^{n-}$: A. Ceriotti, A. Fait, G. Longoni, G. Piro, F. Demartin, M. Manassero, N. Masciocchi, M. Sansoni, *J. Am. Chem. Soc.* **1986**, *108*, 8091; c) $[H_{6-n}Ni_{34}C_4(CO)_{38}]^{n-}$: A. Ceriotti, A. Fait, G. Longoni, G. Piro, L. Resconi, F. Demartin, M. Manassero, N. Masciocchi, M. Sansoni, *J. Am. Chem. Soc.* **1986**, *108*, 5370; d)$[Ni_{32}C_6(CO)_{36}]^{6-}$: F. Calderoni, F. Demartin, M. C. Iapalucci, G. Longoni, *Angew. Chem.* **1996**, *108*, 2393; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2225; e) $[Pd_{38}(CO)_{28}(PEt_3)_{12}]$: E. G. Mednikov, N. K. Eremenko, Yu. L. Slovakhotov, Yu. T. Struchkov, *J. Chem. Soc. Chem. Commun.* **1987**, 218; f) $[Pd_{34}(CO)_{24}(PEt_3)_{12}]$: E. G. Mednikov, N. I. Kanteeva, *Russ. Chem. Bull.* **1995**, *44*, 163; g) $[Ni_9Pd_{33}(CO)_{41}(PPh_3)_6]^{4-}$: M. Kawano, J. W. Bacon, C. F. Campana, L. F. Dahl, *J. Am. Chem. Soc.* **1996**, *118*, 7869; h) $[H_{12}Pd_{28}Pt_{13}(CO)_{27}(PMe_3)(PPh_3)_{12}]$: J. M. Bemis, L. F. Dahl, *J. Am. Chem. Soc.* **1997**, *119*, 4545.

[4] J. M. van Ruitenbeek, D. A. van Leeuwen, L. J. de Jongh in *Physics and Chemistry of Metal Cluster Compounds, Vol. 18* (Ed.: L. J. de Jongh), Kluwer Academic, Dordrecht, **1994**, p. 277.

[5] N. Rösch, G. Pacchioni in *Clusters and Colloids: From Theory to Applications* (Ed.: G. Schmid), VCH, Weinheim, **1994**, p. 5.

[6] P. Zanello in *Stereochemistry of Organometallic and Inorganic Compounds, Vol. 5* (Ed.: P. Zanello), Elsevier, Amsterdam, **1994**, p. 163.

[7] F. Calderoni, F. Demartin, F. Fabrizi De Biani, C. Femoni, M. C. Iapalucci, G. Longoni, P. Zanello, *Inorg. Chem.*, submitted.

[8] D. A. Nagaki, L. D. Lower, G. Longoni, P. Chini, L. F. Dahl, *Organometallics* **1986**, *5*, 1764.

[9] A. Ceriotti, F. Demartin, G. Longoni, M. Manassero, G. Piva, G. Piro, M. Sansoni, B. T. Heaton, *J. Organomet. Chem.* **1986**, *301*, C5.

[10] B. K. Teo, H. Zhang, *J. Cluster Sci.* **1990**, *1*, 155.

[11] Crystal data for $0.5\,[NMe_3CH_2Ph]_6[Ni_{36}Pt_4(CO)_{45}]/0.5\,[NMe_3CH_2Ph]_6$-$[Ni_{37}Pt_4(CO)_{46}]\cdot C_3H_8O$: hexagonal, space group $P6_3$ (no. 173), $a=17.853(9)$, $c=27.127(13)$ Å, $V=7488(6)$ Å^3, $Z=2$, $\rho_{calcd}=2.29$ g cm^{-3}, graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å), $\mu(Mo_{K\alpha})=82.5$ cm^{-1}. A total of 86976 reflections with $3<\theta<29°$ were measured on a Siemens CCD area-detector SMART diffractometer at 210 K on a crystal of approximate dimensions $0.10\times0.15\times0.08$ mm, mounted in air but protected by the cooling N_2 stream during data collection. Data were corrected for Lorentzian polarization and absorption effects (empirical absorption correction with SADABS;[12] transmission factors in the range 0.61 – 1.00). The structure was solved by direct methods (SIR97[13]) and refined with full-matrix least-squares (SHELX93[14]) on 9209 independent reflections with $I>3\sigma(I)$. Anisotropic displacement parameters were assigned to all atoms of the anions. The final R value was 0.057 ($R_w=0.128$). Maximum $\Delta\rho=2.2$ e Å^{-3} close to the Pt atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102917. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] G. M. Sheldrick, SADABS, Universität Göttingen, Germany, unpublished results.

