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Article

Controlled Binding of a L-Cysteinato Cobalt(III) Octahedron to a Cadmium(II) Center

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The binding ability of a chiral L-cysteinato cobalt(III) complex, [Co(L-cys-*N*,*S*)(en)$_2$]$^+$ (L-H$_2$cys = L-cysteine, en = ethylenediamine), toward a cadmium(II) center, together with the construction of S-bridged Co^{III}Cd^{II} structures that are controlled by anions and pH, is reported. The reaction of Λ_{L}-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ having a pendent COOH group with CdCl$_2$ in a 1:1 ratio in water, followed by the addition of NaCl, gave an S-bridged Co^{III}Cd^{II} dinuclear complex, Λ_{L}-[CdCl$_4${Co(L-Hcys-*N*,*S*)(en)$_2$}] (**1$_{\text{Cl}}$**), in which a cadmium(II) ion is weakly coordinated by a thiolato group from a Λ_{L}-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ unit, besides four Cl$^-$ anions. The corresponding 1:1 reaction with CdBr$_2$ and NaBr yielded an S-bridged Co^{III}Cd^{II}Co^{III} trinuclear complex composed of an S-bridged Co^{III}Cd^{II}Co^{III} trinuclear cation and a [CdBr$_4$]$^{2-}$ anion, (Λ_{L})$_2$-[CdBr$_3${Co(L-Hcys-*N*,*S*)(en)$_2$}{Co(L-cys-*N*,*S*)(en)$_2$}][CdBr$_4$] (**2**), while a Co^{III}Cd^{II} dinuclear complex analogous to **1$_{\text{Cl}}$**, Λ_{L}-[CdBr$_4${Co(L-Hcys-*N*,*S*)(en)$_2$}] (**1$_{\text{Br}}$**), was obtained by the addition of HBr instead of NaBr. In the Co^{III}Cd^{II}Co^{III} cation of **2**, a Cd^{II} center is very weakly coordinated by two thiolato groups from Λ_{L}-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ and Λ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units, besides three Br$^-$ anions, with the trinuclear structure being sustained by an intramolecular COOH···OOC hydrogen bond. On the other hand, no S-bridged structure was obtained by the corresponding 1:1 reaction with CdI$_2$ and NaI, giving only a mononuclear Co^{III} species with a [CdI$_4$]$^{2-}$ counteranion, Λ_{L}-[Co(L-Hcys-*N*,*S*)(en)$_2$][CdI$_4$] (**3**). When Λ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]ClO$_4$ having a deprotonated pendent COO$^-$ group was reacted with CdCl$_2$ in a 1:1 ratio in water, followed by the addition of NaCl, a one-dimensional (Co^{III}Cd^{II})$_n$ polymeric complex, (Λ_{L})$_n$-[CdCl$_3${Co(L-cys-*N*,*S*)(en)$_2$}]$_n$ (**4$_{\text{Cl}}$**), in which Λ_{L}-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units are alternately linked by [CdCl$_3$]$^-$ moieties through thiolato and carboxylate groups, was constructed. An analogous (Co^{III}Cd^{II})$_n$ polymeric structure having [Cd(NCS-*N*)$_3$]$^-$ moieties, (Λ_{L})$_n$-[Cd(NCS-*N*)$_3$-{Co(L-cys-*N*,*S*)(en)$_2$}]$_n$ (**4$_{\text{NCS}}$**), was also produced by the use of Cd(ClO$_4$)$_2$ and NaSCN.

Introduction

Over the past few decades, cadmium(II) compounds with thiolate ligands have attracted considerable attention not only in the field of coordination chemistry, because of their intriguing structural versatility,[1] but also in the field of bioinorganic and biochemistry, in connection with metallothioneins that contain cadmium(II) ions.[2,3] The structures of some cadmium-containing metallothioneins have been investigated by X-ray structural analyses,[4] as well as NMR and extended X-ray absorption fine structure (EXAFS) spectroscopies,[5,6] and the presence of two cadmium(II) cluster units, [Cd$_4$(S-cys)$_{11}$]$^{3-}$ (cluster A) and [Cd$_3$(S-cys)$_9$]$^{3-}$ (cluster B), in which cadmium(II) centers are bridged by S atoms from L-cysteine residues of peptides, has been clarified. In parallel with these investigations, a number of S-bridged

