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Self-Assembly of L-Cysteinato Trinuclear Cations into Metallosupramolecular Architectures Controlled by Protons, Metal Ions, and Chirality

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During the past decade, metallosupramolecular architectures such as coordination rings, cages, and tubes have attracted considerable attention because of their structural characteristics and potential applications, which include the recognition and inclusion of small molecules and ions.[1,2] In many cases, metallosupramolecules have been synthesized by means of metal-assisted assembly of organic molecules with several metal-binding sites,[1] which leads to the formation of thermodynamically stable assembled structures. On the other hand, examples of metallosupramolecular species created by the self-assembly of one kind of building block are relatively rare,[2] although this method is advantageous for the reversible control of assembled and disassembled structures by external factors. One way to achieve this is to design coordination compounds with vacant acceptor sites at a metal center, together with free donor groups that come to bind to another metal center in response to external factors. A mercury(II) coordination compound with free carboxyl groups is a potential candidate for creating a reversible self-assembly system because 1) a mercury(II) ion can adopt several coordination geometries, such as two-coordinated linear, three-coordinated T-shape, and four coordinated tetrahedron; 2) a mercury(II) ion has a good affinity not only for soft sulfur donors but also for hard oxygen donors;[3] and 3) the donating ability of carboxyl groups toward a metal center can be controlled by changing the pH of the solution. Thus, as part of our research project on the rational construction of chiral metallosupramolecular architectures based on thiolato metal complexes,[4] we newly prepared three diastereomers ($\Delta_L\Delta_L$, $\Lambda_L\Lambda_L$, and $\Delta_L\Lambda_L$) of a chiral $Co^{III}Hg^{II}Co^{III}$ trinuclear complex with two pendent COOH groups, $[Hg\{Co(\text{L-Hcys})(en)_2\}_2](ClO_4)_6$ (**1**; $\text{L-}H_2cys$ = L-cysteine), and investigated the possibility of their self-assembly induced by the deprotonation of the COOH groups in water. As a result, we found that the $\Lambda_L\Lambda_L$ isomer of **1** is self-assembled into a unique $(\Lambda_L\Lambda_L\text{-}Co^{III}Hg^{II}Co^{III})_n$ metallohelix structure (**3**), whereas its $\Delta_L\Delta_L$ isomer was converted into a $(\Delta_L\Delta_L\text{-}Co^{III}Hg^{II}Co^{III})_2$ dimeric structure (**2**). In addition, the $\Lambda_L\Lambda_L$ isomer of **1** was found to be assembled into a $(\Lambda_L\Lambda_L\text{-}Co^{III}Hg^{II}Co^{III})_6$ metallocage structure ($\mathbf{4_{Cr}}$) in the presence of Cr^{3+}, encapsulating an aqua chromium(III) ion in its cavity. To our surprise, this $(\Lambda_L\Lambda_L\text{-}Co^{III}Hg^{II}Co^{III})_6$ metallocage compound was exclusively isolated when the *meso*-like $\Delta_L\Lambda_L$ isomer of **1** was treated under the same conditions. Herein we report on these remarkable results, together with the incorporation of another aqua metal ion in the metallocage structure (Scheme 1).

Compound $\Delta_L\Delta_L$-**1** was isolated as dark-red needle crystals from the 2:1 reaction of $\Delta_L\text{-}[Co(\text{L-Hcys})(en)_2](ClO_4)_2$[5] and $Hg(ClO_4)_2$ in aqueous $HClO_4$. The IR spectrum of $\Delta_L\Delta_L$-**1** showed a relatively sharp C=O stretching band at 1725 cm^{-1},[6] which suggests the presence of COOH groups.[7] Single-crystal X-ray analysis demonstrated that $\Delta_L\Delta_L$-**1** is an expected S-bridged $Co^{III}Hg^{II}Co^{III}$ trinuclear complex with two pendent COOH groups, $\Delta_L\Delta_L\text{-}[Hg\{Co(\text{L-Hcys})(en)_2\}_2](ClO_4)_6$ (Figure 1a). In $\Delta_L\Delta_L$-**1**, the two thiolato groups from two $\Delta_L\text{-}[Co(\text{L-Hcys})(en)_2]^{2+}$ units coordinate to the central Hg^{II} atom in a roughly linear geometry (Hg–S = 2.381(2) Å; S-Hg-S = 174.0(1)°), whereas the COOH groups that adopt an equatorial orientation do not participate in the coordination. When $\Delta_L\Delta_L$-**1** was dissolved in water, followed by the addition of $NaClO_4$, dark-red crystals with a

