[Rh$_{28}$N$_4$(CO)$_{41}$H$_x$]$^{4-}$, a Massive Carbonyl Cluster with Four Interstitial Nitrogen Atoms

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Main group atoms (C, N, P, etc.), when occupying interstitial positions within the carbonyl clusters, have unusual stereochemistries and coordination numbers, stabilize new and unusual cluster shapes, and play a particularly relevant role in the buildup of the higher nuclearities.[2] In the growing area of molecular interstitial nitrides, only a few polynitrido clusters have been synthesized: [Co$_{14}$N$_3$(CO)$_{24}$]$^{3-}$,[3] [Rh$_{12}$N$_2$(CO)$_{23}$H]$^{3-}$,[4] [Rh$_{14}$N$_2$(CO)$_{25}$]$^{2-}$,[5] and [Rh$_{23}$N$_4$(CO)$_{38}$]$^{3-}$.[6] They all derive from the pyrolysis of the respective hexanuclear [M$_6$N(CO)$_{15}$]$^-$ (M = Co,[7] Rh[8]) species. We now report on [Rh$_{28}$N$_4$(CO)$_{41}$H$_x$]$^{4-}$, which is to date the largest structurally characterized rhodium cluster.

Pyrolysis of [Rh$_6$N(CO)$_{15}$]$^-$ as the K$^+$ or Na$^+$ salt in diglyme yields, within 6−8 h at 140−150 °C, essentially the dianion [Rh$_{14}$N$_2$(CO)$_{25}$]$^{2-}$; prolonging the process with a temperature increase to *ca.* 170 °C for an additional 20−30 h gives, together with an abundant precipitation of uncharacterized products and rhodium metal, a residual diluted solution containing several products. The filtered solution was worked-up to separate the components by fractional precipitation of the alkali metal salts in water; thus, after separation of some residual Na$_2$[Rh$_{14}$N$_2$-(CO)$_{25}$], a potassium salt fraction of a new anion (**1**) was obtained with minimal yields (3−5%). This same product **1** was obtained in higher yields (*ca.* 30%) and in milder conditions (100 °C, 3−5 h) directly from Na$_2$[Rh$_{14}$N$_2$(CO)$_{25}$] in a buffered aqueous solution (Na$_2$HPO$_4$/NaOH, pH ≈ 11).[9] Metathesis of the potassium salt with bulky cations afforded many different salts of anion **1**, but none had crystals suitable for X-ray diffraction. All these derivatives show the same IR in acetone, independent of the cation (2032 m, 1998 s, 1965 mw, 1890 m, 1868 ms, 1846 m, 1836 m, 1788 w ± 2 cm^{-1}).

Treatment of **1** with acids (H$_3$PO$_4$, CF$_3$COOH) gives the new anionic species **2**, which, in the presence of a base (Na$_2$CO$_3$,
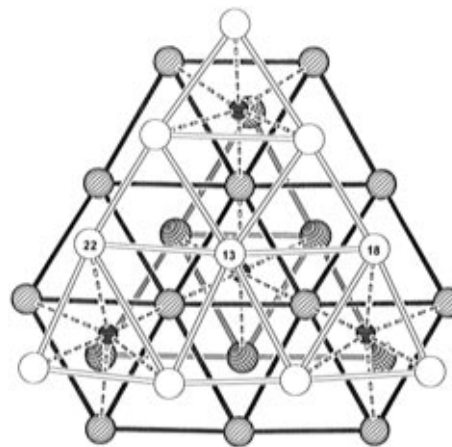

Figure 1. The bare metallic skeleton of idealized C_{3v} symmetry, within the [Rh$_{28}$N$_4$(CO)$_{41}$H$_x$]$^{4-}$ anion, view down the C_3 axis. The three layer sequence of supertriangles is clearly distinguished: T^3 (top empty bonds and atoms), tT^4 (middle, black bonds) and T^2 (bottom, triple line bonds). A supertriangle T^n is a triangle (of edge *n*) composed by (n^2) "unitary" triangles, while tT^n is a truncated supertriangle, lacking the three vertex atoms.

t-BuOK), regenerates **1**. The IR spectra in acetone of **1** and **2** (2044 m, 2013 s, 1980 mw, 1905 m, 1883 ms, 1867 m, 1858 m, 1800 w ± 2 cm^{-1}) appear identical in shape and relative band intensities but shifted 14−15 cm^{-1}; this suggests that the parent anion **1** is a closely related, more reduced species, in connection to **2** through the dissociation−association of a proton. Variable temperature ^{1}H FT-NMR gave for **1** ([NEt$_4$]$^+$ salt in acetone-d_6), an hydrido resonance: a doublet of septets (δ = −22.8 ppm, J_{HRh} = 20.7 (d) Hz and J_{HRh} = 7.3 (sept) Hz) which gradually lost resolution from room temperature to 183 K. Dubious results were obtained for **2**.

