



**Conversion of 12-Membered  $D_3$ - and  $L_3$ - $Co^{III}_3Cd^{II}_3$  Metallorings into a 24-Membered  $D_3L_3$ - $Co^{III}_6Cd^{II}_6$  Metalloring**

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## Conversion of 12-Membered $D_3$ - and $L_3$ - $Co^{III}Cd^{II}_3$ Metallorings into a 24-Membered $D_3L_3$ - $Co^{III}_6Cd^{II}_6$ Metalloring

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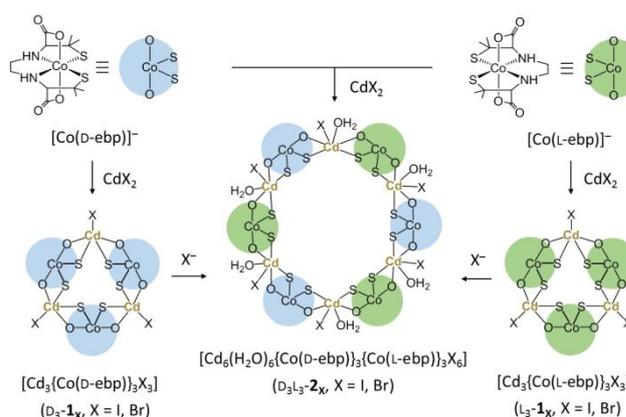
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The treatment of  $[Co(D\text{- or }L\text{-ebp})]^-$  with  $CdX_2$  ( $X = Br^-, I^-$ ) gave a cyclic  $Co^{III}Cd^{II}_3$  complex with a 12-membered metalloring,  $[Cd_3X_3\{Co(D\text{- or }L\text{-ebp})\}_3]$  ( $D_3$ - or  $L_3$ - $1_x$ ). The use of a 1:1 mixture of  $[Co(D\text{-ebp})]^-$  and  $[Co(L\text{-ebp})]^-$ , instead of  $[Co(D\text{- or }L\text{-ebp})]^-$ , led to the creation of a cyclic  $Co^{III}_6Cd^{II}_6$  complex with a 24-membered metalloring,  $[Cd_6X_6(H_2O)_6\{Co(D\text{-ebp})\}_3\{Co(L\text{-ebp})\}_3]$  ( $D_3L_3$ - $2_x$ ). Compounds  $D_3L_3$ - $2_x$  were also produced when  $D_3$ - $1_x$  and  $L_3$ - $1_x$  were mixed in water in a 1:1 ratio, illustrating the conversion of a pair of homochiral metallorings into a double-sized heterochiral metalloring.

Metalloring compounds are polygonal architectures constructed by the alternating assembly of metal ions and organic ligands through coordination bonds.<sup>1</sup> One of the most attractive aspects of this class of compounds is that their structures are convertible to other cyclic structures or polyhedrons,<sup>2,3</sup> unlike covalently bridged organic macrocycles such as cyclic oligosaccharides and crown ethers. To date, the structural conversions induced by external chemical/physical factors, such as the solvent,<sup>4</sup> temperature,<sup>5</sup> pH,<sup>6</sup> light,<sup>7</sup> concentration,<sup>8</sup> and guest molecules/ions,<sup>9</sup> have extensively been investigated, with the aim of potential applications as molecular machines and sensing devices.<sup>10</sup> Recent interesting examples of structural conversions involve the intercrossing of metal ions or ligands between two types of metallorings.<sup>3,11,12</sup> While the intercrossing reactions are beneficial for creating mixed-metal (heterometallic) or mixed-ligand (heteroleptic) metallorings, these reactions have normally proceeded while keeping the sizes of the original rings and have rarely been applied for expanding/contracting metallorings.<sup>13</sup>