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cadmium(II) clusters related to the active sites of metallothioneins have been prepared.[7−9] For example, an anionic adamantanoid structure in $[\mathrm{Cd_4(SPh)_{10}}]^{2-}$[7a] and a neutral polyadamantanoid structure in $[\mathrm{Cd_4(SPh)_8}]$[7f] with bridging and terminal thiolate $\mathrm{PhS^-}$ ligands have been synthesized by the reactions of cadmium(II) salts with PhSH in the presence of base. Furthermore, it has been shown that the addition of elemental sulfur or $\mathrm{Na_2S}$ for these reactions leads to the formation of several S-bridged anionic clusters, such as $[\mathrm{S_4Cd_{10}(SPh)_{16}}]^{4-}$, $[\mathrm{S_4Cd_{17}(SPh)_{28}}]^{2-}$, and $[\mathrm{SCd_8(SPh)_{16}}]^{2-}$, in which cadmium(II) centers are capped by sulfide $\mathrm{S^{2-}}$ ion(s).[8] Thus, the bridging ability of thiolate ligands between cadmium(II) centers to form S-bridged polycadmium(II) structures has been well established.

On the other hand, examples of heterometallic polynuclear complexes, in which thiolate ligands bridge cadmium(II) and another transition metal center, are much less common,[10] and the rational construction of this kind of polynuclear species is still a great challenge in cadmium−thiolate chemistry. This seems to be responsible for the inherent binding ability of a thiolate group toward a cadmium(II) center, which is weaker than that toward another thiophilic metal center. In fact, Deutsch and co-workers[11] reported that a thiolato donor group in $[\mathrm{Co(aet)(en)_2}]^{2+}$ or $[\mathrm{Co(tga)(en)_2}]^{+}$ (Haet = 2-aminoethanethiol, $\mathrm{H_2tga}$ = thioglycolic acid, en = ethylenediamine) does not bind with cadmium(II) ion in solution, despite the binding with other thiophilic metal ions, such as silver(I), mercury(II), and platinum(II), to form S-bridged heterometallic structures. Recently, we have shown that $[\mathrm{Co(aet)(en)_2}]^{2+}$ forms S-bridged structures with cadmium(II) ions in the solid state, assisted by the introduction of chloride ions in a cadmium(II) coordination sphere, although Cd−S bonds are much weaker than Co−S bonds in these S-bridged structures.[12] Interestingly, the reaction of the optically active Λ-$[\mathrm{Co(aet)(en)_2}]^{2+}$ with $\mathrm{CdCl_2}$ was found to give a $\mathrm{Co^{III}{}_2Cd^{II}{}_2}$ tetranuclear structure in $\Lambda\Lambda$-$[\mathrm{Cd_2Cl_7\{Co(aet)(en)_2\}_2}]^{+}$, while the corresponding reaction of its racemic isomer produced an S-bridged $\mathrm{Co^{III}{}_2Cd^{II}}$ trinuclear structure in $\Delta\Lambda$-$[\mathrm{CdCl_4\{Co(aet)(en)_2\}_2}]^{2+}$. These results suggested that S-bridged heterometallic $\mathrm{Co^{III}Cd^{II}}$ structures constructed from thiolato cobalt(III) complexes and cadmium(II) halides could be controlled by some external factors owing to the relatively weak Cd−S bonds. Thus, as part of our recent efforts to rationally construct chiral heterometallic aggregates based on thiolato metal complexes,[13−15] we investigated the reactions of optically active cobalt(III) complexes of L-cysteinate, Δ_L- or Λ_L-$[\mathrm{Co(L\text{-}cys\text{-}\mathit{N,S})(en)_2}]^{+}$, with cadmium(II) salts. As a result, we found that the Λ_L isomer of $[\mathrm{Co(L\text{-}cys\text{-}\mathit{N,S})(en)_2}]^{+}$ can form S-bridged structures with $\mathrm{Cd^{II}}$ under appropriate conditions, while none of the S-bridged $\mathrm{Co^{III}}$-$\mathrm{Cd^{II}}$ products were isolated by use of its Δ_L isomer.

