

Preliminary communication / Communication

# Nanoscale ensembles using building blocks inspired by the [FeFe]-hydrogenase active site

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## Abstract

The hydrogenase model  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]^{2-}$  was employed as a molecular tecton for the construction of supramolecular aggregates. IR spectroscopy indicated that cyanide bridged aggregates are formed when  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]^{2-}$  was treated with Lewis acids such as Zn(tetraphenylporphyrinate),  $[\text{Cu}(\text{NCMe})(2,2'\text{-bipyridine})]\text{PF}_6$  and  $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ . Condensation of  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]^{2-}$  with the tritopic Lewis acid  $[\text{Cp}^*\text{Rh}]^{2+}$  afforded the novel expanded tetrahedron cage,  $\{[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]_6[\text{Cp}^*\text{Rh}]_4\}^{4-}$ . The tetrahedron cage was characterized crystallographically as the PPN salt. **To cite this article:** Julie L. Boyer et al., C. R. Chimie 11 (2008).

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**Keywords:** Cyanide; Supramolecular chemistry; Cage compounds; Lewis acids; Carbonyl ligands

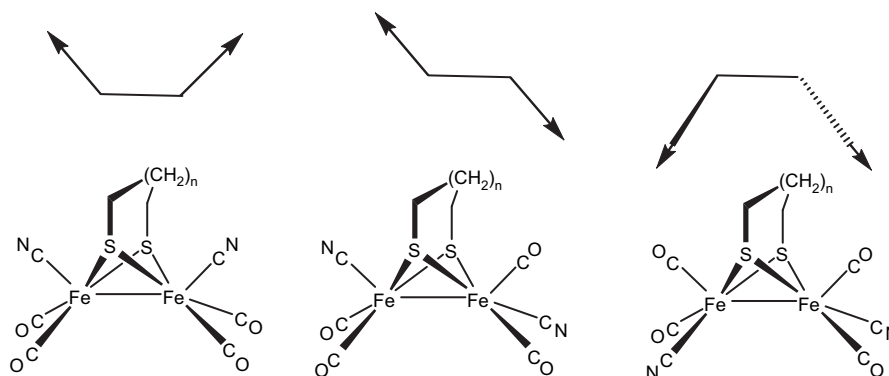
## 1. Introduction

Cyanometallates are well known to serve as ligands for Lewis acidic metal centers [1–4]; this area dates back to the synthesis of Prussian Blue and the Hofmann clathrates [5–9]. Inspired by these precedents, researchers have recently learned how to generate molecular cuboidal cages via condensations of cyanometallates and the Lewis acids wherein both bear blocking coligands [10,11]. With certain coligands, one can obtain molecular cages that display distinctive host–guest or magnetic properties [12–15]. The invention of new cyanometallate cages depends on the development of new cyanometallate building blocks [16–19].

In evaluating new cyanometallate building blocks, we focused on the dianions  $[\text{Fe}_2(\text{SR})_2(\text{CN})_2(\text{CO})_4]^{2-}$ , which have been of intense interest as models for the active site of the [FeFe]-hydrogenases [20–22]. Such species exhibit Bronsted basicity, redox activity, and an ambidentate cyanide ligand. In addition to the possibility of incorporated functionality into multimetallic ensembles, such species are attractive building blocks for several reasons: (i) they are readily prepared with a range of thiolate bridges and counter cations [23], (ii) the  $\text{Fe}(\text{CN})(\text{CO})_2$  vertices are fluxional via a turnstile rotation (Scheme 1) [24] which allows the cyanide ligands to readily reorient to accommodate the geometric preference of templating Lewis acids, and possibly to correct non-optimally folded cages of the annealing structure and (iii) the Bronsted basicity of the Fe–Fe bond in these dianionic species has been demonstrated. We were particularly intrigued by the prospect of

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Scheme 1.

elucidating pathways to potentially multifunctional ensembles that could open the door to the realm of catalytically active coordination cages.