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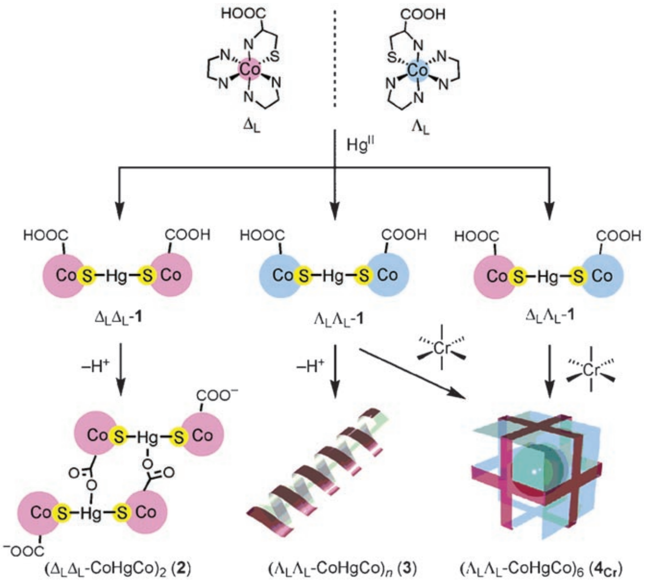

Scheme 1. Synthetic routes for $\mathrm{Co^{III}Hg^{II}Co^{III}}$ trinuclear ($\Delta_L\Delta_L$-, $\Lambda_L\Lambda_L$-, and $\Delta_L\Lambda_L$-**1**), ($\Delta_L\Delta_L$-$\mathrm{Co^{III}Hg^{II}Co^{III}}$)$_2$ dimeric (**2**), ($\Lambda_L\Lambda_L$-$\mathrm{Co^{III}Hg^{II}Co^{III}}$)$_n$ helix (**3**), and ($\Lambda_L\Lambda_L$-$\mathrm{Co^{III}Hg^{II}Co^{III}}$)$_6$ cage (**4$_{Cr}$**) complexes.

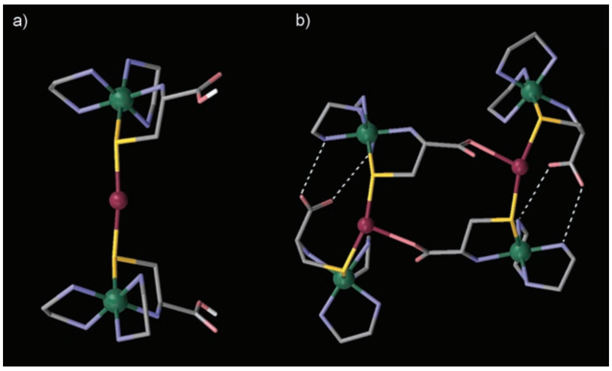

Figure 1. Perspective views of the complex cations of a) $\Delta_L\Delta_L$-**1** and b) **2**. Co = green, Hg = purple, C = gray, N = blue, O = red, and S = yellow.

blocklike shape (**2**) were produced. The presence of deprotonated COO$^-$ groups in **2** was suggested by its IR spectrum, which gives a C=O stretching band at 1620 cm^{-1}.[6] X-ray analysis revealed that **2** has a ($\Delta_L\Delta_L$-$\mathrm{Co^{III}Hg^{II}Co^{III}}$)$_2$ dimeric structure composed of two $\Delta_L\Delta_L$-[Hg{Co(L-cys)(en)$_2$}$_2$]$^{4+}$ trinuclear units with deprotonated COO$^-$ groups (Figure 1b). In **2**, one of the two COO$^-$ groups of each $\mathrm{Co^{III}Hg^{II}Co^{III}}$ trinuclear unit adopts an equatorial orientation and binds to the Hg^{II} atom of another trinuclear unit, such that each Hg^{II} center is situated in a T-shaped geometry with an $\mathrm{O_1S_2}$ donor set (average Hg–S = 2.412(2), Hg–O = 2.496(4) Å; S-Hg-S = 164.28(5), S-Hg-O = 97.7(1)°). The other COO$^-$ group of each $\mathrm{Co^{III}Hg^{II}Co^{III}}$ trinuclear unit has an axial orientation and is hydrogen bonded with two en amine groups of the adjacent Δ_L-[Co(L-cys)(en)$_2$]$^+$ mononuclear unit. This hydrogen-bonding interaction appears to prevent the pendent COO$^-$ group from binding to another $\mathrm{Co^{III}Hg^{II}Co^{III}}$ trinuclear unit to construct a higher assembled structure.

