Structural Chemistry of “Defect” Cyanometalate Boxes:  
\{\text{Cs}[\text{CpCo(CN)}]_{3}\} \text{ and } \{\text{MC}[\text{Cp}^{*}\text{Rh(CN)}]_{3}\}  
(\text{M} = \text{NH}_{4}, \text{Cs})

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Abstract: A series of heptametallic cyanide cages are described; they represent soluble analogues of defect-containing cyanometalate solid-state polymers. Reaction of 0.75 equiv of [Cp*Ru(NCMe)$_{3}$]PF$_{6}$, Et$_{3}$N-[Cp*Rh(CN)$_{3}$], and 0.25 equiv of CsOTf in MeCN solution produced \{Cs[Cp*Rh(CN)]$_{3}$][Cp*Ru]$_{3}$\} (Cs$_{3}$-R$_{7}$Ru$_{3}$). H and $^{133}$Cs NMR measurements show that Cs$_{3}$-R$_{7}$Ru$_{3}$ exists as a single Cs$_{7}$ isomer. In contrast, \{Cs[CpCo(CN)$_{3}$]$_{3}$Cp*Ru$_{3}$\} (Cs$_{3}$Co$_{3}$R$_{3}$), previously lacking crystallographic characterization, adopts both Cs$_{7}$ isomers in solution. In situ ESI-MS studies on the synthesis of Cs$_{3}$-R$_{7}$Ru$_{3}$ revealed two Cs-containing intermediates, Cs$_{3}$-R$_{7}$Ru$_{3}^{+}$ (1239 m/z) and Cs$_{3}$-R$_{7}$Ru$_{3}^{+}$ (1791 m/z), which underscore the participation of Cs$_{7}$ in the mechanism of cage formation. $^{133}$Cs NMR shifts for the cages correlated with the number of CN groups bound to Cs$^{+}$: Cs$_{3}$-Co$_{3}$Ru$_{3}^{+}$ (δ 1 vs δ 34 for CsOTf), Cs$_{3}$-R$_{7}$Ru$_{3}$ where Cs$^{+}$ is surrounded by ten CN ligands (δ 91), Cs$_{3}$-Co$_{3}$Ru$_{3}$, which consists of isomers with 11 and 10 x-bonded CNs (δ 42 and δ 89, respectively). Although (K$_{3}$[Cp*Rh(CN)$_{3}$]$_{3}$)[Cp*Ru]$_{3}$ could not be prepared, (NH$_{4}$)[Cp*$\text{Co}^{*}$\text{CN}]$_{3}$[Cp*Ru]$_{3}$ (NH$_{4}$-R$_{0}$C$_{0}$R$_{3}$) forms readily by NH$_{4}^{-}$-template cage assembly. IR and NMR measurements indicate that NH$_{4}^{-}$ binding is weak and that the site symmetry is low. CsOTf quantitatively and rapidly converts NH$_{4}$-R$_{0}$C$_{0}$R$_{3}$ into Cs$_{3}$-R$_{7}$Ru$_{3}$, demonstrating the kinetic advantages of the M$_{7}$ cages as ion receptors. Crystallographic characterization of Cs$_{3}$Co$_{3}$Ru$_{3}$ revealed that it crystallizes in the C$_{1}$-template cage assembly. IR and NMR revealed that it crystallizes in the C$_{1}$-template cage assembly. 

Introduction

Molecular containers are of continuing interest for synthetic chemists due to their realized uses as catalysts,$^{1,2}$ sorters,$^{3}$ sensors,$^{4-5}$ and in cavity directed synthesis.$^{6,7}$ Most molecular containers are based on hydrocarbon frameworks.$^{8}$ An advantage of inorganic frameworks is their potential rigidity, which should impart size-based selectivity to these supermolecules.$^{9}$ It has, however, proven difficult to synthesize inorganic molecular cages that exhibit host–guest behavior. Our approach to inorganic cages entails the use of the rigid organometallic cyanides. Cyanometalate building blocks indeed give rise to diverse structures such as chains,$^{10,11}$ triangles,$^{12,13}$ squares,$^{14}$ boxes,$^{15}$ and extended solid frameworks$^{20}$ which have been discussed as sensors,$^{21}$ molecular magnets,$^{22,23}$ and sieves.$^{24}$

Much work on cyanometalate-based cages is inspired by Prussian Blue (PB), the inorganic polymer Fe$_{6}$(CN)$_{6}$H$_{2}$O$^{x-}$ and Fe(III) salts (eq 1). $^{3}$

\[3\text{Fe(CN)}_{6}^{x-} + 4\text{Fe}^{3+} \rightarrow \text{Fe}_{6}\text{(CN)}_{6}^{x-} + \text{Fe}^{3+}\]  