As part of our long-standing interest in the rational construction of S-bridged polynuclear and metallosupramolecular structures by using thiolato metal

complexes as S-donating metalloligands,<sup>14-16</sup> we previously reported that  $trans(N)$ - $[Co(D\text{-pen})_2]^-$  binds to a  $Cd^{II}$  centre in a bidentate-S,S chelating mode to form an S-bridged  $Co^{III}Cd^{II}$  trinuclear complex,  $[Cd(H_2O)\{Co(D\text{-pen})_2\}_2]$ .<sup>17</sup> To construct S-bridged polynuclear structures that have a cyclic form, it is necessary to employ a thiolato complex that can bridge two metal centres through sulfur donors, instead of  $trans(N)$ - $[Co(D\text{-pen})_2]^-$ . The complex  $trans(O)$ - $[Co(D\text{-ebp})]^-$ , which has been synthesized by us,<sup>18</sup> meets this requirement because of its  $trans(O)$  geometry suitable for adopting a bridging coordination mode,<sup>19</sup> as well as its  $N,N$ -bridged structure that enlarges the S-Co-S angle to prevent it from chelating to a metal centre. Here, we report that the reactions of  $trans(O)$ - $[Co(D\text{- or }L\text{-ebp})]^-$  with  $CdX_2$  ( $X = Br^-, I^-$ ) indeed afford cyclic  $Co^{III}Cd^{II}_3$  complexes with a 12-membered metalloring,  $[Cd_3X_3\{Co(D\text{- or }L\text{-ebp})\}_3]$  ( $D_3$ - $1_x$  or  $L_3$ - $1_x$ ) (Scheme 1). Remarkably, the 1:1 mixing of  $D_3$ - $1_x$  and  $L_3$ - $1_x$  led to the production of heterochiral complexes with a 24-membered metalloring,  $[Cd_6X_6(H_2O)_6\{Co(D\text{-ebp})\}_3\{Co(L\text{-ebp})\}_3]$  ( $D_3L_3$ - $2_x$ ). To the best of our knowledge, this is the first example of a metalloring expansion due to the conversion of a pair of enantiomeric metallorings via a heterochiral recognition event.



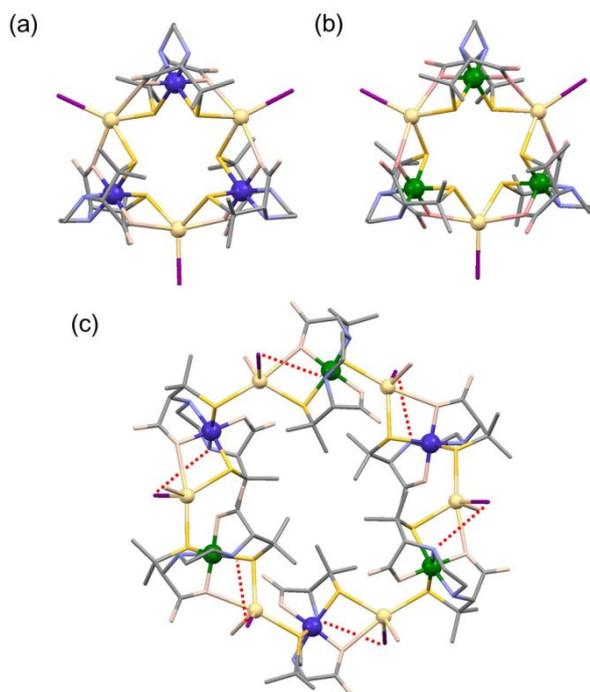
Scheme 1. Reactions of  $[Co(ebp)]^-$  with  $CdX_2$ .

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Complexes Na[Co(D-ebp)] and Na[Co(L-ebp)] were prepared according to a procedure similar to that used in the literature,<sup>18</sup> employing Na<sub>3</sub>[Co(CO<sub>3</sub>)<sub>3</sub>] as a Co<sup>III</sup> source instead of [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> to prevent the contamination of NaCl in the product. The reaction of Na[Co(D-ebp)] with a slight excess of CdI<sub>2</sub> in water gave a purple solution, from which purple block crystals (D<sub>3</sub>-1<sub>i</sub>) were isolated with a satisfactory yield (73%).<sup>†</sup> The fluorescence X-ray analysis of this product showed the presence of Cd, Co, S, and I atoms, and its elemental analytical data were in good agreement with the formula for a 1:1:1 adduct of [Co(ebp)]<sup>-</sup>, Cd<sup>2+</sup>, and I<sup>-</sup>.<sup>†</sup> The structure of D<sub>3</sub>-1<sub>i</sub> was determined by single-crystal X-ray crystallography (space group: C222<sub>1</sub>, Flack parameter: 0.030(6)), which revealed the presence of neutral complex molecules and water molecules of crystallization. As shown in Figure 1a, the complex molecule consists of three [Co(D-ebp)]<sup>-</sup> octahedral units that are alternately bridged by three {CdI}<sup>+</sup> moieties through S and O atoms (av. Cd–S = 2.54 Å, av. Cd–O = 2.53 Å), forming a cyclic Co<sup>III</sup><sub>3</sub>Cd<sup>II</sup><sub>3</sub> structure in [Cd<sub>3</sub>I<sub>3</sub>{Co(D-ebp)}<sub>3</sub>] having a 12-membered Co<sub>3</sub>Cd<sub>3</sub>S<sub>6</sub> metalloring. In D<sub>3</sub>-1<sub>i</sub>, each Cd<sup>II</sup> atom is coordinated by two thiolato S and two carboxyl O atoms from two [Co(D-ebp)]<sup>-</sup> units and one terminal I<sup>-</sup> ion (av. Cd–I = 2.68 Å) in a distorted trigonal-bipyramidal geometry. The cyclic structure in D<sub>3</sub>-1<sub>i</sub> possesses a cavity with the largest S...S separation of 5.29 Å. This cavity size is similar to that found in the S<sub>6</sub> thioether cage that can encapsulate a metal ion.<sup>20</sup>