The $\Lambda_L\Lambda_L$ isomer of **1** was also prepared by a similar 2:1 reaction of Λ_L-[Co(L-Hcys)(en)$_2$](ClO$_4$)$_2$ with Hg(ClO$_4$)$_2$, and its deprotonated species (**3**) was isolated as dark-red needle crystals by dissolving $\Lambda_L\Lambda_L$-**1** in water, followed by the addition of NaClO$_4$. The structures of $\Lambda_L\Lambda_L$-**1** with COOH groups and **3** with COO$^-$ groups were established by single-crystal X-ray analyses, along with their IR spectra, which show C=O stretching bands at 1721 and 1620 cm^{-1}, respectively. As shown in Figure 2a, $\Lambda_L\Lambda_L$-**1** has an S-bridged $\mathrm{Co^{III}Hg^{II}Co^{III}}$ trinuclear structure in $\Lambda_L\Lambda_L$-[Hg{Co(L-Hcys)(en)$_2$}$_2$]$^{6+}$, in which two Λ_L-[Co(L-Hcys)(en)$_2$]$^{2+}$ mononuclear units with equatorially orientated COOH groups are linked by a linear Hg^{II} atom through thiolato groups (average Hg–S = 2.371(2) Å; S-Hg-S = 176.11(5)°). This trinuclear structure in $\Lambda_L\Lambda_L$-**1** corresponds well with that in $\Delta_L\Delta_L$-**1**, apart from the chirality about two Co^{III} centers. On the other hand, the structure of **3** derived from $\Lambda_L\Lambda_L$-**1** is markedly different from the dimeric structure in **2** derived from

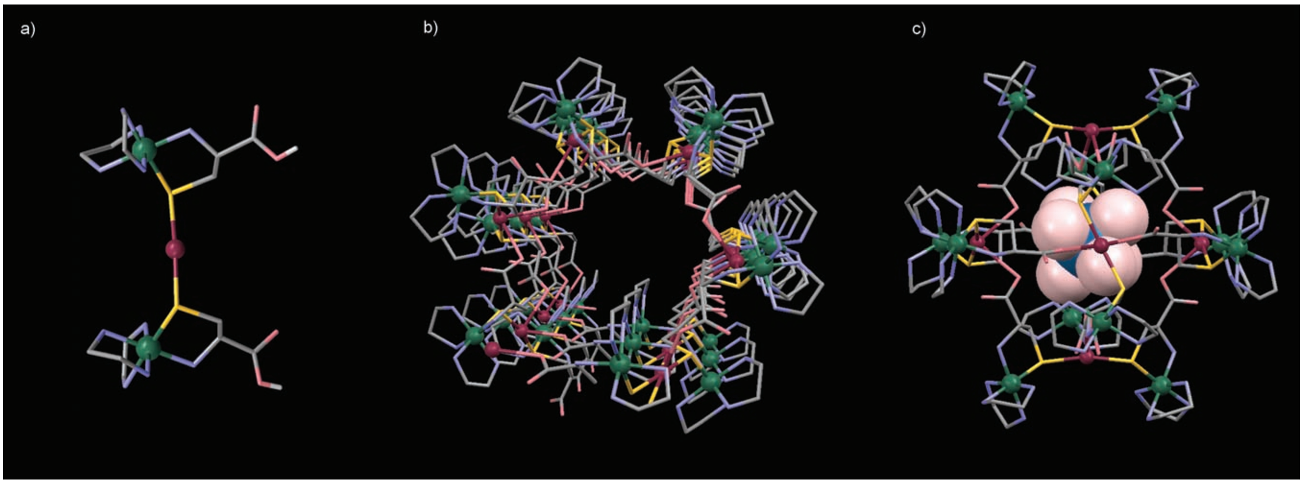

Figure 2. Perspective views of the complex cations of a) $\Lambda_L\Lambda_L$-**1**, b) **3**, and c) **4$_{Cr}$**. Co = green, Hg = purple, Cr = dark blue, C = gray, N = blue, O = red, S = yellow.