In this paper, we report on the synthesis, characterization, and crystal structures of a series of heterometallic $\mathrm{Co^{III}Cd^{II}}$ compounds consisting of Λ_L-$[\mathrm{Co(L\text{-}cys\text{-}\mathit{N,S})(en)_2}]^{+}$ and/or Λ_L-$[\mathrm{Co(L\text{-}Hcys\text{-}\mathit{N,S})(en)_2}]^{2+}$ units and cadmium(II) ions (Scheme 1). The binding ability of L-cysteinate in a chiral cobalt(III) octahedron toward a cadmium(II) center, which can be tuned by the change of halide anions ($\mathrm{Cl^-}$, $\mathrm{Br^-}$, and $\mathrm{I^-}$), as well as the pH of reaction solutions, is also reported.

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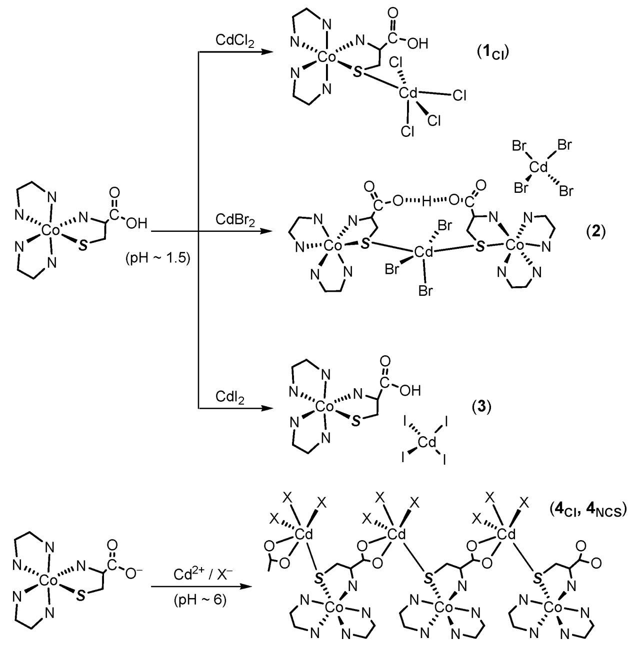
Scheme 1



Experimental Section

Preparation of Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]ClO$_4$ and Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$. Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]ClO$_4$ and Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ were prepared by modified methods described in the literature.[16] To a solution containing 16.0 g (67 mmol) of $CoCl_2\cdot 6H_2O$ in 50 cm^3 of water was added a solution containing 8.0 g (33 mmol) of L-(−)-cystine and 13.4 cm^3 (200 mmol) of ethylenediamine in 83 cm^3 of water. The mixture was stirred at room temperature for 5 h under a N_2 gas bubbling. To the almost black reaction solution was added 33 g (240 mmol) of $NaClO_4\cdot H_2O$, which was kept in a refrigerator for 1 h. The resulting dark brown microcrystals of Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]ClO$_4$ were collected by filtration. Yield: 8.0 g. Anal. Calcd for [Co(cys)(en)$_2$]ClO$_4$, $C_7H_{21}ClCoN_5O_2S$: C, 21.14; H, 5.32; N, 17.61. Found: C, 21.12; H, 5.23; N, 17.47.

To a solution containing 10.0 g (25 mmol) of Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]ClO$_4$ in 50 cm^3 of water was added 10.0 cm^3 of 60% aqueous HClO$_4$. The mixture was stirred at 60 °C for 10 min, and the dark brown solution was allowed to stand in a refrigerator for 1 day. The resulting dark brown stick crystals of Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2\cdot$1.5H$_2$O were collected by filtration. Yield: 11.3 g. Anal. Calcd for [Co(Hcys)(en)$_2$](ClO$_4$)$_2\cdot$1.5H$_2$O, $C_7H_{25}Cl_2CoN_5O_{11.5}S$: C, 16.01; H, 4.80; N, 13.33. Found: C, 15.83; H, 4.56; N, 13.37.