PB consists of CN-interconnected octahedral Fe centers, the

framework of which defines a series of boxlike subunits (Figure 1). As indicated by its formula, PB consists of many defects, and these defects are integrally related to PB’s host–guest behavior.26,27 Thus, whereas (LM)CN12 cages have been mentioned as molecular representations of PB,28 lower symmetry derivatives of such cubic cages in fact would be more faithful representations of PB, with regards to both structure and function. Such a defect structure provides context for the present project, which describes a series of heptametallic cyano-bridged cages. PB and some of its analogues exhibit a particular affinity for Cs+ because of the relative stereochemistry of the three terminal cyanide ligands (CN) in defect cages, their M7-CN12 frameworks are not true subunits of the completed M8-(CN)12 boxes. Addition of [Cp*Rh(NCMe)3]2+ to {[Cp*Rh(CN)]3+[Cp*Rh]3}2+ does not lead to cage closure.

The following lessons were learned from our initial studies on Cp*Rh3+-based cages:

(1) Cationic cages failed to exhibit detectable host–guest behavior. This finding led to our interest in anionic or charge-neutral cages.

(2) The stoichiometry of the condensing partners significantly influences the course of the condensation.

(3) The steric bulk of the ancillary ligands (e.g., Cp vs Cp*) can be used to modify the box-forming tendencies of these cyanometalates. Because of the relative stereochemistry of the three terminal cyanide ligands (CN) in defect cages, their M7-CN12 frameworks are not true subunits of the completed M8-(CN)12 boxes. Addition of [Cp*Rh(NCMe)3]2+ to {[Cp*Rh(CN)3]+[Cp*Rh]3}2+ does not lead to cage closure.

(4) The M–CN–M’ linkages are ordered in all known cyanometalate boxes and defect boxes, as shown by 13C NMR and crystallographic studies. Metals with labile M–CN linkages do not form box or defect-box structures.33,34

These four points underpin the present study, which originated with our recently reported synthesis of [CpCo(CN)3]3+/[Cp*Ru]2+ cages.35 These Co–Ru cages, which are less cationic than related Cp*Rh3+-derived species, require the presence of a templating cation, Cs+ being particularly versatile in this regard. We found that the [CpCo(CN)3]3+/[Cp*Ru]2+/Cs+ reaction affords both CsM7 defect boxes and CsM8 boxes, depending on the reaction stoichiometry.35 We confirmed that Cs[CpCo(CN)3]3+[Cp*Ru]4+ (CsCo4Ru4) adopts the boxlike structure anticipated by its more labile analogue [Cs[Cp*(CN)3]3+[Cp*Rh]3]2+ because it was unclear exactly how the Cs+ was accommodated by the CN1 (terminal) ligands. NMR studies indicated Cs[CpCo(CN)3]3+[Cp*Ru]4+ exists as a mixture of two unsymmetrical isomers, which were proposed to differ in terms of the relative stereochemistry of the Cp and CN ligands on the “rim” of the cage (Figure 2). The structure proposed for CsCo4Ru13 was unprecedented because it involved terminal CN ligands π-bonded to Cs+. Interest in this cage was enhanced because, despite its existence as isomers, it behaves as a tridentate ligand, somewhat akin to trispyrazolyl borates, triazacyclononane, etc., enabling the formation of novel heterotrinuclear boxes and double boxes (Scheme 2).

The defect boxes represent a novel motif for ion sequestration, as they possess a pocket for guest ions.28 Whereas the ion exchange rates for the guest in guestCsM4M4 are quite slow.28


Figure 1. Unit cell for Prussian Blue, Fe₃[Fe(CN)₆]·3(H₂O)₉, as proposed by Ludi et al.26 Fe(III) (N and O coordination); ●, Fe(II) (C coordination); and □, H₂O. The blue highlighted area represents a defect box subunit.
the ion exchange rates for the defect boxes should be high because of their more open structure. This motif is potentially relevant to the design of new sequestering agents for radio-waste materials.36,37

Results and Discussion

I. Synthesis and Reactivity. Synthesis and Characterization of \( \text{Cs}[[\text{Cp}^*\text{Rh}((\mu-\text{CN})_3\text{C}N)_{3}]_{4}[[\text{Cp}^*\text{Ru}]_3] \).

Reaction of 0.75 equiv of \([\text{Cp}^*\text{Ru}((\mu-\text{CN})_3\text{C}N)]_{3}\)PF\(_6\) with Et\(_4\)N[\text{Cp}^*\text{Rh}((\mu-\text{CN})_3\text{C}N)]_{3} \) and 0.25 equiv of CsOTf in MeCN solution produced \( \text{Cs}[\text{Cp}^*\text{Rh}((\mu-\text{CN})_3\text{C}N)]_{4}[[\text{Cp}^*\text{Ru}]_3] \). Golden yellow crystals of the product were obtained in excellent yield (eq 2).