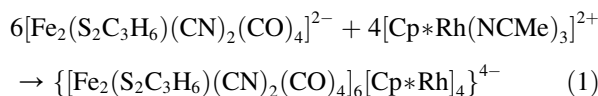
## 2. Results and discussion

We initially surveyed the ability of  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]^{2-}$  to serve as a ligand by screening its interaction with several metal ions, using FT-IR spectroscopy as an assay.<sup>1</sup> Solutions of  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]^{2-}$  were found to react with MeCN solutions of Lewis acids such as  $[\text{Cu}(\text{NCMe})(\text{bipy})]\text{PF}_6$  and  $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$  in a 1:1 ratio to give soluble adducts. In each case, adduct formation was signaled by shifts in the  $\nu_{\text{CN}}$  band,  $37\text{ cm}^{-1}$ , to higher energy. A shift in the  $\nu_{\text{CO}}$  bands to higher energy was also observed, indicative of a Lewis acid adduct formation [25]. Similarly, the highly lipophilic salt  $(\text{PPN})_2[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]$  ( $\text{PPN}^+ = \text{Ph}_3\text{PNPPH}_3^+$ ) was found to form 1:2 adducts with ZnTPP (TPP = *meso*-tetraphenylporphyrin dianion). IR spectra for  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4][\text{ZnTPP}]_2^{2-}$  exhibited  $\nu_{\text{CN}}$  band at  $2100\text{ cm}^{-1}$ , a shift of  $25\text{ cm}^{-1}$  vs.  $(\text{PPN})_2[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]$ , consistent with the formation of FeCN–Zn linkages.

The preceding condensations clearly indicated the ability of this dimetallic dicyanide as a supramolecular tecton. We therefore directed our attention to the more challenging possibility of generating three-dimensional ensembles. In this case, we turned to the use of  $\text{Cp}^*\text{Rh}^{2+}$ , which is a versatile reagent in stabilizing high molecular weight coordination cages [26]. In the diaxial orientation, the two cyanide vectors in  $[\text{Fe}_2$

$(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]^{2-}$  define an angle of  $\sim 115^\circ$ , which should favor the formation of adamantoid or extended tetrahedral cages when reacted with the half-sandwich  $[\text{Cp}^*\text{Rh}(\text{NCMe})_3](\text{PF}_6)_2$  [27].

IR spectral analysis demonstrated that 1.5 equiv  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]^{2-}$  condensed readily with  $[\text{Cp}^*\text{Rh}(\text{NCMe})_3](\text{PF}_6)_2$  in acetonitrile solution (Eq. (1)). The IR spectrum of the product solution featured a band assigned to  $\nu_{\mu\text{-CN}}$  at  $2108\text{ cm}^{-1}$ , shifted to higher energy vs. starting  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]^{2-}$  ( $2075\text{ cm}^{-1}$ ). The three  $\nu_{\text{CO}}$  bands ( $1979$ ,  $1935$ ,  $1913\text{ cm}^{-1}$ ) were also shifted to higher energy vs. starting  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]^{2-}$  ( $1963$ ,  $1922$ ,  $1884\text{ cm}^{-1}$ ). Titrations indicated that cage formation was strongly favored since the treatment of  $(\text{NEt}_4)_2[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]$  with 0.5 equiv of  $[\text{Cp}^*\text{Rh}(\text{NCMe})_3](\text{PF}_6)_2$  gave aggregates and unreacted  $(\text{NEt}_4)_2[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]$ . At 1/0.67 ratio of  $(\text{NEt}_4)_2[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]$  to  $[\text{Cp}^*\text{Rh}(\text{NCMe})_3](\text{PF}_6)_2$ , the IR spectrum indicated the presence of a single condensed aggregate (Fig. 1). ESI-MS analysis of the reaction  $(\text{PPN})_2[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4] + 0.67 [\text{Cp}^*\text{Rh}(\text{NCMe})_3](\text{PF}_6)_2$  showed a strong current at  $m/z = 811$  and  $1261$ , corresponding to  $\{[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]_6[\text{Cp}^*\text{Rh}]_4\}^{4-}$  and  $\{\text{PPN}\{[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]_6[\text{Cp}^*\text{Rh}]_4\}^{3-}$ , respectively.



Fragile crystals of the  $\text{Fe}_{12}\text{Rh}_4(\text{CN})_{12}$  cage were obtained using a variety of different counter ions Q ( $\text{Q} = \text{NEt}_4$ ,  $\text{NBU}_4$ ,  $\text{PPN}$ ). The tetra-PPN<sup>+</sup> salt afforded the highest quality crystals. Crystallographic analysis indicates that cage consists of an expanded tetrahedron as predicted by the Stang analysis (Fig. 2) [27]. Four  $\text{Cp}^*\text{Rh}$  vertices are connected by six  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)$

<sup>1</sup> IR spectra of the titration of  $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$  and  $[\text{bipyCu}(\text{NCMe})]\text{PF}_6$  to  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CN})_2(\text{CO})_4]^{2-}$  are given in the supplementary material.

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