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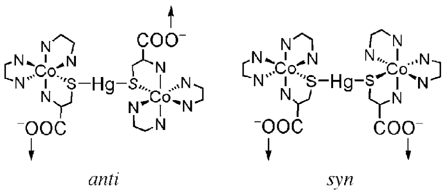
$\Delta_L\Delta_L$-**1**. That is, in **3** the two COO^- groups of each $Co^{III}Hg^{II}Co^{III}$ trinuclear unit adopt an axial orientation and bind to two Hg^{II} atoms from two adjacent $Co^{III}Hg^{II}Co^{III}$ units in an *anti* fashion (Scheme 2).[8] This binding mode leads to the construction of a $(\Lambda_L\Lambda_L\text{-}Co^{III}Hg^{II}Co^{III})_n$ tubular helix structure in $\{\Lambda_L\Lambda_L\text{-}[Hg\{Co(\textsc{l}\text{-cys})(en)_2\}_2]^{4+}\}_n$ with a diameter of around 20 Å, as illustrated in Figure 2b. The helix turn of **3** consists of the six $Co^{III}Hg^{II}Co^{III}$ trinuclear units with a pitch of 16.6 Å, and a large tubular channel is formed insides the helix. In crystal **3**, the tubular helices uniformly adopt a left-handedness and are arranged parallel to one another along the *a* axis.[6] The Hg^{II} atoms in **3** are each situated in a seesaw-type geometry bound by two thiolato and two carboxylato donors (average Hg–S = 2.410(6), Hg–O = 2.541(7) Å; S-Hg-S = 171.4(2), O-Hg-O = 74.8(3)°).



anti *syn*

Scheme 2. a) *Syn* and b) *anti* configurational orientations of carboxyl groups in the $Co^{III}Hg^{II}Co^{III}$ unit.

When $Cr(ClO_4)_3$ was added to an aqueous solution of $\Lambda_L\Lambda_L$-**1**, instead of $NaClO_4$, dark-red block crystals ($\mathbf{4_{Cr}}$) that contain Co, Hg, and Cr atoms were produced. The IR spectrum of $\mathbf{4_{Cr}}$ was similar to that of **3**, giving a C=O stretching band at 1624 cm^{-1} due to deprotonated COO^- groups. X-ray analysis revealed that the entire complex cation of $\mathbf{4_{Cr}}$ consists of six $\Lambda_L\Lambda_L\text{-}[Hg\{Co(\textsc{l}\text{-cys})(en)_2\}_2]^{4+}$ units with deprotonated COO^- groups (Figure 2c). Like in **3**, the two COO^- groups of each $Co^{III}Hg^{II}Co^{III}$ trinuclear unit in $\mathbf{4_{Cr}}$ bind to two Hg^{II} atoms from two adjacent $Co^{III}Hg^{II}Co^{III}$ units and each Hg^{II} atom has a seesaw-type geometry with an S_2O_2 donor set (average Hg–S = 2.340(1), Hg–O = 2.633(3) Å; S-Hg-S = 168.84(4), O-Hg-O = 82.21(9)°). However, the two COO^- groups of each $Co^{III}Hg^{II}Co^{III}$ unit are directed to an equatorial orientation and their binding mode toward two Hg^{II} atoms is *syn* (Scheme 2). As a result, each $Co^{III}Hg^{II}Co^{III}$ unit in $\mathbf{4_{Cr}}$ is connected to four $Co^{III}Hg^{II}Co^{III}$ units through two donating COO–Hg and two accepting Hg–OOC bonds to construct a discrete $(\Lambda_L\Lambda_L\text{-}Co^{III}Hg^{II}Co^{III})_6$ metallocage structure with the largest Co···Co separation of 15.9 Å. In $\mathbf{4_{Cr}}$, one octahedral $[Cr(H_2O)_6]^{3+}$ cation (average Cr–O = 1.971(4) Å) is encapsulated into a cavity of the cationic $(\Lambda_L\Lambda_L\text{-}Co^{III}Hg^{II}Co^{III})_6$ metallocage with a total formal charge of +24.[9] There exist multiple O–H···O hydrogen bonds between H_2O molecules of the $[Cr(H_2O)_6]^{3+}$ cation and COO^- groups of the surrounding $Co^{III}Hg^{II}Co^{III}$ units (average O···O = 2.613(6) Å), which might be responsible for the formation and stabilization of the metallocage structure in $\mathbf{4_{Cr}}$.[10] Here it should be noted that dark-red needle crystals of $\Lambda_L\Lambda_L$-**1** were regenerated on adding $HClO_4$ to an aqueous solution of **3** or $\mathbf{4_{Cr}}$. This result clearly indicates that the metallohelix structure in **3** and the metallocage structure in $\mathbf{4_{Cr}}$ are disassembled to the parental $\Lambda_L\Lambda_L$-**1** by changing the pH of the solution.