The IR spectrum of \( \text{Cs}[\text{Cp}^*\text{Rh}((\mu-\text{CN})_3\text{C}N)]_{4}[[\text{Cp}^*\text{Ru}]_3] \) features \( \nu_{\text{CN}} \) bands at 2158, 2142, 2124, and 2121 cm\(^{-1}\), which are shifted to higher frequencies versus 2124 and 2114 cm\(^{-1}\) for free \((\text{Et}_4\text{N})[\text{Cp}^*\text{Rh}((\mu-\text{CN})_3\text{C}N)]_{3}\). ESI-MS measurements confirmed the formula (m/z = 2107 amu). Signals were not detected for the corresponding box \( \text{Cs}[\text{Cp}^*\text{Rh}((\mu-\text{CN})_3\text{C}N)]_{4}[[\text{Cp}^*\text{Ru}]_4]^+ \). Purified samples of \( \text{Cs}[\text{Cp}^*\text{Rh}((\mu-\text{CN})_3\text{C}N)]_{4}[[\text{Cp}^*\text{Ru}]_4]^+ \) proved unreactive toward additional \([\text{Cp}^*\text{Ru}((\mu-\text{CN})_3\text{C}N)]_{3}\)^\(^+\). Consequently, the stoichiometry of the reaction in eq 2 is not as critical as the synthesis of \( \text{Cs}[\text{Cp}^*\text{Co}((\mu-\text{CN})_3\text{C}N)]_{4}[[\text{Cp}^*\text{Ru}]_3] \).

Attempted syntheses of the empty (or voided) anionic bowl \( \{[\text{Cp}^*\text{Rh}((\mu-\text{CN})_3\text{C}N)]_{3}[[\text{Cp}^*\text{Ru}]_4] \) were unsuccessful. Reaction of 0.75 equiv of \([\text{Cp}^*\text{Ru}((\mu-\text{CN})_3\text{C}N)]_{3}\)PF\(_6\) with \((\text{Et}_4\text{N})[\text{Cp}^*\text{Rh}((\mu-\text{CN})_3\text{C}N)]_{3} \) resulted in insoluble solids. Such negative results, which are reminiscent of the untemplated reactions of \([\text{Cp}^*\text{Ru}((\mu-\text{CN})_3\text{C}N)]_{3}\)^\(^+\) and \([\text{Cp}^*\text{Co}((\mu-\text{CN})_3\text{C}N)]_{3}\)^\(^-\), underscore the important role of the Cs\(^+\) template.

ESI-MS Studies on Cage Assembly. In contrast to \( \text{Cs}[\text{Cp}^*\text{Co}((\mu-\text{CN})_3\text{C}N)]_{4}[[\text{Cp}^*\text{Ru}]_3] \), the all-Cp\(^*\) cage \( \text{Cs}[\text{Cp}^*\text{Rh}((\mu-\text{CN})_3\text{C}N)]_{4}[[\text{Cp}^*\text{Ru}]_3] \) exhibits good solubility in MeCN despite the fact that it is charge-neutral. This property enabled us to monitor the cage-forming process by ESI-MS measurements on homogeneous MeCN solutions. Analysis of the crude reaction mixture by ESI-MS was hindered by the presence of \((\text{Et}_4\text{N})[\text{Cp}^*\text{Rh}((\mu-\text{CN})_3\text{C}N)]_{3}\), which dominates the ion current. ESI-MS analysis of reaction mixtures revealed no anionic cage intermediates in the cage formation process — only PF\(_6\)^\(^-\) was detected.
observed. Under normal synthesis conditions, the formation of CsR₁₃Ru₁₃ requires 24 h, and, during this time, three intermediates were observed, Cs₃Ru₄₂⁺ (1239 amu), Rh₂Ru₃⁺ (1342 amu), Cs₃Ru₄₁⁺ (1791 amu), as well as the product [Cs₃Rh₂Ru₃] (2107amu). The first product to appear is Rh₃Ru₁⁺ (Figure 3). Over the course of hours, this intermediate is consumed concomitant with the appearance of both Cs₃Rh₂Ru₃⁺ and Cs₃Rh₂Ru₃⁺, as well as the final product. Monitoring the reaction revealed that the amount of final product increased concomitant with the decrease in the proposed intermediates, suggesting they are true intermediates and not a side product; however, the reaction revealed that the amount of final product increased concomitant with the decrease in the proposed intermediates, suggesting they are true intermediates and not a side product. Monitoring the course of hours, this intermediate is consumed concomitant with the appearance of both Cs₃Rh₂Ru₃⁺ and Cs₃Rh₂Ru₃⁺, as well as the final product. Monitoring the reaction revealed that the amount of final product increased concomitant with the decrease in the proposed intermediates, suggesting they are true intermediates and not a side product.