**Figure 1.** Perspective views of (a) D<sub>3</sub>-1<sub>i</sub>, (b) L<sub>3</sub>-1<sub>i</sub>, and (c) D<sub>3</sub>L<sub>3</sub>-2<sub>i</sub>, viewed from virtual C<sub>3</sub> or S<sub>6</sub> axes. Colour code: Cd, beige; I, purple; Co, blue for [Co(D-ebp)]<sup>-</sup> unit and green for [Co(L-ebp)]<sup>-</sup> unit; S, yellow; O, pink; N, pale blue; C, grey. H atoms are omitted for clarity. Red dashed lines indicate NH...I hydrogen bonds.

To check the stability of the cyclic structure in D<sub>3</sub>-1<sub>i</sub>, we measured the electronic absorption, CD, and <sup>1</sup>H NMR spectra in solution. The absorption spectrum of D<sub>3</sub>-1<sub>i</sub> in water exhibits a visible band ca. 530 nm, with a shoulder at a lower wavelength, assignable to the d-d transition of a Co<sup>III</sup> centre (Figure S1).<sup>†</sup> In this d-d band region, positive bands are observed in the CD spectrum (Figure S1).<sup>†</sup> The absorption and CD spectra of D<sub>3</sub>-1<sub>i</sub> are almost identical with those of the parental Na[Co(D-ebp)] in water. This is also the case for the <sup>1</sup>H NMR spectrum of D<sub>3</sub>-1<sub>i</sub>, which gives a single set of proton signals identical to those for Na[Co(D-ebp)] (Figure S2).<sup>†</sup> Thus, we conclude that D<sub>3</sub>-1<sub>i</sub> is dissociated into [Co(D-ebp)]<sup>-</sup> and Cd<sup>2+</sup> ions in water due to the cleavage of Cd–S and Cd–O bonds, considering that appreciable differences in the diffuse reflection and CD spectra of D<sub>3</sub>-1<sub>i</sub> and Na[Co(D-ebp)] were found in the solid state (Figures S3, S4).<sup>†</sup>

A similar reaction with CdI<sub>2</sub> using Na[Co(L-ebp)], instead of Na[Co(D-ebp)], also produced purple block crystals (L<sub>3</sub>-1<sub>i</sub>). Based on the single-crystal X-ray analysis (space group: C222<sub>1</sub>, Flack parameter: 0.011(5)), together with the spectroscopic measurements (Figures S2–S4), L<sub>3</sub>-1<sub>i</sub> was confidently determined to have a cyclic Co<sup>III</sup><sub>3</sub>Cd<sup>II</sup><sub>3</sub> structure in [Cd<sub>3</sub>I<sub>3</sub>{Co(L-ebp)}<sub>3</sub>], which is enantiomeric to the structure in D<sub>3</sub>-1<sub>i</sub> (Figure 1b). On the other hand, the use of a 1:1 mixture of Na[Co(D-ebp)] and Na[Co(L-ebp)] gave purple crystals with a hexagonal plate shape (D<sub>3</sub>L<sub>3</sub>-2<sub>i</sub>).<sup>†</sup> The fluorescence X-ray and elemental analyses indicated that D<sub>3</sub>L<sub>3</sub>-2<sub>i</sub> is a 1:1:1 adduct of [Co(ebp)]<sup>-</sup>, Cd<sup>2+</sup>, and I<sup>-</sup>, as is also the case for D<sub>3</sub>-1<sub>i</sub> and L<sub>3</sub>-1<sub>i</sub>. The CD spectrum of D<sub>3</sub>L<sub>3</sub>-2<sub>i</sub> in the solid state, as well as in water, is completely silent, indicative of the presence of [Co(D-ebp)]<sup>-</sup> and [Co(L-ebp)]<sup>-</sup> units in a 1:1 ratio. However, the assignment of D<sub>3</sub>L<sub>3</sub>-2<sub>i</sub> as a racemic compound consisting of D<sub>3</sub>-1<sub>i</sub> and L<sub>3</sub>-1<sub>i</sub> is excluded because the diffuse reflection spectral feature of D<sub>3</sub>L<sub>3</sub>-2<sub>i</sub> is not the same as that of D<sub>3</sub>-1<sub>i</sub> or L<sub>3</sub>-1<sub>i</sub> (Figure S5).<sup>†</sup>