Preparation of Λ_L-[CdCl$_4${Co(L-Hcys-*N*,*S*)(en)$_2$}] (1_{Cl}). To a solution containing 0.20 g (0.38 mmol) of Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2\cdot$1.5H$_2$O in 5 cm^3 of water was added 0.09 g (0.40 mmol) of $CdCl_2\cdot 2.5H_2O$. This mixture was stirred at room temperature for 1 h. To the dark brown reaction solution (pH 1.3) was added 2.0 cm^3 of a saturated aqueous solution of NaCl, and the mixture was allowed to stand at room temperature for several hours. The resulting dark red plate crystals ($1_{Cl}\cdot H_2O$) suitable for X-ray analysis were collected by filtration. Yield: 0.17 g (78%). Anal. Calcd for [CdCl$_4${Co(Hcys)(en)$_2$}]$\cdot$H$_2$O ($1_{Cl}\cdot H_2O$), $C_7H_{24}CdCl_4CoN_5O_3S$: C, 14.71; H, 4.23; N, 12.25. Found: C, 14.57; H, 4.02; N, 12.24.

Preparation of (Λ_L)$_2$-[CdBr$_3${Co(L-Hcys-*N*,*S*)(en)$_2$}{Co(L-cys-*N*,*S*)(en)$_2$}][CdBr$_4$] (2). To a solution containing 0.20 g (0.38 mmol) of Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2\cdot$1.5H$_2$O in 10 cm^3 of water was added 0.11 g (0.40 mmol) of CdBr$_2$. This mixture was stirred at room temperature for 1 h. To the dark brown reaction solution (pH 1.6) was added 1.0 cm^3 of a saturated aqueous solution of NaBr, and the mixture was allowed to stand at room temperature for 1 day. The resulting dark brown block crystals (**2**) suitable for X-ray analysis were collected by filtration. Yield: 0.19 g (72%). Anal. Calcd for [CdBr$_3${Co(Hcys)(en)$_2$}{Co(cys)(en)$_2$}][CdBr$_4$] (**2**), $C_{14}H_{43}Br_7Cd_2Co_2N_{10}O_4S_2$: C, 12.17; H, 3.14; N, 10.14. Found: C, 12.11; H, 2.99; N, 10.04.

Preparation of Λ_L-[CdBr$_4${Co(L-Hcys-*N*,*S*)(en)$_2$}] (1_{Br}). To a solution containing 0.20 g (0.38 mmol) of Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2\cdot$1.5H$_2$O in 18 cm^3 of water were added 0.11 g (0.40 mmol) of CdBr$_2$ and 2.0 cm^3 of 1 M aqueous HBr. This mixture (pH < 1) was stirred at room temperature for 1 h and then allowed to stand at room temperature for 1 week. The resulting dark brown plate crystals ($1_{Br}\cdot H_2O$) suitable for X-ray analysis were collected by filtration. Yield: 0.25 g (87%). Anal. Calcd for [CdBr$_4${Co(Hcys)(en)$_2$}]$\cdot$H$_2$O ($1_{Br}\cdot H_2O$), $C_7H_{24}Br_4CdCoN_5O_3S$: C, 11.22; H, 3.23; N, 9.35. Found: C, 11.22; H, 3.07; N, 9.34.

Conversion of 2 to 1_{Br}. To a solution containing 0.10 g (0.07 mmol) of **2** in 3 cm^3 of water was added 2.0 cm^3 of 1 M aqueous HBr. This mixture was stirred at room temperature for 1 h and then allowed to stand at room temperature for 1 day. The resulting red plate crystals of $1_{Br}\cdot H_2O$ were collected by filtration. Yield: 0.05 g (50%).

Conversion of 1_{Br} to 2. To a solution containing 0.10 g (0.13 mmol) of $1_{Br}\cdot H_2O$ in 3 cm^3 of water was added 2.0 cm^3 of saturated aqueous NaBr. This mixture was stirred at room temperature for 1 h and then allowed to stand at room temperature for 1 day. The resulting dark brown block crystals of **2** were collected by filtration. Yield: 0.07 g (78%).

Preparation of Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$][CdI$_4$] (3). To a solution containing 0.20 g (0.38 mmol) of Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2\cdot$1.5H$_2$O in 20 cm^3 of water was added 0.15 g (0.40 mmol) of CdI$_2$. This mixture was stirred at room temperature for 30 min. To the dark brown reaction solution (pH 1.6) was added 2.0 cm^3 of saturated aqueous NaI. An insoluble dark brown residue was filtered off, and the dark brown filtrate was allowed to stand at room temperature for 2 days. The resulting dark brown block crystals ($3\cdot H_2O$) suitable for X-ray analysis were collected by filtration. Yield: 0.16 g (46%). Anal. Calcd for [Co(Hcys)(en)$_2$][CdI$_4$]$\cdot$H$_2$O ($3\cdot H_2O$), $C_7H_{24}CdCoI_4N_5O_3S$: C, 8.97; H, 2.58; N, 7.47. Found: C, 8.92; H, 2.54; N, 7.51.