In contrast to the case for $\Lambda_L\Lambda_L$-**1**, the addition of $Cr(ClO_4)_3$ to an aqueous solution of $\Delta_L\Delta_L$-**1** resulted in the isolation of the $(\Delta_L\Delta_L\text{-}Co^{III}Hg^{II}Co^{III})_2$ dimeric compound **2**. Notably, the $(\Lambda_L\Lambda_L\text{-}Co^{III}Hg^{II}Co^{III})_6$ metallocage compound $\mathbf{4_{Cr}}$, which consists only of the Λ_L configurational $[Co(\textsc{l}\text{-cys})(en)_2]^+$ mononuclear units, was exclusively isolated from an aqueous solution of the *meso*-like $\Delta_L\Lambda_L$ isomer of **1**,[11] assisted by the addition of $Cr(ClO_4)_3$. The predominant existence of the deprotonated species of $\Delta_L\Delta_L$-**1** in the remaining solution was confirmed by the absorption and circular dichroism (CD) spectral measurements.[6] Thus, $\Delta_L\Lambda_L$-**1** is subject to disproportionation to give the $\Delta_L\Delta_L$ and $\Lambda_L\Lambda_L$ configurational $Co^{III}Hg^{II}Co^{III}$ units, and only the $\Lambda_L\Lambda_L$ units are self-assembled around a templating $[Cr(H_2O)_6]^{3+}$ cation to construct the thermodynamically stable metallocage structure in $\mathbf{4_{Cr}}$.

Compound $\mathbf{4_{Cr}}$ was also produced by the direct 2:1 reaction of $\Lambda_L\text{-}[Co(\textsc{l}\text{-cys})(en)_2](ClO_4)$ and $Hg(ClO_4)_2$ in water, followed by the addition of $Cr(ClO_4)_3$. When another metal perchlorate, $M(ClO_4)_{2\text{ or }3}$ (M = Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}), was added to the reaction solution, instead of $Cr(ClO_4)_3$, a series of $(Co^{III}Hg^{II}Co^{III})_6$ metallocage compounds encapsulating an aqua metal ion ($\mathbf{4_M}$) was produced.[12] On the other hand, the addition of $Ca(ClO_4)_2$ or $Cd(ClO_4)_2$ under the same conditions led to the isolation of **3** with a tubular metallohelix structure. It has been shown that the averaged $M\text{–}O_{water}$ distances in the first hydration shell for M = Cd^{II} (2.30 Å) and Ca^{II} (2.42 Å) are appreciably larger than those for M = Cr^{III} (1.97 Å), Fe^{III} (2.03 Å), Ni^{II} (2.06 Å), Zn^{II} (2.10 Å), Co^{II} (2.11 Å), Cu^{II} (equatorial = 1.97 Å, apical = 2.40 Å), and Mn^{II} (2.19 Å).[13] Thus, the presence of an aqua metal ion with an appropriate size is essential for the construction of the $(Co^{III}Hg^{II}Co^{III})_6$ metallocage structure. Note that the addition of a 1:1 mixture of a perchlorate salt of M1 = Fe^{III}, Ni^{II}, or Zn^{II} and a perchlorate salt of M2 = Cr^{III}, Cu^{II}, or Mn^{II} afforded $(Co^{III}Hg^{II}Co^{III})_6$ metallocage compounds that selectively encapsulate an aqua M1 ion. This result implies that an aqua metal ion with $M\text{–}O_{water}$ distances of approximately 2.05–2.10 Å is best fitted for the cavity of the $(Co^{III}Hg^{II}Co^{III})_6$ metallocage to act as an effective template.