The IR spectrum of NH₄PF₆ indicated that the reaction resulted in a signal at δ 42 which is assigned as the isomer with a Cs(CN)₁₁ site, that is, the isomer that crystallizes. The CR₁₃Ru₃ is surrounded by only 10 CN ligands, the 133Cs signal occurs at δ 91. Key interpolations come from measurements on Cs₃Co₄Ru₃, which consists of two isomers, one of which has 11 CN ligands interacting with Cs⁺ and the other with 10 (vide infra). The dominant signal at δ 42 is assigned as the isomer with a Cs(CN)₁₁ site, that is, the isomer that crystallizes (allowing us to assign the 1H NMR signals to particular isomers). The minor signal (δ 89) is assigned to the isomer with a Cs(CN)₁₀ site, as for Cs₃Rh₂Ru₃. The 133Cs MAS NMR spectrum for a solid sample of Cs₃Rh₂Ru₃ was inconclusive, showing one broad peak within the range of both isomers (δ 63).

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\text{CsNMR Measurements.} \quad \text{133Cs NMR spectroscopy provided a useful tool for characterizing these Cs-containing cage compounds. Not only do the spectra allow one to assay the purity of cage samples, the chemical shift was found to correlate with the number of } \eta²-\text{CN ligands surrounding the Cs}^+ \text{ ion (Figure 4). Cs₃Co₄Ru₃}^+ \text{ with all 12 cyanides interacting with Cs}^+ \text{ resulted in a signal at } \delta 1 \text{ versus } \delta 34 \text{ for CsOTf, which we attribute to maximal shielding relative to the other cases. In Cs₃Rh₂Ru₃, where Cs}^+ \text{ is surrounded by only 10 CN ligands, the } 133\text{Cs signal occurs at } \delta 91. \text{ Key interpolations come from measurements on Cs₃Co₄Ru₃, which consists of two isomers, one of which has 11 CN ligands interacting with Cs}^+ \text{ and the other with 10 (vide infra). The dominant signal at } \delta 42 \text{ is assigned as the isomer with a Cs(CN)₁₁ site, that is, the isomer that crystallizes (allowing us to assign the } 1\text{H NMR signals to particular isomers). The minor signal (} \delta 89 \text{) is assigned to the isomer with a Cs(CN)₁₀ site, as for Cs₃Rh₂Ru₃. The } 133\text{Cs MAS NMR spectrum for a solid sample of Cs₃Rh₂Ru₃ was inconclusive, showing one broad peak within the range of both isomers (} \delta 63).}
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\text{[NH₄}[(\text{Cp*Rh(CN)})_{3}]_4[(\text{Cp*Ru})_{3}]]\]. \quad \text{The fact that the voided cage } [\text{Rh₃Ru₁}^- \text{] could not be synthesized indicates that complexation to cations is important for cage stability, as well as cage formation (see above). On the basis of our inability to synthesize } \text{K₃Rh₃Ru₃}, \text{ we concluded that K}^+ (r_{ionic} = 1.52 \text{ Å}) \text{ is too small. In contrast, NH₄}^+ (r_{ionic} = 1.75 \text{ Å}), \text{ which is only 0.06 Å smaller than Cs}^+, \text{ does template the formation of a defect box. The addition of 0.75 equiv of } \text{[Cp*Ru(NCMe)₃]}^+ \text{ to a McCN solution of Et₃N[} \text{Cp*Rh(CN)₃}]^- \text{ in the presence of 0.25 equiv of NH}_4\text{PF}_6 \text{ efficiently produced NH}_4\text{[CpCo(CN)₃]}^-\text{[Cp*Ru]}_4\text{ (NH}_4\text{[Rh₃Ru₃], eq 2). ESI-MS measurements confirmed the formula, with } M^+ + m/z = 1992 \text{ amu. With regards to the less hindered cages, we have been unable to synthesize M₃C₄O₄Ru₃ \text{ for any } M \text{ other than Cs.}}
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The IR spectrum of NH₄[Rh₃Ru₃] in the νNH region indicated...
that the cation is bound in an unsymmetrical environment. Peaks were observed at 3196, 3246, and 3270 (sh) cm$^{-1}$. In contrast, the IR spectrum of $\text{NH}_4^+$ shows only one peak at 3250 cm$^{-1}$ assigned to the $T_2$ mode reflecting a symmetrical environment (Figure 5). In $\text{NH}_4 \text{Rh}_4 \text{Ru}_3$, the $T_2$ mode has split into $E$ and $A_1$ modes, while the $A_1$, previously only Raman-active, becomes IR-active due to the decreased site symmetry. This low site symmetry arises not only from the overall cage structure, but more specifically from the unique N–H...NC interaction between the endo CN and one of four NH bonds (vide infra). Typical strong X–HNNH$_3^+$ hydrogen bonds exhibit two energetically distinct v$_{N\cdots H}$ bands. Isolated N–H units exhibit v$_{N\cdots H} \approx 3400$–3260 cm$^{-1}$, whereas for N–H...X-containing species v$_{N\cdots H} \approx 2975$–3110 cm$^{-1}$. For $\text{NH}_4 \text{Rh}_4 \text{Ru}_3$, $\Delta v_{\text{NH}} = 50$ cm$^{-1}$, which indicates a weak interaction between NH$_4^+$ and the π-bond of CN. The $T_2$ bending mode of NH$_4^+$ is obscured by the v$_{C\cdots H}$ bands for the facially capping Cp and Cp* ligands at 1600–1200 cm$^{-1}$.