Crystals of **2** were obtained from a solution used for the NMR and prepared from the K$^+$ salt of **1** and 1% H$_3$PO$_4$ in acetone-d_6, by addition of [NEt$_4$]BF$_4$ in 2-propanol. The structure of the [NEt$_4$] salt, which crystallized with a clathrated molecule of acetone, was elucidated by X-ray diffraction and revealed the presence of a tetraanion [Rh$_{28}$N$_4$(CO)$_{41}$H$_x$]$^{4-}$ (*x* = 0 or, more likely, 2).[10] The bare metallic cluster (Figure 1) has an idealized C_{3v} symmetry, which is also substantially retained in the overall CO disposition. However, the local stereochemistry of Rh(13), which lies on the idealized C_3 axis but bears only two semi-bridging CO ligands and perhaps two bridging hydrides, reduces the overall idealized symmetry to C_s (Figure 2).[11] The Rh$_{28}$ array is a slightly distorted chunk of *ccp* lattice containing a fully encapsulated metal triangle; it is formed by the superposition of three pieces of compact layers with, respectively, 6, 12, and 10 metal atoms in a A/B/C sequence. The three-layer sequence can also be described as T^2/tT^4/T^3, that is, two supertriangles of order 2 and 3 (T^2 and T^3, respectively) sandwiching a truncated supertriangle of order 4 (tT^4).

(1) (a) CNR. (b) Dipartimento di Chimica Inorganica, Metallorganica e Analitica. (c) Dipartimento di Chimica Strutturale e Stereochimica Inorganica.

(2) As a cluster grows, the maximum number of carbonyls per metal atom is reduced only for steric reasons (Chini, P. *Gazz. Chim. Ital.* **1979**, *109*, 225). Interstitial atoms contribute electrons to the total cluster valence electrons, without steric requirements on the cluster surface.

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(6) Martinengo, S.; Ciani, G.; Sironi A. *J. Chem. Soc., Chem. Commun.* **1992**, 1405.

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(9) The choice of a medium with the proper acidity stabilizes the anions within a particular range of ratios of anionic charge/metal atoms. (Fumagalli, A. *Mater. Chem. Phys.* **1991**, *29*, 211. Also, work in progress).

(10) Crystal Structure Analysis: C$_{76}$H$_{86}$N$_8$O$_{42}$Rh$_{28}$, M_r 4665.0; triclinic; space group $P\overline{1}$ (No. 2); a = 14.766(1), b = 16.287(2), and c = 25.284(2) Å; α = 85.70(1), β = 86.19(1), and γ = 69.34(1)°; V = 5668.4(9) Å^3; D_{calc} = 2.733 g cm^{-3}; Z = 2. A total of 19 845 intensities (6° < 2θ < 50°, Mo Kα radiation) were recorded at 293K on an Enraf-Nonius CAD4 automated diffractometer, by the ω-scan method, and corrected for Lorentz, polarization, and decay (15%) effects. An empirical absorption correction, based on ψ-scans, was applied (relative transmission factors in the range of 0.53−1.00). The structure was solved by direct methods (SIR92), completed from subsequent difference Fourier syntheses, and refined (SHELX93) by full-matrix least-squares (on F$_o$^{2}) on the basis of 15 679 independent significant [I > 1σ(I)] reflections (1367 parameters). Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The final values of the agreement indices R$_1$ and wR$_2$ were 0.030 and 0.069, respectively. All the diagrams were obtained with SCHAKAL program.

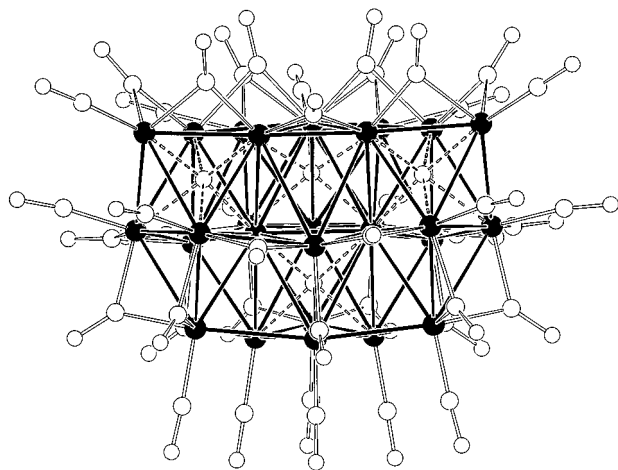(11) The presence of a third semibridging CO ligand on Rh(13) would in any case lower the actual symmetry to C_3.

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Figure 2. Drawing of the $[Rh_{28}N_4(CO)_{41}H_x]^{4-}$ anion. Note the idealized C_s symmetry of the full anion.