In summary, we developed a remarkable self-assembly system based on the chiral $Co^{III}Hg^{II}Co^{III}$ trinuclear complex with two pendent L-cysteinato carboxyl groups. This is the first example that shows reversible self-assembly of a single kind of building units into two different metallosupramolecular architectures (metallohelix and metallocage), controlled by the solution pH, the presence/absence of an appropriate metal ion, and the chirality of an octahedral metal center. Not only their aesthetically appealing homochiral structures, but the selective uptake and encapsulation of a cationic aqua metal ion in the cationic $(Co^{III}Hg^{II}Co^{III})_6$ metallocage

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with a formal charge of +24 are noteworthy. The versatility of coordination geometry about a mercury(II) center in combination with the tunable binding ability and orientation of L-cysteinato carboxyl groups is a key to the self-assembly/disassembly of this system. Finally, the present results should provide valuable insight into the design and creation of self-assembly systems that reversibly afford functional metallosupramolecular species in response to external factors.

Experimental Section

Experimental details, together with spectroscopic data, are given in the Supporting Information.

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Keywords: cage compounds · helical structures · cysteine · mercury · supramolecular chemistry

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[8] Molecular model examinations reveal that each COO^- group in the $\Lambda_L\Lambda_L$-$\mathrm{Co^{III}Hg^{II}Co^{III}}$ trinuclear unit can not form intramolecular hydrogen bonds with amine groups because of the steric demand, unlike the case for the $\Delta_L\Delta_L$-$\mathrm{Co^{III}Hg^{II}Co^{III}}$ trinuclear unit.

[9] The X-band EPR spectrum of a solid sample of $\mathbf{4_{Cr}}$ at 77 K displayed a sharp signal centered at $g = 1.99$ (Figure S7). This spectral behavior corresponds well with that of $[\mathrm{Cr(H_2O)_6}]^{3+}$ in water ($g = 1.98$),[14] which indicates that the interactions among aqua $\mathrm{Cr^{III}}$ ions in solid $\mathbf{4_{Cr}}$ are fully blocked by the encapsulation in the diamagnetic $(\mathrm{Co^{III}Hg^{II}Co^{III}})_6$ metallocage and by the large separation (20.6–23.6 Å) between these metal ions.

[10] The CD spectrum of $\mathbf{4_{Cr}}$ in acetone, which is the same as that in the solid state, remained unchanged at least for 1 d, whereas its spectrum in water or in dimethyl sulfoxide quickly changed to the spectrum for the $\Lambda_L\Lambda_L$-$\mathrm{Co^{III}Hg^{II}Co^{III}}$ species within 30 min. These results suggest that the metallocage structure in $\mathbf{4_{Cr}}$ is retained in a non-coordinating solvent, but not in a coordinating solvent. Consistent with this, the ^{1}H NMR spectrum of $\mathbf{4_{Cr}}$ in [D$_6$]acetone showed very broad signals, whereas that in D_2O gave sharp signals that corresponds well with those for $\Delta_L\Lambda_L$-**1**.

[11] Compound $\Delta_L\Lambda_L$-**1** was prepared by the reaction of a 1:1 mixture of Δ_L- and Λ_L-$[\mathrm{Co(L\text{-}Hcys)(en)_2}](\mathrm{ClO_4})_2$ with $\mathrm{Hg(ClO_4)_2}$ in aqueous $HClO_4$, and its S-bridged $\mathrm{Co^{III}Hg^{II}Co^{III}}$ trinuclear structure, in which Δ_L- and Λ_L-$[\mathrm{Co(L\text{-}Hcys)(en)_2}]^{2+}$ mononuclear units are linked by a linear $\mathrm{Hg^{II}}$ atom (av. Hg–S = 2.386(5) Å, S-Hg-S = 173.2(2)°), was determined by single-crystal X-ray analysis.

[12] These compounds were characterized by X-ray fluorescence spectrometry, elemental analyses, solid state absorption, CD, and IR spectroscopies, along with preliminary X-ray analyses for $\mathbf{4_{Mn}}$, $\mathbf{4_{Fe}}$, $\mathbf{4_{Co}}$, $\mathbf{4_{Ni}}$, $\mathbf{4_{Cu}}$. See the Supporting Information.

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