Preparation of (Λ_L)$_n$-[CdCl$_3${Co(L-cys-*N*,*S*)(en)$_2$}]$_n$ (4_{Cl}). To a solution containing 0.16 g (0.40 mmol) of Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]ClO$_4$ in 5 cm^3 of water was added 0.09 g (0.40 mmol) of $CdCl_2\cdot 2.5H_2O$. This mixture was stirred at room temperature for 1 h. To the dark brown reaction solution (pH ∼ 6) was added 4.0 cm^3 of saturated aqueous NaCl, and the mixture was allowed to stand at room temperature for 2 days. The resulting dark red needle crystals ($4_{Cl}\cdot 0.25NaCl\cdot 3H_2O$) suitable for X-ray analysis were collected by filtration. Yield: 0.15 g (62%). Anal. Calcd for [CdCl$_3${Co(cys)(en)$_2$}]$\cdot$0.25NaCl$\cdot$3H$_2$O ($4_{Cl}\cdot 0.25NaCl\cdot 3H_2O$), $C_7H_{27}CdCl_{3.25}CoN_5Na_{0.25}O_5S$: C, 14.35; H, 4.65; N, 11.96. Found: C, 14.26; H, 4.58; N, 12.26.

Conversion of 1_{Cl} to 4_{Cl}. To a solution containing 0.10 g (0.17 mmol) of $1_{Cl}\cdot H_2O$ in 3 cm^3 of water was added 0.18 cm^3 of 1 M aqueous NaOH. This mixture was stirred at room temperature for 1 h. To the dark brown reaction solution (pH ∼ 6) was added 3.0 cm^3 of saturated aqueous NaCl, and the mixture was allowed to

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[16] Freeman, H. C.; Moore, C. J.; Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1978**, *17*, 3513−3521.

Table 1. Crystallographic Data for Complexes

	$1_{Cl}\cdot H_2O$	$1_{Br}\cdot H_2O$	**2**	$3\cdot H_2O$	$4_{Cl}\cdot 0.25NaCl\cdot 3H_2O$	$4_{NCS}\cdot 2H_2O$
empirical formula	$C_7H_{24}Cd_1Cl_4Co_1N_5$	$C_7H_{24}Br_4Cd_1Co_1N_5O_3S_1$	$C_7H_{21.5}Br_{3.5}Cd_1Co_1N_5O_2S_1$	$C_7H_{24}Cd_1Co_1I_4N_5O_3$	$C_7H_{27}N_5CdCl_{3.25}CoNa_{0.25}O_5S$	$C_{10}H_{25}Cd_1Co_1N_8O_4S_4$
fw	571.52	749.34	690.87	937.30	585.69	620.95
space group	$P2_1$ (no. 4)	$P2_1$ (no. 4)	$P4_12_12$ (no. 92)	$P2_1$ (no. 4)	$C2$ (no. 5)	$P2_12_12_1$ (no. 19)
a, Å	8.4196(9)	8.572(2)	12.230(2)	8.773(1)	27.032(1)	13.233(2)
b, Å	12.297(2)	12.608(2)		15.067(2)	12.7921(5)	13.365(2)
c, Å	9.8194(8)	10.165(2)	24.401(5)	8.937(1)	23.552(1)	12.723(2)
β, deg	109.048(7)	108.48(2)		102.767(9)	98.243(1)	
V, Å^3	961.0(2)	1041.9(3)	3649.8(9)	1152.2(2)	8060.3(6)	2250.1(6)
Z	2	2	8	2	16	4
T, K	296(1)	296(1)	296(1)	296(1)	153(1)	296(1)
ρ_{calcd}, g cm^{-1}	1.975	2.389	2.515	2.702	1.931	1.833
μ (Mo Kα), cm^{-1}	26.48	96.00	98.59	71.05	24.44	20.88
$2\theta_{max}$	60	60	60	60	54.0	60
total no. of reflns	3088	3362	3867	3692	14 024	3663
no. of unique reflns	2914	3176	3232	3496	8761	3663
no. of parameters	204	200	191	237	535	256
goodness of fit on F^2	1.070	1.022	1.017	1.064	1.279	1.003
$R\ [I > 2\sigma(I)]^a$	0.022	0.032	0.043	0.028	0.053	0.046
$R_w{}^b$	0.055	0.076	0.125	0.076	0.184	0.112