Figure 4. Plot of $^{133}\text{Cs}$ NMR chemical shift vs number of π-CN$^-$ ligands interacting with the Cs$^+$. Data: $\text{CsC}_4\text{Ru}_4$ (δ 1), two isomers of $\text{CsC}_4\text{Co}_4$ (δ 89 for minor isomer, 42 for major isomer), $\text{CsC}_3\text{Rh}_3$ (δ 91), and $\text{CsC}_7\{[\text{Cp}^*\text{Rh}($CN$)_3]$[\text{Mo}($CO$)$_3$]$\}_3^{1-}$ (−δ 3).

Figure 5. IR spectra (KBr pellets) in the v$_{\text{NH}}$ region for $\text{Co}_4\text{Ru}_4$ (A) as a blank, $\text{NH}_4\text{Co}_4\text{Ru}_4^+$ (B),$^{29}$ and $\text{NH}_4\text{Rh}_4\text{Ru}_3$ (C).

Figure 6. 500 MHz $^1\text{H}$ NMR spectrum of $\text{NH}_4\text{Rh}_4\text{Ru}_3$ (THF solution). The 1:1:2 Cp*Rh and 2:1 Cp*Ru patterns are consistent with one $C_s$ isomer.

As for $\text{CsC}_3\text{Rh}_3$, $\text{NH}_4\text{C}_4\text{Rh}_4\text{Ru}_3$ exists as one isomer in MeCN solution as shown by $^1\text{H}$ NMR spectroscopy (Figure 6). A broad multiplet is observed at δ 5.40 for the NH$_4^+$ signal. The $^1\text{H}$ NMR spectrum of $^{15}\text{NH}_4\text{C}_4\text{Rh}_4\text{Ru}_3$ exhibits a doublet at δ 5.40, demonstrating that the cation is tumbling fast on the NMR time scale inside of the cage (Figure 7). In MeCN solutions, $\text{NH}_4\text{C}_4\text{Rh}_4\text{Ru}_3$ undergoes rapid exchange H–D exchange with D$_2$O, demonstrating that the ammonium ion is

highly accessible to the solution. Similar experiments show that NH₄CoRu₄⁺ is unreactive toward H–D exchange under these conditions, reflecting the chemical shielding afforded by the completed box. Addition of CsOTf to a MeCN solution of NH₄Rh₂Ru₃ quantitatively affords Cs⁺Rh₂Ru₃ within 20 min.

Affinity of NH₄⁺ for Cs⁺. The affinity of NH₄⁺ for Cs⁺ was qualitatively examined in a competition experiment using calix[4]arene-bis(benzocrown-6) (BC6B, Figure 8), a representative member for high-affinity (K = 10⁶) cesium-selective calix[4]arene-crown-6 ligands. 40-44 A MeCN solution of [Cs(BC6B)]⁺ (133 Cs NMR: δ 76 MHz) was treated with 1 equiv of NH₄⁺, resulting within the time required for NMR analysis in quantitative conversion to Cs⁺Rh₂Ru₃ (δ 88, see eq 3, Figure 8). The Cs⁺/K⁺ and Cs⁺/Na⁺ selectivities have not been determined, but our inability to synthesize K⁺Rh₂Ru₃ suggests these selectivity values are quite high.