The molecular structure of D<sub>3</sub>L<sub>3</sub>-2<sub>i</sub> was established by a single-crystal X-ray analysis (space group: R $\bar{3}$ ). As shown in Figure 1c, D<sub>3</sub>L<sub>3</sub>-2<sub>i</sub> has a cyclic Co<sup>III</sup><sub>6</sub>Cd<sup>II</sup><sub>6</sub> structure in [Cd<sub>6</sub>I<sub>6</sub>(H<sub>2</sub>O)<sub>6</sub>{Co(D-ebp)}<sub>3</sub>{Co(L-ebp)}<sub>3</sub>], in which three [Co(D-ebp)]<sup>-</sup> and three [Co(L-ebp)]<sup>-</sup> units are alternately spanned by {CdI(H<sub>2</sub>O)}<sup>+</sup> moieties in the meso form with an S<sub>6</sub> symmetry. Like in D<sub>3</sub>-1<sub>i</sub> and L<sub>3</sub>-1<sub>i</sub>, the [Co(ebp)]<sup>-</sup> units in D<sub>3</sub>L<sub>3</sub>-2<sub>i</sub> each bind to two Cd<sup>II</sup> centres in a bis(bidentate-O,S) mode. However, each Cd<sup>II</sup> atom adopts a distorted octahedral geometry, coordinated by two S and two O atoms from two [Co(ebp)]<sup>-</sup> units (av. Cd–S = 2.58 Å, av. Cd–O<sub>COO</sub> = 2.75 Å), one I<sup>-</sup> ion (Cd–I = 2.8269(3) Å), and one water molecule (Cd–O<sub>H<sub>2</sub>O</sub> = 2.2174(18) Å). Importantly, the Co<sup>III</sup><sub>6</sub>Cd<sup>II</sup><sub>6</sub> structure in D<sub>3</sub>L<sub>3</sub>-2<sub>i</sub> comprises a 24-membered Co<sub>6</sub>Cd<sub>6</sub>S<sub>12</sub> metalloring that is twice as large as the metalloring in the homochiral D<sub>3</sub>-1<sub>i</sub> or L<sub>3</sub>-1<sub>i</sub>. The metalloring cavity in D<sub>3</sub>L<sub>3</sub>-2<sub>i</sub> is occupied by 12 ebp methyl groups by forming hydrophobic interactions (Figure S6).<sup>†</sup> In the cyclic structure in D<sub>3</sub>L<sub>3</sub>-2<sub>i</sub>, there exist six intramolecular hydrogen bonds (NH...I = 3.5966(18) Å) between amine groups and iodide ligands (Figure 1c). Such intramolecular hydrogen bonds are not found in D<sub>3</sub>-1<sub>i</sub> and L<sub>3</sub>-1<sub>i</sub>; the closest N...I separation is 5.07 Å. We assume that the intramolecular NH...I hydrogen bonds, together with the hydrophobic interactions due to methyl groups, lead to the heterochiral assembly of D<sub>3</sub>L<sub>3</sub>-2<sub>i</sub> from [Co(D-ebp)]<sup>-</sup> and [Co(L-ebp)]<sup>-</sup> on crystallization. The ESI-mass spectrum of D<sub>3</sub>L<sub>3</sub>-2<sub>i</sub> in

