

# The Design of Cyanometallate Cages for Alkali Ion Separation

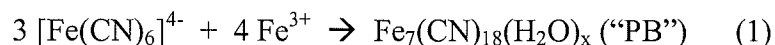
Matthew L. Kuhlman

Final Defense

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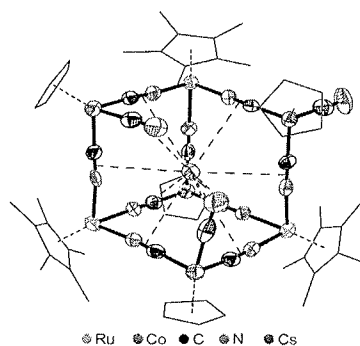
Molecular containers are of continuing interest for synthetic chemists due to their realized uses as catalysts,<sup>1,2</sup> sorters,<sup>3</sup> sensors,<sup>4</sup> and in cavity directed synthesis.<sup>5</sup> Most molecular containers are based on hydrocarbon derived frameworks.<sup>6</sup> An advantage of inorganic frameworks is their potential rigidity, which should impart size-based selectivity to these supermolecules.<sup>7</sup>

Much work on cyanometallate-based cages is inspired by Prussian Blue (PB), the inorganic polymer  $\text{Fe}_7(\text{CN})_{18}(\text{H}_2\text{O})_x$ .<sup>8</sup> PB is prepared by the building block approach, the condensation of  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $\text{Fe}(\text{III})$  salts (eq 1).



PB consists of CN-interconnected octahedral Fe centers, the framework of which defines a series of box-like subunit. As indicated by its formula, PB consists of many defects, and these defects are integrally related to PB's host-guest behavior.<sup>9</sup> PB and some of its analogues exhibit a particular affinity for  $\text{Cs}^+$ .<sup>10</sup> Improved understanding of cyanometallate- $\text{Cs}^+$  interactions provides a context for our work, i.e. the design of new classes of ion selection agents for nuclear waste remediation ( $^{137}\text{Cs}$ ).<sup>11</sup>

Our approach to inorganic cages entails the use of the rigid organometallic cyanides. The reaction between  $[\text{K}(18\text{-crown-6})][\text{CpCo}(\text{CN})_3]$  and  $[\text{Cp}^*\text{Ru}(\text{NCMe})_3]^+$  in the presence of  $\text{CsOTf}$  produced the molecular box and defect box,  $\{\text{Cs} \llcorner [\text{CpCo}(\text{CN})_3]_4\text{-}[\text{Cp}^*\text{Ru}]_4\}^+$ ,  $\text{Cs} \llcorner \text{Co}_4\text{Ru}_4^+$ , and  $\text{Cs} \llcorner [\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3$ ,  $\text{Cs} \llcorner \text{Co}_4\text{Ru}_3$ , respectively. The  $^1\text{H}$  NMR spectrum of  $\text{Cs} \llcorner \text{Co}_4\text{Ru}_3$  indicates that it exists as a mixture of two low symmetry isomers ( $C_s$ ). The two isomers are proposed to differ in terms of the relative stereochemistry of the Cp and  $\text{CN}_t$  (terminal) ligands on the upper "rim" of the cage. Crystallographic characterization of  $\text{Cs} \llcorner \text{Co}_4\text{Ru}_3$  revealed that it crystallizes in the  $C_s$ -(exo)<sub>1</sub>(endo)<sub>2</sub> isomer (Figure 1).



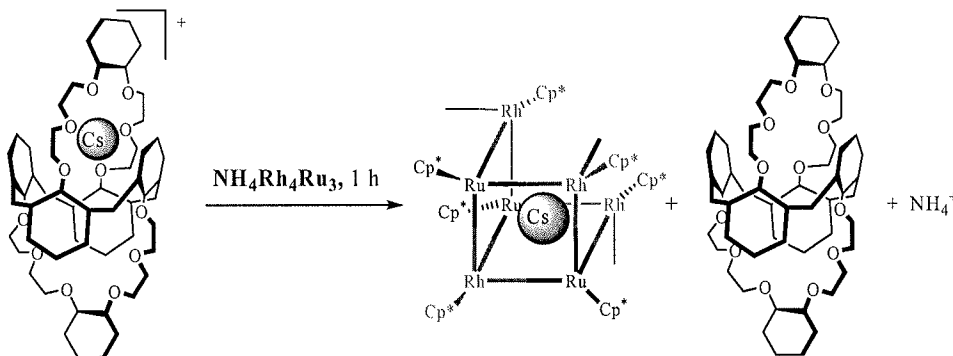
**Figure 1.** Molecular structure of  $\text{Cs} \llcorner [\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3$  showing the atom labeling scheme. Thermal ellipsoids are drawn at the 50% level.

Aside from its novel structure, an exciting aspect of  $\text{Cs}\llcorner\text{Co}_4\text{Ru}_3$  is its potential as a well-defined building block for the assembly of novel molecular cages via the condensation of  $\text{Cs}\llcorner\text{Co}_4\text{Ru}_3$  with another metal fragment (M) to give  $\text{Cs}\llcorner\text{Co}_4\text{Ru}_3\text{M}$ , a box-completion process. The reactions of  $\text{Cs}\llcorner\text{Co}_4\text{Ru}_3$  with:  $\text{Cp}^*\text{Rh}(\text{NCMe})_3^{2+}$ ,  $\text{VCl}_3(\text{THF})_3$ , or  $(\text{cym})\text{Ru}(\text{NCMe})_3^{2+}$  all resulted in complete conversion to the corresponding completed box product.