II. Structural Analyses. Isomerism in the Defect Boxes.

Defect boxes could, in principle, adopt four isomeric structures, depending on the relative orientation of the three CN⁻ ligands (see Figure 2). ¹H NMR measurements show that Cs⁺Rh₂Ru₃ exists as one of the two C₄ isomers, as demonstrated by the observation of five Cp⁺ signals in a ratio 1:1:2:2:1. In contrast, ¹H NMR spectra for solutions of Cs⁺Co₄Ru₃ revealed the presence of two unsymmetrical (C₇) isomers, each of which show characteristic subspectra, which can now be assigned on the basis of the ¹H NMR data (see above). ¹H NMR experiments (−60 to 60 °C) did not reveal any line-broadening. If coalescence temperature is conservatively estimated to be 20 °C above 60 °C, this would imply that the rate constant for exo–endo isomerization would have an upper limit of 50 s⁻¹. In solution, the cage Cs⁺Co₄Ru₃ is rapidly capped (box-completion reaction) with various electrophiles, 35 such as Na⁺ and Cp⁺Rh⁺, and this process is complete within minutes at room temperature (the time required to prepare sample for NMR analysis). Assuming that the rate of complexation is determined by the unimolecular rate of exo–endo isomerization, the speed of the box completion reaction indicates that the speed of the exo–endo isomerization is 0.05 s⁻¹.

The dynamic structure of Cs⁺Co₄Ru₃ is evident from the ¹H NMR spectrum of a solution freshly prepared from single crystals of Cs⁺Co₄Ru₃ revealed the presence of the same two C₃ isomers in the equilibrium ratio. The rapid isomerization of the cage is related to the ease with which it undergoes box-completion reactions.

The dynamic structure of Cs⁺Co₄Ru₃ is evident from the fact that we only isolate one isomer when we can observe two in solution. Furthermore, the facility with which this cage undergoes box-completion reactions implies that all three CN⁻ ligands can transiently, at least, adopt the all-endo geometry, thereby presenting incoming electrophiles with a tridentate ligand. These assumptions and facts can be accommodated by an atom labeling scheme. Thermal ellipsoids are drawn at the 50% level.

**Scheme 3**

![Scheme 3](image)

**Figure 9.** Molecular structure of Cs⁺Co₄Ru₃ showing the atom labeling scheme. Thermal ellipsoids are drawn at the 50% level.

Table 1. Selected Bond Distances (Å) for the Cations in Cs\textsubscript{5}Co\textsubscript{4}Ru\textsubscript{3} and Cs\textsubscript{5}Ru\textsubscript{4}Ru\textsubscript{3}

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The crystallographic analysis of Cs\textsubscript{5}Co\textsubscript{4}Ru\textsubscript{3} and Cs\textsubscript{5}Ru\textsubscript{4}Ru\textsubscript{3} indicated the presence of both C\textsubscript{1} isomers in solution, only one isomer crystallizing. Three types of C\textsubscript{1}Co\textsubscript{3}(CN)\textsubscript{3} centers are observed in a 1:1:2 ratio as well as two types of C\textsubscript{1}Ru centers. Nine of the twelve CN ligands form Co–CN–Ru bridges; the remaining three CN groups are terminal with two endo and one exo. The endo CN\textsubscript{r} groups interact with Cs\textsuperscript{+}, with average N\textsubscript{r}–Cs\textsubscript{r} and Cs\textsubscript{r}–Cs\textsubscript{r} distances of 3.56 and 3.67 Å, respectively. The nine μ-CN ligands are slightly less strongly bound to Cs\textsuperscript{+} with Cs–N distances (3.61 Å) again being shorter than the Cs–Cs distances (3.66 Å), although it appears that the CN\textsubscript{r} is slightly more strongly bound to Cs than is μ-CN. Typical Cs–μ-CN distances range from 3.113 to 3.678 Å with an average distance of 3.28 ± 0.16 Å. With respect to distortions of the overall M\textsubscript{4}(CN)\textsubscript{12} framework, the CoRu\textsubscript{2}(CN)\textsubscript{12} face bearing the exo-CN is slightly bowed inward (Figure 10). The extent of this distortion is indicated by the Co–Co distances within the

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(48) Cambridge Structural Database version 5.24, search of Cs–NC distances (16 examples).

Figure 10. The view is approximately parallel to two of the Co\textsubscript{3}Ru\textsubscript{2}(CN)\textsubscript{4} faces so as to show the outward or inward bending of the terminal M(CN)\textsubscript{3} units (M = Co, Rh). (A) Cs\textsubscript{5}Co\textsubscript{4}Ru\textsubscript{3}; (B) Cs\textsubscript{5}Ru\textsubscript{4}Ru\textsubscript{3}; (C) NH\textsubscript{4}Rh\textsubscript{3}Ru\textsubscript{4}.