MeOH/H<sub>2</sub>O (v/v = 1/1) shows a divalent signal corresponding to [Cd<sub>6</sub>L<sub>4</sub>{Co(ebp)}<sub>6</sub>]<sup>2+</sup> and a monovalent signal corresponding to [Cd<sub>3</sub>L<sub>2</sub>{Co(ebp)}<sub>3</sub>]<sup>+</sup> at *m/z* = 1729 in an approximate intensity ratio of 2:1, although these signals are weak (Figure S7).<sup>†</sup> For D<sub>3</sub>-**1**<sub>i</sub> or L<sub>3</sub>-**1**<sub>i</sub>, a monovalent signal corresponding to [Cd<sub>3</sub>L<sub>2</sub>{Co(ebp)}<sub>3</sub>]<sup>+</sup> (*m/z* = 1729) is observed, but no apparent signal corresponding to [Cd<sub>6</sub>L<sub>4</sub>{Co(ebp)}<sub>6</sub>]<sup>2+</sup> is detected. These mass spectral features suggest the preferential formation of the cyclic Co<sup>III</sup><sub>6</sub>Cd<sup>III</sup><sub>6</sub> structure, rather than the Co<sup>III</sup><sub>3</sub>Cd<sup>III</sup><sub>3</sub> structure, when [Co(D-ebp)]<sup>-</sup> and [Co(L-ebp)]<sup>-</sup> coexist in solution.

Prompted by these results, we carried out the 1:1 mixing of D<sub>3</sub>-**1**<sub>i</sub> and L<sub>3</sub>-**1**<sub>i</sub> in water, expecting the selective formation of D<sub>3</sub>L<sub>3</sub>-**2**<sub>i</sub> via the scrambling of the [Co(D-ebp)]<sup>-</sup> and [Co(L-ebp)]<sup>-</sup> units. When aqueous NaI was added to the brown solution of D<sub>3</sub>-**1**<sub>i</sub> and L<sub>3</sub>-**1**<sub>i</sub>, we were able to isolate purple hexagonal crystals of D<sub>3</sub>L<sub>3</sub>-**2**<sub>i</sub> in high yield (84%).<sup>†,‡</sup> Since other species were not crystallized from the mixed solution, D<sub>3</sub>-**1**<sub>i</sub> and L<sub>3</sub>-**1**<sub>i</sub> are fused to produce D<sub>3</sub>L<sub>3</sub>-**2**<sub>i</sub> exclusively in the course of the crystallization process. Notably, green block crystals (D<sub>2</sub>L<sub>2</sub>-**3**), besides the purple hexagonal platelet crystals of D<sub>3</sub>L<sub>3</sub>-**2**<sub>i</sub>, appeared when NaI was not added to an aqueous solution of the 1:1 mixture of D<sub>3</sub>-**1**<sub>i</sub> and L<sub>3</sub>-**1**<sub>i</sub>.<sup>§§§</sup> A single-crystal X-ray analysis demonstrated that D<sub>2</sub>L<sub>2</sub>-**3** is composed of two [Co(D-ebp)]<sup>-</sup> and two [Co(L-ebp)]<sup>-</sup> units and two {Cd(H<sub>2</sub>O)}<sup>2+</sup> moieties (space group: *P*<sub>2</sub><sub>1</sub>/*n*) (Figure S8).<sup>†</sup> In D<sub>2</sub>L<sub>2</sub>-**3**, [Co(D-ebp)]<sup>-</sup> and [Co(L-ebp)]<sup>-</sup> units are linked by two Cd<sup>II</sup> atoms to form an S-bridged Co<sup>III</sup><sub>2</sub>Cd<sup>II</sup><sub>2</sub> tetranuclear core with an 8-membered Cd<sub>2</sub>Co<sub>2</sub>S<sub>4</sub> metalloring. To this core, additional [Co(D-ebp)]<sup>-</sup> and [Co(L-ebp)]<sup>-</sup> units each bind to a Cd<sup>II</sup> centre in a bidentate-S,O mode, completing a meso Co<sup>III</sup><sub>4</sub>Cd<sup>II</sup><sub>2</sub> hexanuclear structure in [Cd<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>{Co(D-ebp)}<sub>2</sub>{Co(L-ebp)}<sub>2</sub>]. Each Cd<sup>II</sup> atom in D<sub>2</sub>L<sub>2</sub>-**3** has a square-pyramidal geometry coordinated by three thiolato S and a carboxyl O atom from three [Co(ebp)]<sup>-</sup> units (av. Cd–S = 2.56 Å, Cd–O<sub>COO</sub> = 2.787(3) Å), besides one water molecule (Cd–O<sub>H<sub>2</sub>O</sub> = 2.403(4) Å). The formation of D<sub>2</sub>L<sub>2</sub>-**3** is a result of the lack of iodide ions bound to each Cd<sup>II</sup> centre, which is indicative of the importance of the iodide coordination to construct the Co<sup>III</sup><sub>6</sub>Cd<sup>III</sup><sub>6</sub> structure in D<sub>3</sub>L<sub>3</sub>-**2**<sub>i</sub> from D<sub>3</sub>-**1**<sub>i</sub> and L<sub>3</sub>-**1**<sub>i</sub>.

