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A new multivalent cluster: synthesis, electrochemistry, solid state structure and computational studies on the iron–nickel mixed-metal nitride anions $[Fe_6Ni_6N_2(CO)_{24}]^{n-}$ ($n = 2$–4)

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Abstract

The three clusters $[Fe_6Ni_6N_2(CO)_{24}]^{n-}$ ($n = 2$–4) have been isolated, and their solid-state structures determined. The clusters are composed by three face-sharing octahedra, with the external ones filled by two interstitial nitride. The addition of electrons brings about swelling of the central, empty octahedron. Cyclic voltammetry shows that redox conversions of the three clusters are totally reversible. Extended Hückel and density functional calculations have been performed, to explain this behavior. ***To cite this article: R. Della Pergola et al., C.R. Chimie 8 (2005)***.

Résumé

Les trois clusters $[Fe_6Ni_6N_2(CO)_{24}]^{n-}$ ($n = 2$–4) ont été isolés et leurs structures déterminées a l'état solide. Les clusters sont composés de trois octaèdres, avec deux faces en commun à l'intérieur ; les deux octaèdres externes ont deux nitrures interstitiels. L'addition de électrons cause un grossissement de l'octaèdre central vide. La voltamétrie cyclique montre que les transformations rédox des trois clusters sont complètement réversibles. Les calculs de Hückel étendus et de la densité fonctionnelle ont été achevés pour expliquer ce comportement. ***Pour citer cet article : R. Della Pergola et al., C.R. Chimie 8 (2005)***.

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The vast majority of cluster compounds are supposed to be diamagnetic, and to possess a definite (even) number of valence electron, mainly dependent on their geometry [1]. This conviction was so strong that paramagnetic behavior was normally associated with odd number of electrons, even in the absence of experimental evidences [2]. However, in recent years, electrochemical experiments have shown that many cluster cores are able to add/release electrons without disruption [3]. At the same time, an increasing number of clusters violating electron counting rules have been isolated and characterized. Some of them have been isolated only as paramagnetic compounds [4], only a few are sufficiently stable that could be isolated in multiple oxidation states [5]. For this peculiar behavior of metal clusters, frequently referred as electron sponges [6], a molecular (rather than atomic) type of magnetism was claimed, since they can store unpaired spin on molecular orbital delocalized over the entire metallic particles (which can approach nano-sized dimensions), instead of single metallic ions [7]. One example of this sort are the $[Fe_3Pt_3(CO)_{15}]^{n-}$ clusters ($n = 0–2$). The structure of the three congeners [5,8], the ESR of the monoanion [9], the computational explanation for their behavior [10,11], and peculiar electrochemical [8,10] and magnetic properties have been described [7].

In this paper the new family of multivalent $[Fe_6Ni_6N_2(CO)_{24}]^{n-}$ ($n = 1–4$) clusters is reported. The three stable anions $[Fe_6Ni_6N_2(CO)_{24}]^{n-}$ ($n = 2–4$) have been synthesized by the reaction between $(NEt_4)_2[Ni_6(CO)_{12}]$ and the preformed nitride $(NEt_4)[Fe_4N(CO)_{12}]$, in acetonitrile. The exact composition of the final reaction mixture is strongly dependent from the experimental details (molar ratio of the reagents, temperature, solvents, etc.). Subsequent extraction of the reaction mixture with MeOH, THF, acetone and MeCN allowed isolating a large variety of mixed-metal clusters, which are not, as yet, fully characterized. Some of them contain an interstitial nitride (such as $[HFe_4Ni_2N(CO)_{13}]^{2-}$ or $[HFe_5NiN(CO)_{14}]^{2-}$) [12] some others are homoleptic carbonyl compounds (such as $[FeNi_5(CO)_{13}]^{2-}$ and $[Fe_3Ni(CO)_{12}]^{2-}$) [13].

When the reaction is carried at room temperature, in acetonitrile, with a $Fe_4N/Ni_6 = 2:1$ molar ratio, the main products are the anions $[Fe_6Ni_6N_2(CO)_{24}]^{n-}$ ($n = 2–4$), which can be fractionated easily, owing to their different solubility in MeOH, acetone and acetonitrile, brought about by their different negative charge[1]. Therefore, the three anions could all be examined by single crystal X-ray analysis[2].

Later on, we could interconvert smoothly and selectively the three anions, by using conventional redox reagents (H^+, atmospheric oxygen, tropilium or ferrocenium cations were proved suitable for oxidations, cobaltocene for the reduction to $[Fe_6Ni_6N_2(CO)_{24}]^{3-}$ and sodium-ketyl for the obtainment of the tetraanion), or controlled potential electrolysis.

As clearly demonstrated by the cyclic voltammogram shown in Fig. 1, the dianion $[Fe_6Ni_6N_2(CO)_{24}]^{2-}$ exhibits in MeCN solution either a (coulometrically measured) one-electron oxidation ($E°'_{2-/-} = +0.17$ V, vs. SCE; $\Delta E_p = 74$ mV at 0.2 V s^{-1}), which possesses features of partial chemical reversibility (at 0.2 V s^{-1}: $i_{pc}/i_{pa} = 0.7$), or two stepwise (coulometrically measured) one-electron reductions ($E°'_{2-/3-} = -0.40$ V, $E°'_{3-/4-} = -0.90$ V; $\Delta E_p = 66$ and 62 mV, respectively, at 0.2 V s^{-1}), which are chemically reversible both in the cyclic voltammetric (i_{pa}/i_{pc} constantly equal to 1.0) and in the macroelectrolysis time scales [14].

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[1] $(NEt_4)_2[Ni_6(CO)_{12}]$ (0.49 g; 0.52 mmol) and $(NEt_4)[Fe_4N(CO)_{12}]$ (0.75 g; 1.07 mmol) were dissolved in 45 ml of MeCN and stirred at room temperature for 72 h: the solvent was then removed in vacuum, and the black residue was suspended overnight in MeOH (mixed NEt_4^+/PPh_4^+ salts were obtained, if PPh_4Br was added ad this stage). The solution contained fairly pure $[Fe_6Ni_6N_2(CO)_{24}]^{2-}$, which was precipitated by the addition of PPh_4Br and water, filtered, dried and crystallized from THF/2-propanol. The solid residue was extracted with acetone and then acetonitrile. The two solutions were layered with 2-propanol and di-isopropyl ether, respectively, yielding variable amounts of $[Fe_6Ni_6N_2(CO)_{24}]^{3-}$ and $[Fe_6Ni_6N_2(CO)_{24}]^{4-}$. ν(CO) for $[Fe_6Ni_6N_2(CO)_{24}]^{2-}$: 2016vs, 2003vs, 1954m, 1911w cm^{-1}, in THF. ν(CO) for $[Fe_6Ni_6N_2(CO)_{24}]^{3-}$: 1993vs, 1978vs, 1924m, 1882w cm^{-1}, in MeCN. ν(CO) for $[Fe_6Ni_6N_2(CO)_{24}]^{4-}$: 1974vs, 1951vs, 1930m, 1884w cm^{-1}, in MeCN.

[2] *Crystal data* are reported in table 2. Bruker SMART CCD area-detector, T 223 K, Mo Kα radiation ($\lambda = 0.71073$ Å), ω scan mode, $\theta_{min} = 3°$, $\theta_{max} = 26°$. Structures solved by direct methods and refined by full-matrix least squares. Program used was Personal SDP on a Pentium III computer.