Figure 11. Molecular structure of Cs\textsubscript{5}[Cp\textsuperscript{+}Rh(CN)\textsubscript{3}][Cp\textsuperscript{-}Ru\textsubscript{3}] showing the atom labeling scheme. Thermal ellipsoids are drawn at the 50% level.
while the unique $r_{\text{Rh-Rh}}$ is 0.46 Å (6.1%) longer than $(r_{\text{Rh-Rh}})_{\text{avg}}$. The distortion is also evident in the comparison of Rh···N distances. The NH$_4^+$ is unsymmetrically situated with respect to the four Rh atoms: N···Rh$_{\text{min}}$(CN)$_{\text{exo}}$ = 4.78 Å versus N···Rh$_{\text{min}}$(CN)$_{\text{endo}}$ = 4.38 Å, while the “nonrim” Rh has a N···Rh = 4.14 Å. Thus, the cation in NH$_4$Rh$_4$Ru$_3$ is more deeply embedded into the M$_4$(µ-CN)$_6$ cavity (Figure 13).

The four protons of NH$_4^+$ were located with an average N···H distance of 0.80 Å. The H$_2$N···H···N$_2$C distance is 2.95 Å, and the H$_2$N···H···N$_2$C distance is 2.14 Å (Figure 12), which is typical of H$_2$N···H···N hydrogen bonds.\(^{(50)}\) In contrast to Cs$_2$Rh$_4$Ru$_3$, all three of the M$_4$(CN)$_4$ faces in [Cp*Rh(CN)$_3$]$_4$[Cp*Rh(CN)$_3$]$_2$PF$_6$ are significantly bowed outward, apparently due to repulsions between Cp*Rh(CN)$_3$ centers. The Ru$_2$Rh$_2$(CN)$_6$endo face of Cs$_2$Rh$_4$Ru$_3$ is bowed inward toward Cs$^+$, arising from a short Cs···N distance of 3.25 Å (vs van der Waals radii for Cs···N, ~3.3 Å).

**Summary**

In this work, the structural chemistry of cation-containing defect cyanometalates was elucidated. The less bulky derivative Cs$_2$Co$_4$Ru$_3$ is an interesting building block for new boxlike and double box cage structures.\(^{(35)}\) The defect box also represents a promising motif for cation receptors because, unlike the corresponding completed boxes,\(^{(28)}\) these cations are more solvent-accessible and hence more kinetically labile.

Specific conclusions follow:

1. Whereas the first example of a defect box, [Cp*Rh(CN)$_3$]$_4$-[Cp*Rh]$_2$$^2+$, featured all exo-CN$_t$ ligands,\(^{(32)}\) the cation-containing defect boxes have one or two endo-CN$_t$ ligands. These endo-CN$_t$ ligands interact ionically with the guest cation.

2. The steric profile of the coligands (Cp$^*$ vs Cp) allows one to enforce the defect box motif without box formation. Whereas Cs$_2$Co$_4$Ru$_3$ is reactive toward metal electrophiles to give boxlike cages, the all-Cp$^*$ species Cs$_2$Rh$_4$Ru$_3$ show no affinity for “capping” metal electrophiles.

3. $^{133}$Cs NMR spectroscopy provides a convenient indicator of the Cs$^+$ coordination environment in cyanometalates.

4. The successful synthesis of NH$_4$Rh$_4$Ru$_3$ defines the dimensions critical for cage formation: NH$_4^+$ ($r_{\text{ionic}}$ = 1.75 Å) being intermediate in size between K$^+$ ($r_{\text{ionic}}$ = 1.52 Å), which does not react, and Cs$^+$ ($r_{\text{ionic}}$ = 1.81 Å). NH$_4$Rh$_4$Ru$_3$ binds Cs$^+$ tightly and, in contrast to NH$_4$Co$_4$Ru$_3$,\(^{(28)}\) ion-exchanges rapidly.

5. Structural analyses of the two defect boxes, Cs$_2$Co$_4$Ru$_3$, NH$_4$Rh$_4$Ru$_3$, and Cs$_2$Rh$_4$Ru$_3$, reveal that cage distortion increases as the cationic guest becomes smaller or the Cp groups become larger.

6. A competition experiment between a well-known cesium selective complexant demonstrates that NH$_4$Rh$_4$Ru$_3$ has a high affinity for cesium.