[13] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *24*, 435.

[14] G. M. Sheldrick, SHELX93, program for the refinement of crystal structures, Universität Göttingen, Germany, **1993**.

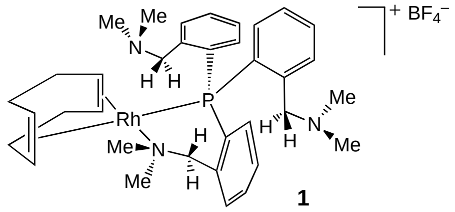
[15] a) A. Ceriotti, G. Longoni, M. Manassero, M. Perego, M. Sansoni, *Inorg. Chem.* **1985**, *24*, 117; b) A. Ceriotti, G. Longoni, M. Manassero, L. Resconi, M. Sansoni *J. Chem. Soc. Chem. Commun.* **1985**, 181; c) A. Ceriotti, G. Longoni, M. Manassero, N. Masciocchi, G. Piro, L. Resconi, M. Sansoni *J. Chem. Soc. Chem. Commun.* **1985**, 1402; d) A. Ceriotti, G. Longoni, G. Piro, M. Manassero, N. Masciocchi, M. Sansoni, *New J. Chem.* **1988**, *12*, 501.

A Chelate with Conformational Memory?**

M. Aránzazu Alonso, Juan A. Casares, Pablo Espinet,*
and Katerina Soulantica

Advances in NMR techniques have enabled detailed observation of some dynamic phenomena at the molecular level. One problem that has attracted attention is restricted rotation around single bonds,[1] particularly in chiral molecules. Because of their movements, some molecular systems have been referred to as molecular motors, brakes, ratchets, etc.[2–5] The possible selective directionality of these restricted rotations is governed by the principle of microscopic reversibility: Rotations that interconvert degenerate states cannot have a preferred sense.[3, 6] An illustrative case of this and other related basic aspects is presented here.

The complexes $[Rh(diene)\{P(bzN)_3\}]BF_4$ (**1**: diene = 1,5-cyclooctadiene (cod), **2**: diene = tetrafluorobenzobarrelene (tfb); bzN = 2-(dimethylaminomethyl)phenyl) are square planar in solution, and the $P(bzN)_3$ ligand acts as a P,N chelate with two pendant amino group arms. The chelate ring has a boat conformation, which makes the complexes chiral (racemic).[7] Racemization by inversion of the boat is slow on the NMR time scale at room temperature, as can be seen in the ^1H COSY spectrum of **1** (Figure 1). The four olefinic hydrogen atoms are inequivalent, the CH_2 groups give rise to three AB systems, and the methyl groups give four singlets (3:3:6:6); hence, the two methyl groups on the coordinated N center are inequivalent, and those at each pendant N atom are equivalent owing to fast inversion of the amino group, although the two pendant arms are inequivalent.[8] The coordination plane clearly defines two half-spaces, one concave and one convex,[9] which contain the two possible positions for nucleophilic attack by an entering ligand (Scheme 1).



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[*] Prof. Dr. P. Espinet, M. A. Alonso, Dr. J. A. Casares,
Dr. K. Soulantica
Departamento de Química Inorgánica, Facultad de Ciencias
Universidad de Valladolid
E-47005 Valladolid (Spain)
Fax: (+349)983-423013
E-mail: espinet@qi.uva.es

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