

Aggregation of L-Cysteinato Tricobaltate(III) Anions by Lanthanide(III) Cations into Dimensional Structures That are Controlled by Diastereoisomerism and Ionic Size

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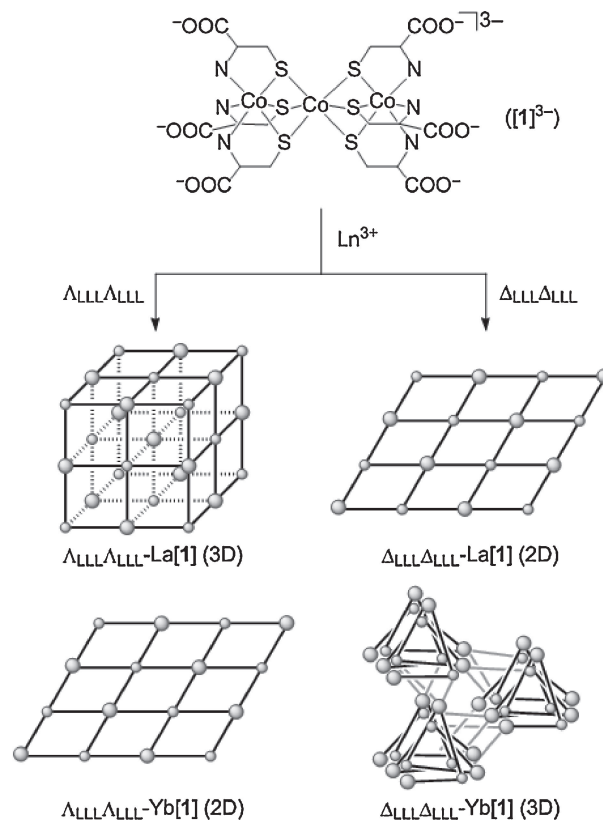
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Treatment of the $\Delta_{LLL}\Delta_{LLL}$ and $\Delta_{LLL}\Delta_{LLL}$ isomers of $K_3[Co\{Co(L-cys-N,S)_3\}_2]$ ($K_3[1]$, L-cys: L-cysteinate) with $Ln(NO_3)_3$ ($Ln = La$ and Yb) in water gave coordination polymers, $\Delta_{LLL}\Delta_{LLL}-Ln[1]$ and $\Delta_{LLL}\Delta_{LLL}-Ln[1]$, respectively, in which $[1]^{3-}$ binds to Ln^{3+} through carboxylate groups in a 1:1 ratio. It was found that the dimensional structures of $Ln[1]$ are controlled not only by the diastereoisomerism of $[1]^{3-}$ ($\Delta_{LLL}\Delta_{LLL}$ vs. $\Delta_{LLL}\Delta_{LLL}$) but also by the ionic size of Ln^{3+} (La^{3+} vs. Yb^{3+}).

Rational creation of coordination polymers that consist of metal ions and organic and/or inorganic ligands has received much attention in the past decades because of their multifunctional properties resulting from specific structures.¹ The most common approach to create coordination polymers is the use of multidentate organic ligands as building blocks.² On the other hand, the use of metalloligands instead of organic ligands is much less common, although it is expected that the resulting structures are more easily controlled thanks to the predetermined directionality of coordination sites of metalloligands.³ We have been interested in the use of thiolato metal complexes as an S-donating metalloligand in order to create systematically S-bridged polynuclear complexes with specific structures and properties.⁴ Recently, we have found that a S-bridged $Co^{III}Au^I$ trinuclear complex, $[Au\{Co(L-cys-N,S)(en)_2\}_2]^{3+}$ (L-cys: L-cysteinate), prepared from $[Co(L-cys-N,S)(en)_2]^+$ and Au^I , binds to $MnCl_2$ using free carboxylate groups to form a 1D ($Co^{III}_2Mn^II Au^I$)_n coordination polymer.⁵ This shows that multinuclear complexes with free carboxylate groups can function as effective O-donating metalloligands. In this context, we thought it worthwhile to investigate the binding ability of a tricobaltate(III) complex with L-cysteinate, $[Co\{Co(L-cys-N,S)_3\}_2]^{3-}$ ($[1]^{3-}$),⁶ toward metal ions not only because of the existence of six free carboxylate groups available for the coordination to metal centers but also because of the existence of diastereoisomers, $\Delta_{LLL}\Delta_{LLL}$ and $\Delta_{LLL}\Delta_{LLL}$, capable of controlling the resulting structures by chirality (Δ and Δ) at metal centers. Indeed, we found that $[1]^{3-}$ binds to La^{3+} ions through carboxylate groups to form coordination polymers, the dimensional structures of which are changed by the diastereoisomers employed. In addition, the use of Yb^{3+} instead of La^{3+} as a linking lanthanide ion also resulted in the drastic change of their structures. In this paper, we report on these intriguing stereochemical properties that were established by single-crystal X-ray analyses (Scheme 1).