Table 1. Rh−Rh Interactions Partitioned into Topologically Homogeneous Classes

	class[a]	i/e[e]	b/n[f]	bond no.	range (Å)[h]	average (Å)
1	T² layer	e, i	n	9	2.821−2.891	2.84(2)
2	tT⁴ layer[b]	i	n	3	2.738−2.772	2.76(1)
3	tT⁴ layer	e	b	6	2.777−2.829	2.80(2)
4	tT⁴ layer	i	n	12	2.857−2.911	2.89(1)
5	tT⁴ layer	e	n	3	2.954−3.016	2.98(2)
6	T³ layer	e	b	3	2.578−2.590	2.584(5)
7	T³ layer[c]	e	b	6	2.757−2.766	2.764(6)
8	T³ layer[d]	i	b	2	2.860−2.864	2.862(1)
9	T³ layer[d]	i	n[g]	4	2.861−2.950	2.91(4)
10	T³ layer	i	n	3	3.100−3.266	3.17(7)
11	T²/tT⁴ interlayer	e	b	3	2.806−2.830	2.82(1)
12	T²/tT⁴ interlayer[c]	i	n	3	2.806−2.835	2.82(1)
13	T²/tT⁴ interlayer[c]	e	b	6	2.858−2.904	2.88(2)
14	T²/tT⁴ interlayer	i	n	6	2.985−3.043	3.02(2)
15	tT⁴/T³ interlayer[c]	e	n	12	2.802−2.917	2.86(4)
16	tT⁴/T³ interlayer	i	n	9	2.938−3.076	2.98(4)
17	tT⁴/T³ interlayer	e	n	6	3.004−3.069	3.03(2)

[a] Topological characterization of the classes. [b] Within the encapsulated triangle. [c] Involving some corner atom of the layer(s). [d] Involving the central atom of the layer. [e] Internal (i); external (e). [f] CO-bridged (b); non-bridged (n). [g] "Long" distances (two) are possibly due to H-bridging. [h] The esd values for the individual Rh−Rh interaction are less than 0.001 Å.

The pattern of the Rh−Rh bond distances obeys the overall idealized C_{3v} symmetry and can be partitioned into 17 topologically independent classes, as reported in Table 1. From class to class, there is large variability of the average Rh−Rh bond distances (from 2.58 to 3.17 Å), their actual value depending on the local electron book-keeping, the presence of bridging ligands, and the perturbations due to nearby nitrides. This last factor is clearly the most relevant, as can be deduced by comparison with the largest non-interstitial rhodium cluster, $[Rh_{22}(CO)_{37}]^{4-}$, where the Rh−Rh bond distances range from 2.729 to 2.883, only.[12]

Fifteen carbonyl ligands, out of 41, are terminally bound, one for each metal on T² (6 CO) and one for each vertex on tT⁴ (6

(12) Martinengo, S.; Ciani, G.; Sironi A. *J. Am. Chem. Soc.* **1980**, *102*, 7565.

CO) and T³ (3 CO). Twenty-four carbonyls bridge, with some small asymmetry, the nine T²/tT⁴ interlayer surface edges and the external edges of tT⁴ (6 out of 9) and T³ (9); two additional ligands are semibridging the Rh(13)−Rh(18) and Rh(13)−Rh(22) bonds, on T³. Space-filling models, showing on the same T³ face some empty space in the CO covering, suggest the possible location of the two hydrides.

The four interstitial nitrogen atoms are all located in octahedral cavities, one in the middle of the T²/tT⁴ slab and three within the tT⁴/T³ slab. The four cavities are markedly distorted, being the pertinent Rh−Rh interactions scattered between 2.73 and 3.24 Å. Moreover, all N atoms lie, more or less, slightly off the cage centers. In fact, the unique N atom is involved in three short and three long Rh−N interactions [average 2.02(2) and 2.086(5) Å, respectively], while the other three N atoms are involved in four short and two long Rh−N interactions [average 1.98(2) and 2.21(2) Å, respectively]. This confirms the distinctive tendency, of interstitial nitrogen atoms in high-nuclearity clusters, to asymmetric and/or incomplete coordination; whether this can be related to the presence of a lone pair on the nitrogen atoms has still to be understood.

The anion **2** (for $x = 2$) has 360 cluster valence electrons, corresponding to 180 cluster valence molecular orbitals (CVO). This number is related, in compact closest-packed clusters, to the nuclearity (N) through the empirical relationship: CVO = $(6N + X)$, where X has in most cases the value of 7.[13] The compactness of a cluster may decrease because interstitial atoms induce some distortions; in these cases X systematically increases. From this point of view, we could then use the increase of X as a measure of the cage distortions. In the present case, where $X = 7 + 5$, the "swelling" effect induced by each N atom would be of 1.25 CVOs, which is the lower value observed in metal nitrides,[6] consistently with the relatively moderate distortions observed.

Species **1** may be reasonably formulated as $[Rh_{28}N_4(CO)_{41}H]^{5-}$, also on the basis of the elemental analysis. It should be essentially isostructural, apart from one hydrogen, with **2**. This also explains the NMR of **1**, arising from the fluxional behavior of the hydrogen around Rh(13) and its six equivalent neighbors on the T³ face. The broadening observed on lowering the temperature agrees with the tendency to reach a fixed position in one of the two coordination holes on this face.

Most transition metal nitrides have approximately, or in some cases exactly, close-packed structures with the nitrogen atoms interstitially located; the arrangement of the metal atoms in these compounds, however, is generally not the same as in the pure metal.[14] The finding of $[Rh_{28}N_4(CO)_{41}H_x]^{4-}$, a massive cluster which reproduces the *ccp* lattice of the bulk metal, with relatively little swelling due to several interstitial nitrogen atoms, suggests the possibility that a binary nitride of rhodium, presently unknown, could exist.

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