To see the generality of this intriguing conversion phenomena, analogous cyclic Co<sup>III</sup><sub>3</sub>Cd<sup>III</sup><sub>3</sub> complexes with bromide ligands, [Cd<sub>3</sub>Br<sub>3</sub>{Co(D-ebp)}<sub>3</sub>] (D<sub>3</sub>-**1**<sub>Br</sub>) and [Cd<sub>3</sub>Br<sub>3</sub>{Co(L-ebp)}<sub>3</sub>] (L<sub>3</sub>-**1**<sub>Br</sub>), were prepared from Na[Co(D- or L-ebp)] and CdBr<sub>2</sub>.<sup>†</sup> The characterization of D<sub>3</sub>-**1**<sub>Br</sub> and L<sub>3</sub>-**1**<sub>Br</sub> was made by fluorescence X-ray and elemental analyses and spectroscopic methods (Figures S9, S10).<sup>†,‡</sup> The single-crystal X-ray analysis confirmed that the overall structures of D<sub>3</sub>-**1**<sub>Br</sub> (space group: *C*222<sub>1</sub>, Flack parameter: 0.032(5)) and L<sub>3</sub>-**1**<sub>Br</sub> (space group: *C*222<sub>1</sub>, Flack parameter: 0.022(8)) are essentially the same as those of D<sub>3</sub>-**1**<sub>i</sub> and L<sub>3</sub>-**1**<sub>i</sub>, respectively, except for the presence of Br<sup>-</sup> ligands (av. Cd–Br = 2.51 Å) (Figure S11).<sup>†</sup> As expected, the 1:1 mixing of D<sub>3</sub>-**1**<sub>Br</sub> and L<sub>3</sub>-**1**<sub>Br</sub> in water in the presence of NaBr, as well as the reaction of a 1:1 mixture of Na[Co(D-ebp)] and Na[Co(L-ebp)] with CdBr<sub>2</sub>, led to the production of a cyclic Cd<sup>II</sup><sub>6</sub>Co<sup>III</sup><sub>6</sub> complex with a 24-membered metalloring, [Cd<sub>6</sub>Br<sub>6</sub>(H<sub>2</sub>O)<sub>6</sub>{Co(D-ebp)}<sub>3</sub>{Co(L-ebp)}<sub>3</sub>] (D<sub>3</sub>L<sub>3</sub>-**2**<sub>Br</sub>). The molecular structure of D<sub>3</sub>L<sub>3</sub>-**2**<sub>Br</sub>, determined by single-crystal X-ray analysis (space group: *R*<sup>3</sup>), corresponds well with that of D<sub>3</sub>L<sub>3</sub>-**2**<sub>i</sub>, with the metalloring cavity being occupied by methyl groups (Figure

S11).<sup>†</sup> Like in D<sub>3</sub>L<sub>3</sub>-**2**<sub>i</sub>, the cyclic structure in D<sub>3</sub>L<sub>3</sub>-**2**<sub>Br</sub> appears to be sustained by intramolecular hydrogen bonds (N...Br = 3.428(5) Å). Here, it should be noted that the use of CdCl<sub>2</sub> in the reaction of Na[Co(D-ebp)] did not afford a cyclic Co<sup>III</sup><sub>3</sub>Cd<sup>III</sup><sub>3</sub> complex but a (Co<sup>III</sup>Cd<sup>II</sup>)<sub>n</sub> 4-fold helix structure in [CdCl{Co(D-ebp)}]<sub>n</sub> (space group: *P*<sub>4</sub><sub>1</sub>2<sub>1</sub>2, Flack parameter: 0.018(5)) (Figure S12).<sup>†</sup> Nevertheless, the reaction of a 1:1 mixture of Na[Co(D-ebp)] and Na[Co(L-ebp)] with CdCl<sub>2</sub> led to the production of a cyclic Cd<sup>II</sup><sub>6</sub>Co<sup>III</sup><sub>6</sub> complex with a 24-membered metalloring, [Cd<sub>6</sub>Cl<sub>6</sub>(H<sub>2</sub>O)<sub>6</sub>{Co(D-ebp)}<sub>3</sub>{Co(L-ebp)}<sub>3</sub>] (D<sub>3</sub>L<sub>3</sub>-**2**<sub>Cl</sub>) (space group: *R*<sup>3</sup>), the structure of which is the essentially same as those of D<sub>3</sub>L<sub>3</sub>-**2**<sub>i</sub> and D<sub>3</sub>L<sub>3</sub>-**2**<sub>Br</sub> (Figure S12).<sup>†</sup>