Treatment of the $\Delta_{LLL}\Delta_{LLL}$ isomer of $K_3[Co\{Co(L-cys-N,S)_3\}_2]$ ($\Delta_{LLL}\Delta_{LLL}-K_3[1]$) with $La(NO_3)_3 \cdot 6H_2O$ in a 1:1 ratio in water quickly gave a dark brown powder, which turned to almost black crystals ($\Delta_{LLL}\Delta_{LLL}-La[1]$) on allowing it to stand at room temperature for one week.⁷ X-ray fluorescence spectrometry indicated that this compound contains Co and La atoms in a



Scheme 1. Schematic representation of coordination polymers derived from $[1]^{3-}$ and Ln^{3+} .

3:1 ratio, and its elemental analytical data were in agreement with the formula for a 1:1 adduct of $[Co\{Co(L-cys-N,S)_3\}_2]^{3-}$ and La^{3+} .⁸ The presence of the $\Delta_{LLL}\Delta_{LLL}$ isomer of $[1]^{3-}$ in $\Delta_{LLL}\Delta_{LLL}-La[1]$ was confirmed by its reflection and CD spectra in the solid state, which are almost the same as those of the parental $\Delta_{LLL}\Delta_{LLL}-K_3[1]$.⁷ In the IR spectrum, $\Delta_{LLL}\Delta_{LLL}-La[1]$ showed a strong C=O stretching band at ca. 1609 cm^{-1} , indicating that all the L-cys carboxyl groups exist as a deprotonated form.⁹ The structure of $\Delta_{LLL}\Delta_{LLL}-La[1]$ was determined by single-crystal X-ray crystallography, which revealed the presence of $\Delta_{LLL}\Delta_{LLL}-[1]^{3-}$ and La^{3+} in a 1:1 ratio, besides water molecules (Figure 1a).¹⁰ All the L-cys carboxylate groups of $\Delta_{LLL}\Delta_{LLL}-[1]^{3-}$ have an axial orientation such that N,S-chelate rings adopt a thermodynamically stable *lel* (δ for Δ) conformation. This orientation appears to be stabilized by the intramolecular hydrogen bonds between amine and carboxylate groups (av $N\cdots O = 3.200(3)\text{ \AA}$). A similar stereochemical feature has been found in $\Delta_{LLL}\Delta_{LLL}-[Co_3(L-cys-N,S)(L-Hcys-N,S)_5]^{2+}$, in which 5 of 6 carboxyl groups exist as

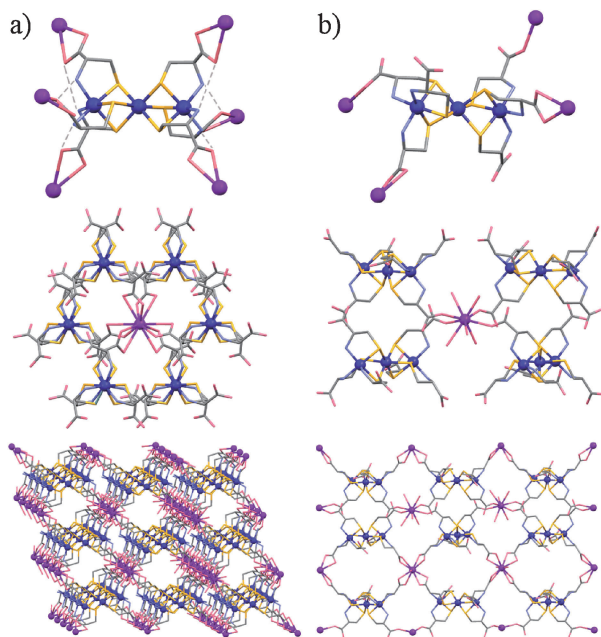


Figure 1. Perspective views of (a) $\Delta_{LLL}\Delta_{LLL}$ -La[1] and (b) $\Delta_{LLL}\Delta_{LLL}$ -La[1]. Hydrogen atoms are omitted for clarity. Co: dark-blue, C: gray, N: blue, O: pale red, S: yellow, La: purple.