**Materials and Methods**

**General.** Standard Schlenk techniques were employed in all syntheses. Et$_4$N[Cp*Rh(CN)$_3$],\(^{(16)}\) [Cp*Ru(NCMe)$_3$]PF$_6$,\(^{(34)}\) [Cs][CpCo(CN)$_3$]$_4$[Cp*Ru$_3$],\(^{(15)}\) CsOTf, and NH$_4$PF$_6$ were either prepared according to literature methods or purchased from Aldrich. Because the purity of [Cp*Ru(NCMe)$_3$]PF$_6$ proved critical, the as-synthesized salt was further recrystallized from CH$_2$Cl$_2$-Et$_2$O to give a bright yellow microcrystalline solid. Elemental analyses were conducted by the School of Chemical Sciences Microanalytical Laboratory. $^{1}$C and $^1$H NMR spectra were acquired on Varian Unity 400 and 500 NMR spectrometers. Infrared spectra were acquired on a Mattson Infinity Gold FTIR spectrometer using CaF$_2$ solution cells or with KBr pellets. Electrospray ionization-mass spectra (ESI-MS) and MS/MS measurements were acquired using a Micromass Quattro QHQ quadrupole–hexapole–quadrupole instrument.

Cs$_2$[Cp*Rh(CN)$_3$]$_4$[Cp*Ru$_3$] (Cs$_2$Rh$_4$Ru$_3$). A solution of 384 mg (0.762 mmol) of purified [Cp*Rh(NCMe)$_3$]PF$_6$ in 20 mL of MeCN was added dropwise to a solution of 72 mg (0.254 mmol) of CsOTf and 457 mg (1.017 mmol) of Et$_4$N[Cp*Rh(CN)$_3$] in 25 mL of MeCN.


After being stirred for 1 h, the solution was allowed to stand for 24 h before the solvent was removed in vacuo. The yellow solid was obtained by a solvent extraction process. Evaporation of the filtrate afforded a fine golden yellow powder. Yield: 610 mg (76%).

IR (MeCN, cm⁻¹): 3297 (m), 3020 (m), 1644 (s), 1608 (s), 1460 (m), 1380 (m), 1320 (m), 1305 (s), 1260 (s), 1205 (s), 1099 (s), 991 (s), 795 (s), 736 (m), 683 (s).

**N.** 7.53. Crystals of Cs₄N₁₂Rh₄Ru₃: C, 46.78; H, 5.02; N, 7.98. Found: C, 45.75; H, 5.20; N, 7.98.

**Crystallographic Data for Cs₄Co₄Ru₃, Cs₄Rh₄Ru₃, and NH₄Rh₄Ru₃**

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</table>

**133 Cs NMR Measurements.**

Conversion of NH₄Rh₄Ru₃ into Cs₄Rh₄Ru₃. A solution of 7 mg (0.025 mmol) of CsOTf in 3 mL of CD₃CN was added to a solution of 50 mg (0.255 mmol) of NH₄Rh₄Ru₃ in 3 mL of CD₃CN, which was immediately (25 min) monitored by 133Cs NMR, showing a single signal at δ 88. A similar experiment was performed by 1H NMR.

**Competition Experiment of BC6B versus NH₄[Rh₃(CN)₆]Cl·[Rh₄Ru₃].** A solution of 7 mg (0.026 mmol) of CsOTf and 24 mg (0.026 mmol) of calix[4]arene-bis(benzo crown-6) in 12 mL of CD₃CN was allowed to stand for 24 h. The solution was then monitored by 133Cs NMR, which revealed one signal at −17 ppm and no free cesium at 34 ppm. A solution of 52 mg (0.026 mmol) of NH₄Rh₄Ru₃ in 3 mL of CD₃CN was added to the initial solution of CsOTf and calix[4]arene-bis(benzo crown-6). The solution was immediately monitored (approximately 1 h) by 133Cs NMR, which revealed one signal at δ 88. A similar experiment was run in THF solvent, which yielded a similar result. The calix[4]arene-bis(benzo crown-6) ligand was obtained from ACROS.

**Crystallography.** Crystals were mounted on thin glass fibers using Paratone-N oil (Exxon) before being transferred to a Siemens Platform/CCD automated diffractometer for data collection. Data processing was performed with SAINT PLUS version 6.22. Structures were solved using direct methods and refined using full matrix least squares on F² using the program Bruker SHELXTL version 6.10. Hydrogen atoms were fixed in idealized positions with thermal parameters 1.5 times those of the attached carbon atoms. The data were corrected for absorption on the basis of Ψ-scans. Specific details for each crystal are given in Table 2. Full crystallographic details have been deposited with the Cambridge Crystallographic Data Center.

**Acknowledgment.** This research was supported by the Department of Energy. We thank Scott Wilson and Teresa Prussak-Wieckowska for assistance with the X-ray crystallography.

**Supporting Information Available:** Crystallographic data (CIF format) including experimental details and complete tables of bond distances and angles, atomic coordinates, and anisotropic displacement parameters (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.