[a] $R = \Sigma|(|F_o| - |F_c|)|/\Sigma(|F_o|)$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)|^2/\Sigma w(|F_o|)^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

stand at room temperature for 1 day. The resulting dark red needle crystals ($\mathbf{4}_{Cl}\cdot 0.25NaCl\cdot 3H_2O$) were collected by filtration. Yield: 0.03 g (30%).

Conversion of $\mathbf{4}_{Cl}$ to $\mathbf{1}_{Cl}$. To a solution containing 0.10 g (0.17 mmol) of $\mathbf{4}_{Cl}\cdot 0.25NaCl\cdot 3H_2O$ in 5 cm^3 of water was added 1.0 cm^3 of 1 M aqueous HCl. This mixture was stirred at room temperature for 1 h. To the dark brown reaction solution (pH < 1) was added 2.0 cm^3 of saturated aqueous NaCl, and the mixture was allowed to stand at room temperature for 1 day. The resulting dark red plate crystals ($\mathbf{1}_{Cl}\cdot H_2O$) were collected by filtration. Yield: 0.08 g (77%).

Preparation of $(\Lambda_L)_n$-[Cd(NCS)$_3${Co(L-cys-*N*,*S*)(en)$_2$}]$_n$ ($\mathbf{4}_{NCS}$). To a solution containing 0.16 g (0.40 mmol) of Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]ClO$_4$ in 30 cm^3 of water was added 0.17 g (0.40 mmol) of $Cd(ClO_4)_2\cdot 6H_2O$. This mixture was stirred at room temperature for 1 h. To the dark brown reaction solution (pH ~ 6) was added 2.0 g (25 mmol) of NaSCN, and the mixture was allowed to stand at room temperature for 3 days. The resulting dark red stick crystals ($\mathbf{4}_{NCS}\cdot 2H_2O$) suitable for X-ray analysis were collected by filtration. Yield: 0.17 g (71%). Anal. Calcd for [Cd(NCS)$_3${Co(cys)(en)$_2$}]$\cdot$2H$_2$O ($\mathbf{4}_{NCS}\cdot 2H_2O$), $C_{10}H_{25}CdCoN_8O_4S$: C, 19.34; H, 4.06; N, 18.05. Found: C, 19.34; H, 3.88; N, 18.26.

Caution: Perchlorate salts of metal complexes are potentially explosive and should be handled with great care.

Measurements. The electronic absorption spectra were recorded on a Ubest-55 spectrophotometer and the CD spectra on a Jasco J-600 spectropolarimeter at room temperature. The electronic absorption and the CD spectra in the solid state were measured by the Nujol mull method.[17] The IR spectra were measured with a Jasco FT/IR-5000 infrared spectrophotometer by use of KBr disks. The elemental analyses (C, H, N) were performed by the Analysis Center of Osaka University. The X-ray fluorescence analyses were made on a Horiba MESA-500 spectrometer.