a protonated form.^{6b} In $\Delta_{LLL}\Delta_{LLL}$ -La[1], each La^{3+} ion is linked by 6 $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ anions in a distorted octahedral arrangement through chelating carboxylate groups to form a 12-coordination environment, while each $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ anion binds to 6 La^{3+} ions using 6 carboxylate groups (av $\text{La-O} = 2.741(18) \text{ \AA}$). As a result of this connection between $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ and La^{3+} , a 3D coordination network is constructed for $\Delta_{LLL}\Delta_{LLL}$ -La[1].

Similar treatment of the $\Delta_{LLL}\Delta_{LLL}$ isomer of $\text{K}_3[\text{Co}\{\text{Co}(\text{L-cys-}N,S)_2\}]^6$ ($\Delta_{LLL}\Delta_{LLL}$ -K₃[1]) with $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ also produced almost black crystals ($\Delta_{LLL}\Delta_{LLL}$ -La[1]) by way of a dark brown powder.⁷ Compound $\Delta_{LLL}\Delta_{LLL}$ -La[1] was assigned to a 1:1 adduct of $\Delta_{LLL}\Delta_{LLL}$ -[Co{Co(L-cys-*N,S*)₂}]³⁻ and La^{3+} , based on the reflection, CD, and IR spectroscopy in the solid state, together with the X-ray fluorescence and elemental analyses.^{7,8} Single-crystal X-ray analysis demonstrated that $\Delta_{LLL}\Delta_{LLL}$ -La[1] consists of the trinuclear anions ($\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻) and La^{3+} in a 1:1 ratio, besides water molecules (Figure 1b), as in the case of $\Delta_{LLL}\Delta_{LLL}$ -La[1].¹¹ However, all the L-cys carboxylate groups of $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ have an equatorial orientation with *lel* conformational N,S-chelate rings. There are two crystallographically independent La^{3+} ions in $\Delta_{LLL}\Delta_{LLL}$ -La[1], each of which are linked by 4 $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ anions in a distorted square-planar arrangement; La1 is nine-coordinated with 4 oxygen atoms from 4 carboxylate groups and 5 water molecules (av $\text{La1-O}_{\text{carboxylate}} = 2.484(8) \text{ \AA}$, av $\text{La1-O}_w = 2.653(9) \text{ \AA}$), while La2 is 10-coordinated with 8 oxygen atoms from 4 carboxylate groups and 2 water molecules (av $\text{La2-O}_{\text{carboxylate}} = 2.610(8) \text{ \AA}$, av $\text{La2-O}_w = 2.583(9) \text{ \AA}$).⁷ In $\Delta_{LLL}\Delta_{LLL}$ -La[1], each $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ anion binds to only 4 La^{3+} ions using 4 carboxylate groups, leaving two non-coordinating carboxylate groups in a trans position. As a result, a 2D sheet-like structure is constructed for $\Delta_{LLL}\Delta_{LLL}$ -La[1],

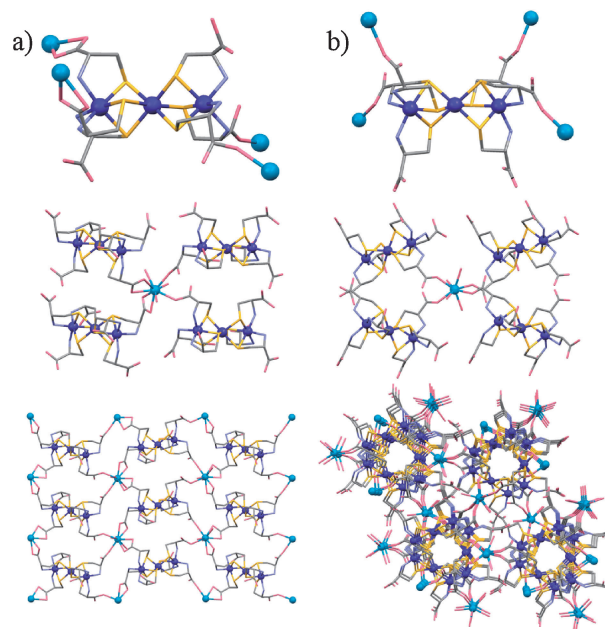


Figure 2. Perspective views of (a) $\Delta_{LLL}\Delta_{LLL}$ -Yb[1] and (b) $\Delta_{LLL}\Delta_{LLL}$ -Yb[1]. Hydrogen atoms are omitted for clarity. Co: dark-blue, C: gray, N: blue, O: pale red, S: yellow, Yb: bright-blue.