In summary, we showed that [Co(ebp)]<sup>-</sup> adopts a bridging mode to Cd<sup>II</sup> to construct S-bridged metalloring structures. While the use of the homochiral [Co(D- or L-ebp)]<sup>-</sup> in the reactions with CdX<sub>2</sub> (X = Br<sup>-</sup>, I<sup>-</sup>) gave Co<sup>III</sup><sub>3</sub>Cd<sup>III</sup><sub>3</sub> complexes with a 12-membered metalloring (D<sub>3</sub>-**1**<sub>X</sub> or L<sub>3</sub>-**1**<sub>X</sub>), the use of a racemic mixture of [Co(D-ebp)]<sup>-</sup> and [Co(L-ebp)]<sup>-</sup> produced a Co<sup>III</sup><sub>6</sub>Cd<sup>II</sup><sub>6</sub> complex with a 24-membered metalloring (D<sub>3</sub>L<sub>3</sub>-**2**<sub>X</sub>). Remarkably, the 1:1 mixing of D<sub>3</sub>-**1**<sub>X</sub> and L<sub>3</sub>-**1**<sub>X</sub> led to the production of D<sub>3</sub>L<sub>3</sub>-**2**<sub>X</sub>, showing the unprecedented conversion of a pair of homochiral metallorings into a double-sized heterochiral metalloring. The presence of halide ligands that can form intramolecular hydrogen bonds, as well as ebp methyl groups that can induce a hydrophobic effect, is a key to the conversion of D<sub>3</sub>-**1**<sub>X</sub> and L<sub>3</sub>-**1**<sub>X</sub> into D<sub>3</sub>L<sub>3</sub>-**2**<sub>X</sub>. While homochiral coordination systems have attracted much attention in recent years due to their relevance to biological systems,<sup>21</sup> the present results demonstrate the availability of a heterochiral system as an alternative way to construct fascinating self-assembled metallosupramolecular architectures.

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## Conflicts of interest

There are no conflicts to declare.

## Notes and references

<sup>‡</sup> The bulk purity of each product was confirmed by powder X-ray diffraction (PXRD), the pattern of which matched well with the pattern simulated from the single-crystal X-ray data (Figures S13, S14).<sup>†</sup>

<sup>§</sup> The TGA data showed that D<sub>3</sub>-**1**<sub>i</sub> and D<sub>3</sub>L<sub>3</sub>-**2**<sub>i</sub> are stable until 250 °C in the solid state, although most of their water molecules of crystallization are released by 100 °C. The PXRD experiments indicated that the crystalline phases of D<sub>3</sub>-**1**<sub>i</sub> and D<sub>3</sub>L<sub>3</sub>-**2**<sub>i</sub> are at least in part maintained after removing of water molecules of crystallization by heating at 100 °C (Figures S16–S18).<sup>†</sup>

<sup>§§</sup> A large cyclic Fe<sup>III</sup><sub>10</sub>Yb<sup>III</sup><sub>10</sub> cluster, in which a pair of enantiomeric ligands are alternately arranged around the ring, has been synthesized from a racemic mixture of chiral ligand.<sup>22</sup>

\$\$\$ Pure  $D_2L_2\text{-3}$  was isolated by the recrystallization of a mixture of  $D_3L_3\text{-2}$  and  $D_2L_2\text{-3}$  from water and characterized by elemental, fluorescence X-ray, and powder and single-crystal X-ray diffraction analyses, as well as diffuse reflection spectral measurements (Figures S13, S15). †

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