

Iron–nickel mixed metal nitrido clusters: Synthesis and solid state structure of the anions $[\text{HFe}_5\text{NiN}(\text{CO})_{14}]^{2-}$ and $[\text{HFe}_4\text{Ni}_2\text{N}(\text{CO})_{13}]^{2-}$

Roberto Della Pergola ^{a,*}, Alessandro Fumagalli ^b, Luigi Garlaschelli ^c, Carlo Manassero ^d, Mario Manassero ^{d,*}, Mirella Sansoni ^d, Annalisa Sironi ^c

^a *Dipartimento di Scienze dell'Ambiente e del Territorio, Università degli Studi di Milano Bicocca, Piazza della Scienza 1, 20126 Milano, Italy*

^b *Dipartimento di Biologia Strutturale e Funzionale, Università degli studi dell'Insubria, Via J. H. Dunant 3, 21100 Varese, Italy*

^c *Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Via G. Venezian 21, 20133 Milano, Italy*

^d *Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Via G. Venezian 21, 20133 Milano, Italy*

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Dedicated to our dear friend P. Zanello, in recognition of his contribution to the chemistry of metal clusters.

Abstract

The two clusters $[\text{HFe}_5\text{NiN}(\text{CO})_{14}]^{2-}$ (**1**) and $[\text{HFe}_4\text{Ni}_2\text{N}(\text{CO})_{13}]^{2-}$ (**2**) were obtained by reaction of $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$ and $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ in refluxing MeCN and EtCN, respectively, along with other Fe–Ni mixed metal clusters. Their solid state structures were determined on the $[\text{PPh}_4]^+$ salts, and both have an octahedral metal cage, containing an interstitial nitrogen atom. The two Ni atoms in **2** are *cis*, with a Ni–Ni separation of 2.724(1) Å. The two anions have different stereochemistry of the carbonyl ligands: in **1**, five CO's are semi-bridging, and the remaining nine are terminal; in **2** there are three asymmetric bridging and ten terminal ligands (two for each iron and one for each nickel). The hydride ligands were located in the final difference maps, both bridging a Ni–Fe edge of the clusters but, thanks to the better quality of the diffraction data, the metal–hydrogen distances were refined only in **2**. In this cluster, the Fe–H and Ni–H bond lengths are 1.77(2) and 1.79(2) Å, respectively.

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1. Introduction

Iron and nickel are well suited for the preparation of transition metal carbonyl clusters, especially for the propensity to incorporate a variety of main group elements such as In [1], C [2], Ge [3,4], Sn [5,4], P [6], As [7], Sb [8], Bi [9]. On that basis, it is remarkable that no nitride clusters of nickel are known [10]. During a systematic investigation aimed to the synthesis of iron-based mixed-metal nitrides, we could isolate in a low yield a family of

trioctahedral clusters, of formula $[\text{Fe}_6\text{Ni}_6(\text{N})_2(\text{CO})_{24}]^{n-}$ ($n = 4, 3, 2$) which can well exemplify the electron-sponge behaviour of large metal clusters, since the three members are all stable. Experimental data, obtained by solid state crystal structure, and computational analyses agree in that they are able to add/release electrons, delocalising them on the entire metallic skeleton [11]. At the same time, from the same reaction mixture, we were able to separate and identify two non-nitridic Fe–Ni clusters, $[\text{FeNi}_5(\text{CO})_{13}]^{2-}$ and $[\text{Fe}_3\text{Ni}(\text{CO})_{12}]^{2-}$, which have been also described [12]. In this paper, we report that the same reaction is the source of at least two other mixed-metal clusters, containing the interstitial nitrogen atom, $[\text{HFe}_5\text{NiN}(\text{CO})_{14}]^{2-}$ and $[\text{HFe}_4\text{Ni}_2\text{N}(\text{CO})_{13}]^{2-}$. The two anions can be obtained

* Corresponding authors.

E-mail addresses: roberto.dellapergola@unimib.it (R. Della Pergola), m.manassero@istm.cnr.it (M. Manassero).

independently, depending upon the reaction temperature, and therefore they have been characterized separately. The syntheses of these two clusters suggest alternative ways for the preparation of ternary Ni–Fe–N alloys, well known materials for magnetic storage [13].

2. Results

2.1. The syntheses

Iron based mixed-metal nitride clusters, containing metals of groups 6–10 have been obtained in the past, most of them synthesized by reaction of the nitrido anion $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$ with nucleophilic metal carbonyl anions. The role of the interstitial nitride is crucial for these syntheses, since it prevents complete demolition of the cluster, and drives the reconstruction of the octahedral cage around it [14]. Therefore, to obtain Fe–Ni nitrido compounds, we explored the condensation between $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$ and $[\text{Ni}_6(\text{CO})_{12}]^{2-}$, the most easily available nickel carbonyl anion. At difference with the syntheses of the other mixed-metal nitrides, this reaction is not at all selective, and mixtures of many new clusters are obtained. Many attempts to drive the reaction toward single products, varying the reagent ratio, the counter-ions, the temperature, or the solvents, have been performed with poor results.

Usually, in similar cases, the anionic cluster products can be separated by exploiting their different solubility in solvents of increasing polarity. In this regard the anionic species which can be more easily purified are those whose solubility can be modified depending upon the counterion, usually a bulky organic cation. They can be dissolved in MeOH as tetraalkylammonium salts, and precipitated as phosphonium salts, eliminating at once the less soluble products and the more soluble ones.