which is in sharp contrast to the 3D structure observed for $\Delta_{LLL}\Delta_{LLL}$ -La[1]. It is reasonable to consider that the difference in the orientations of carboxylate groups between $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ and $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ is responsible for this result. That is, the $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ anion with the axial-oriented carboxylate groups is less bulky than the $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ anion bearing the equatorial-oriented carboxylate groups, and thus each La^{3+} ion can be surrounded by 6 $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ anions to construct the 3D network structure for $\Delta_{LLL}\Delta_{LLL}$ -La[1]. On the other hand, only 4 $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ anions are allowed to bind with each La^{3+} ion, resulting in the formation of a 2D structure for $\Delta_{LLL}\Delta_{LLL}$ -La[1].

To investigate the influence of the ionic size of linking lanthanide(III) ions on the resulting structures, $\Delta_{LLL}\Delta_{LLL}$ - and $\Delta_{LLL}\Delta_{LLL}$ -K₃[1] were treated with $\text{Yb}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, instead of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, which also gave 1:1 coordination polymers, $\Delta_{LLL}\Delta_{LLL}$ -Yb[1] and $\Delta_{LLL}\Delta_{LLL}$ -Yb[1], respectively.⁷ The assignment of these compounds was made by the reflection, CD, and IR spectroscopy in the solid state, together with the X-ray fluorescence and elemental analyses,¹² and their structures were established by single-crystal X-ray analyses (Figure 2).^{7,13,14} Like in $\Delta_{LLL}\Delta_{LLL}$ -La[1] and $\Delta_{LLL}\Delta_{LLL}$ -La[1], the 6 L-cys carboxylate groups of $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ and $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ have axial and equatorial orientations in $\Delta_{LLL}\Delta_{LLL}$ -Yb[1] and $\Delta_{LLL}\Delta_{LLL}$ -Yb[1], respectively. However, in $\Delta_{LLL}\Delta_{LLL}$ -Yb[1], each Yb^{3+} ion is bound by 4 $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ anions through 2 chelating and 2 monodentate carboxylate groups, besides 3 water molecules, to have a nine-coordination environment (av $\text{Yb-O}_{\text{carboxylate}} = 2.37(2) \text{ \AA}$, av $\text{Yb-O}_w = 2.39(2) \text{ \AA}$). In addition, only 4 carboxylate groups of $\Delta_{LLL}\Delta_{LLL}$ -[1]³⁻ participate in the coordination to Yb^{III} ions, while the remaining 2 carboxylate groups, which are located in a trans position, remain uncoordinated. As a result, $\Delta_{LLL}\Delta_{LLL}$ -Yb[1] forms a 2D sheet-like

structure, which is markedly different from the 3D structure in $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-La[1]}$. On the other hand, each Yb^{3+} in $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-Yb[1]}$ is situated in a eight-coordination environment with 4 monodentate carboxylate groups from 4 different $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-[1]}^{3-}$ anions, besides 4 water molecules (av $\text{Yb-O}_{\text{carboxylate}} = 2.301(4)\text{ \AA}$, av $\text{Yb-O}_{\text{w}} = 2.355(4)\text{ \AA}$). The binding of 4 $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-[1]}^{3-}$ anions around each cation in $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-Yb[1]}$ is the same as that in $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-La[1]}$. However, in $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-Yb[1]}$, the four $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-[1]}^{3-}$ anions surround a Yb^{3+} ion in a tetrahedral-like arrangement, rather than a square-planar arrangement found in $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-La[1]}$. Furthermore, each $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-[1]}^{3-}$ anion binds to 4 Yb^{3+} ions through 4 monodentate carboxylate groups such that 2 noncoordinating carboxylate groups locate in a cis position, rather than in a trans position found in $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-La[1]}$. As a result, in $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-Yb[1]}$, $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-[1]}^{3-}$ anions and Yb^{3+} cations are alternately connected with each other to form a 3_1 supramolecular helix, which is further connected to 6 adjacent supramolecular helices through O–Yb–O linkages to complete a unique 3D aggregated structure. Accordingly, the use of Yb^{3+} with an ionic radius smaller than La^{3+} ($\text{Yb}^{3+} = 0.87\text{ \AA}$, $\text{La}^{3+} = 0.98\text{ \AA}$)¹⁵ causes the reduction of the binding number of $[\text{1}]^{3-}$ anions from 6 to 4 for the less bulky $\Delta_{\text{LLL}}\Delta_{\text{LLL}}$ isomer and also causes the change of their binding arrangement from square-plane to tetrahedron for the $\Delta_{\text{LLL}}\Delta_{\text{LLL}}$ isomer, resulting in the drastic change in dimensional structures from 3D to 2D for the $\Delta_{\text{LLL}}\Delta_{\text{LLL}}$ isomer and from 2D to 3D for the $\Delta_{\text{LLL}}\Delta_{\text{LLL}}$ isomer.