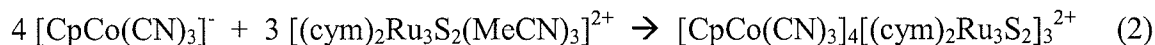
Although analogues of the  $\text{Cs}^+$  compounds such as  $\{\text{K}\llcorner[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3\}$  or  $\text{NH}_4\llcorner[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3$  could not be prepared, the reaction of 0.75 equiv of  $[\text{Cp}^*\text{Ru}(\text{NCMe})_3]\text{PF}_6$ ,  $\text{Et}_4\text{N}[\text{Cp}^*\text{Rh}(\text{CN})_3]$ , and 0.25 equiv of  $\text{NH}_4\text{PF}_6$  produced the ammonium encapsulated species  $\{\text{NH}_4\llcorner[\text{Cp}^*\text{Rh}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3\}$ ,  $\text{NH}_4\llcorner\text{Rh}_4\text{Ru}_3$ .  $\text{CsOTf}$  quantitatively and rapidly converts  $\text{NH}_4\llcorner\text{Rh}_4\text{Ru}_3$  into  $\text{Cs}\llcorner\text{Rh}_4\text{Ru}_3$ , demonstrating the kinetic advantages of the  $\text{M}_7$  cages as  $\text{Cs}^+$  receptors. Crystallographic characterization of  $\text{M}\llcorner\text{Rh}_4\text{Ru}_3$  ( $\text{M} = \text{NH}_4, \text{Cs}$ ) revealed that both crystallize as the second  $C_s$  isomer, i.e.  $(\text{exo})_2(\text{endo})_1$ , wherein only one  $\text{CN}_t$  ligand interacts with the included cation. A competition experiment between a calix[4]arene, that is known to have high affinity for  $\text{Cs}^+$ , and  $\text{NH}_4\llcorner\text{Rh}_4\text{Ru}_3$  reveals  $\text{NH}_4\llcorner\text{Rh}_4\text{Ru}_3$  has a higher affinity for  $\text{Cs}^+$  (Scheme 1).

**Scheme 1.**

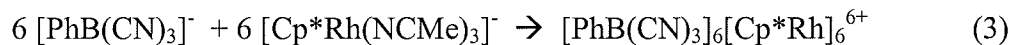
calix[4]arene-bis(benzocrown-6)



We have further exploited this condensation method with *fac*-tricyanide precursors and redox active metal sulfide clusters, which are tritopic Lewis acids (eq 2). Unfortunately, we could not control the host-guest chemistry of the hybrid defect box electrochemically.



The condensation chemistry of tetrahedral tricyanides and tritopic Lewis acids were also investigated, which yielded a larger cyanometallate motif, a hexagonal prism (eq 3).



## References:

- (1) Kang, J.; Santamaria, J.; Hilmersson, G.; Rebek, J., Jr. "Self-Assembled Molecular Capsule Catalyzes a Diels-Alder Reaction" *J. Am. Chem. Soc.* **1998**, *120*, 7389-7390.
- (2) Ito, H.; Kusukawa, T.; Fujita, M. "Wacker oxidation in an aqueous phase through the reverse phase-transfer catalysis of a self-assembled nanocage" *Chem. Lett.* **2000**, 598-599.
- (3) Atwood, J. L.; Koutsantonis, G. A.; Raston, C. L. "Purification of C60 and C70 by selective complexation with calixarenes" *Nature* **1994**, *368*, 229-231.
- (4) Lehaire, M.-L.; Scopelliti, R.; Piotrowski, H.; Severin, K. "Selective recognition of fluoride anion using a Li<sup>+</sup> - metallacrown complex" *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 1419-1422.
- (5) Yoshizawa, M.; Takeyama, Y.; Kusukawa, T.; Fujita, M. "Cavity-directed, highly stereoselective [2+2] photodimerization of olefins within self-assembled coordination cages" *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 1347-1349.
- (6) Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995.
- (7) Huang, S. P.; Kanatzidis, M. G. "Synthesis and structure of the [NaAu<sub>12</sub>Se<sub>8</sub>]<sup>3-</sup>: an inorganic cryptand complex" *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 787-789.
- (8) Herren, F.; Fischer, P.; Ludi, A.; Haelg, W. "Neutron diffraction study of Prussian Blue, Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub>.xH<sub>2</sub>O. Location of water molecules and long-range magnetic order" *Inorg. Chem.* **1980**, *19*, 956-959.
- (9) Lundgren, C. A.; Murray, R. W. "Observations on the composition of Prussian blue films and their electrochemistry" *Inorg. Chem.* **1988**, *27*, 933-939.
- (10) Dunbar, K. R.; Heintz, R. A. "Chemistry of transition metal cyanide compounds: modern perspectives" *Prog. Inorg. Chem.* **1997**, *45*, 283-391.
- (11) Bryan, J. C.; Kavallieratos, K.; Sachleben, R. A. "Unusual Ligand Coordination for Cesium" *Inorg. Chem.* **2000**, *39*, 1568-1572.