In fact, the reaction of $\text{NEt}_4[\text{Fe}_4\text{N}(\text{CO})_{12}]$ and $(\text{NEt}_4)_2[\text{Ni}_6(\text{CO})_{12}]$ in refluxing nitrile solvents (MeCN or EtCN), followed by extraction of the residue with MeOH and addition of PPh_4Cl , resulted in the precipitation of pure $(\text{PPh}_4)_2[\text{HFe}_5\text{NiN}(\text{CO})_{14}]$, $(\text{PPh}_4)_2[\mathbf{1}]$ or $(\text{PPh}_4)_2[\text{HFe}_4\text{Ni}_2\text{N}(\text{CO})_{13}]$, $(\text{PPh}_4)_2[\mathbf{2}]$.

The properties and the infrared spectra of these two salts are very similar, owing to the same charge/metal ratio, and similar structure. Therefore, the best method to establish the course of the reaction, and to judge the purity of the two isolated compounds is the ^1H NMR spectroscopy, because the singlets, attributable to the hydrides, are well distinct (see Section 3). The NMR spectra are invariant down to -90°C , but this may be indicative either of the presence of single isomers in solution, or of a fast fluxional behaviour.

The main difference in the preparations of **1** and **2** is the reaction temperature, that can be selected by the boiling point of the solvent: anion **1** (containing only minor traces of **2**) is best obtained in MeCN ($\sim 80^\circ\text{C}$), whereas pure **2** is obtained by using refluxing EtCN ($\sim 100^\circ\text{C}$). The temperature settings might be counterintuitive, considering that

the composition of **2** ($\text{Fe}_4\text{Ni}_2\text{N}$) matches better with the iron content of the reagent ($[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$), and therefore should require a smaller reorganization of the metals around the nitride (and perhaps a lower temperature than that required for **1**). However, as already pointed out, these reactions never occur with a “clean” addition of two heterometal fragments to the original *arachno* butterfly, to build up the *closo* octahedron. Indeed, the most part of mixed-metal nitride have Fe_5MN cages, suggesting that this composition is the most easily accomplished [14]. Thus, we believe that **1** is an intermediate in the formation of **2**, and a higher temperature is required to substitute one Ni for one Fe in the already formed **1**.

Observing that $[\text{HFe}_6\text{N}(\text{CO})_{15}]^{2-}$ [15], **1** and **2** constitute a cluster family of general formula $[\text{HFe}_{6-x}\text{Ni}_x\text{N}(\text{CO})_{15-x}]^{2-}$ ($x = 0, 1, 2$) some clues can be derived on the mechanism of formation of the trioctahedral di-nitrido cluster $[\text{Fe}_6\text{Ni}_6(\text{N})_2(\text{CO})_{24}]^{4-}$ [11]. As a matter of fact, $[\text{HFe}_3\text{Ni}_3\text{N}(\text{CO})_{12}]^{2-}$ the putative following member of the family ($x = 3$), could be the intermediate that, by dimerization and reductive elimination of a dihydrogen molecule, yields $[\text{Fe}_6\text{Ni}_6(\text{N})_2(\text{CO})_{24}]^{4-}$.

2.2. Solid state structures

The solid state structure of anions **1** and **2** are represented in Figs. 1 and 2, respectively, and the relevant structural parameters are collected in Tables 1 and 2.

Both diffraction analyses were performed on single crystals of the $(\text{PPh}_4)^+$ salts. The crystal lattice of **1** contains two independent anions, and four independent cations. One of the anions could be refined with smaller experimen-

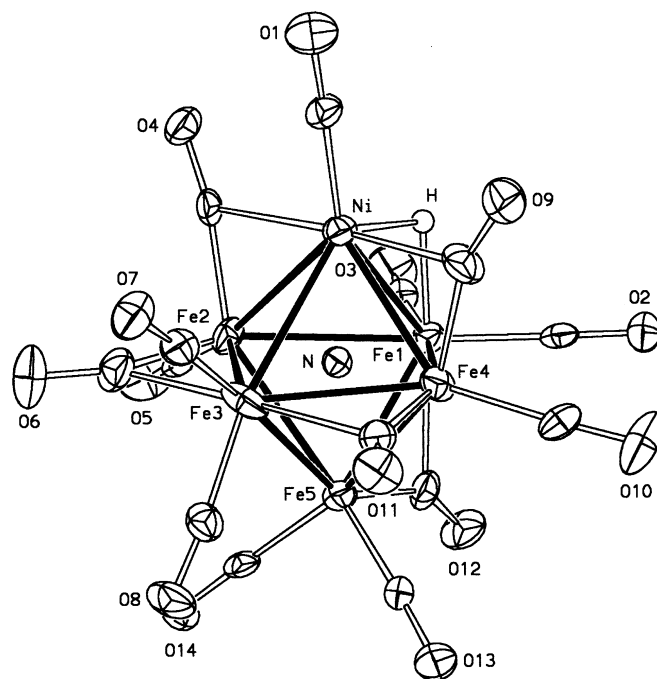


Fig. 1. The solid state structure of $[\text{HFe}_5\text{NiN}(\text{CO})_{14}]^{2-}$. Ellipsoids are drawn at the 30% probability level. The carbon atoms of the carbonyls are labelled as the oxygen to which they are attached.

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