In conclusion, we have shown evidence that the tricobaltate(III) complex with L-cysteinate ($[\text{1}]^{3-}$) acts as a multi-bridging metalloligand toward Ln^{3+} to form carboxylate-bridged heterometallic coordination polymers. While $[\text{1}]^{3-}$ uniformly formed 1:1 coordination polymers with Ln^{3+} , the constructed dimensional structures were found to be highly dependent on the selected diastereoisomerism ($\Delta_{\text{LLL}}\Delta_{\text{LLL}}$ vs. $\Delta_{\text{LLL}}\Delta_{\text{LLL}}$) and Ln^{3+} ion (La^{3+} vs. Yb^{3+}). Note that the control of Ln^{3+} -based dimensional structures by changing the diastereoisomerism of (metallo)ligands has not been reported to date, although several reports that show the structural change in coordination polymers by changing Ln^{3+} have been presented.¹⁶ Further investigations of this system are currently underway by using other Ln^{3+} ions, as well as transition-metal ions.

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- Crystal data for $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-La[1]}\cdot 17\text{H}_2\text{O}$: fw 1336.81, orthorhombic, $P2_12_12_1$, $a = 18.1456(8)\text{ \AA}$, $b = 20.2231(10)\text{ \AA}$, $c = 27.0109(12)\text{ \AA}$, $V = 9911.9(8)\text{ \AA}^3$, $Z = 8$, $D_{\text{calcd}} = 1.792\text{ Mg m}^{-3}$, 96493 reflections measured, 22603 independent. $R_1 = 0.0646$ ($I > 2\sigma(I)$), $wR_2 = 0.1829$ (all data). CCDC: 791192.
- Calcd for $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-Yb[1]}\cdot 7\text{H}_2\text{O}$: C, 18.16; H, 3.72; N, 7.06%. Found: C, 18.16; H, 4.01; N, 6.97%. Yield: 95%. Calcd for $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-Yb[1]}\cdot 17\text{H}_2\text{O}$: C, 15.77; H, 4.71; N, 6.13%. Found: C, 15.59; H, 4.61; N, 5.96%. Yield: 84%.
- Crystal data for $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-Yb[1]}\cdot 7\text{H}_2\text{O}$: fw 1190.78, orthorhombic, $P2_12_12_1$, $a = 18.110\text{ \AA}$, $b = 25.191\text{ \AA}$, $c = 8.829\text{ \AA}$, $V = 4027.9\text{ \AA}^3$, $Z = 4$, $D_{\text{calcd}} = 1.964\text{ Mg m}^{-3}$, 39758 reflections measured, 9232 independent. $R_1 = 0.1220$ ($I > 2\sigma(I)$), $wR_2 = 0.3525$ (all data). The large R_1 and wR_2 values are due to the poor quality of crystal. CCDC: 791193.
- Crystal data for $\Delta_{\text{LLL}}\Delta_{\text{LLL}}\text{-Yb[1]}\cdot 17\text{H}_2\text{O}$: fw 1370.94, trigonal, $P3_21$, $a = 13.5451(7)\text{ \AA}$, $c = 23.0394(14)\text{ \AA}$, $V = 3660.7(3)\text{ \AA}^3$, $Z = 3$, $D_{\text{calcd}} = 1.866\text{ Mg m}^{-3}$, 35078 reflections measured, 5587 independent. $R_1 = 0.0526$ ($I > 2\sigma(I)$), $wR_2 = 0.0965$ (all data). CCDC: 791194.
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