X-ray Structural Determinations. Single-crystal X-ray diffraction experiments for $\mathbf{1}_{Cl}\cdot H_2O$, $\mathbf{1}_{Br}\cdot H_2O$, $\mathbf{3}\cdot H_2O$, and $\mathbf{4}_{NCS}\cdot 2H_2O$ were performed on a Rigaku AFC-5R diffractometer, while those for **2** were performed on a Rigaku AFC-7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) at 23 °C. Unit-cell parameters of these complexes were determined by a least-squares refinement, using the angular setting of 25 centered reflections. The intensity data were collected by the $\omega-2\theta$ scan technique. The intensities were collected for Lorentz and polarization. Empirical absorption corrections based on a series of ψ scans were also applied. Single-crystal X-ray diffraction experiments for $\mathbf{4}_{Cl}\cdot 0.25NaCl\cdot 3H_2O$ were performed on a Rigaku/MSC Mercury charge-coupled device (CCD) with graphite-monochromated Mo Kα radiation (λ = 0.710 70 Å) at −120 °C. Unit cell parameters were determined by a least-squares refinement, and the intensity data were collected by the ω scan technique. Semiempirical absorption corrections with SADABS were also applied. Crystallographic data of the complexes are summarized in Table 1. The positions of Cd, Co, and some other atoms were determined by direct methods (SHELXL-97 or SIR97). The remaining non-H atom positions were found by successive difference Fourier techniques. The structures were refined by full-matrix least-squares techniques with anisotropic thermal parameters for non-H atom. Hydrogen atoms except those of water molecules were placed at calculated positions and were treated as riding models. In **3**, one en chelate ring is disordered over two positions (C6−C7 and C6A−C7A),

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(17) (a) Taniguchi, Y.; Shimura, Y. *Chem. Lett.* **1979**, 1091−1094. (b) Taniguchi, Y.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 754−758. (c) Taniguchi, Y.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2847−2850.

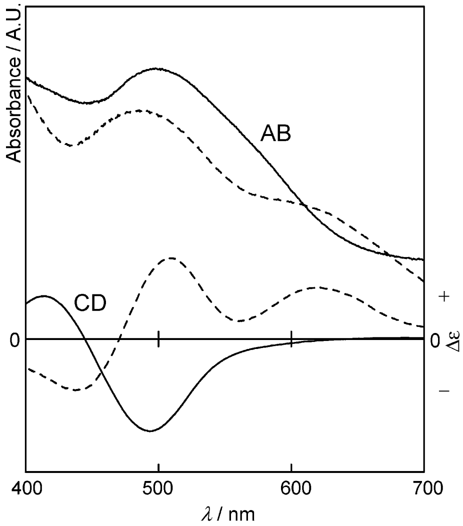

Figure 1. Absorption (AB) and circular dichroic (CD) spectra of Λ_L-[CdCl$_4${Co(L-Hcys-*N*,*S*)(en)$_2$}] ($\mathbf{1_{Cl}}$) (—) and Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ (---) in the solid state.

which were refined with site occupancy of 0.5. In $\mathbf{4_{Cl}}$, Cd, Co, Cl, and S atoms were refined anisotropically, while the other atoms were refined isotropically. Some of the solvated water molecules in $\mathbf{4_{Cl}}$ were disordered and were refined with site occupancy of 0.5 or 0.25. All calculations were carried out with the CrystalStructure software package.[18]

Results and Discussion

Reactions of Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ with CdX$_2$ (X = Cl, Br, I). A dark brown aqueous solution of Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$[16] having a free COOH group was treated with CdCl$_2$ in a 1:1 ratio at room temperature. While the absorption spectrum of the reaction solution was identical with that of the starting Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ in water, the addition of NaCl to the reaction mixture led to the isolation of plate crystals ($\mathbf{1_{Cl}}$·H$_2$O) that are dark red in color. X-ray fluorescence spectrometry indicated the presence of Co and Cd atoms in $\mathbf{1_{Cl}}$, and its elemental analytical data were in good agreement with the formula of [Co(L-Hcys-*N*,*S*)(en)$_2$][CdCl$_4$]. The IR spectrum of $\mathbf{1_{Cl}}$ in the solid state shows a relatively sharp C=O stretching band at 1713 cm^{-1}, as does Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$, indicative of the presence of a protonated COOH group (Figure S1, Supporting Information).[19] In the solid-state absorption spectrum of $\mathbf{1_{Cl}}$, a d−d absorption shoulder (ca. 600 nm) characteristically observed for Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ disappears with the shift of an absorption peak from 484 to 500 nm (Figure 1). This is suggestive of the formation of a Cd−S bond in $\mathbf{1_{Cl}}$, considering the fact that the binding of a thiolato group in [Co(aet)(en)$_2$]$^{2+}$, [Co(tga)(en)$_2$]$^{+}$, or [Co(L-cys-*N*,*S*)(en)$_2$]$^{+}$ toward a second metal center commonly induces the loss of the d−d absorption shoulder at ca. 600 nm.[11−13,15] On the basis of these results, $\mathbf{1_{Cl}}$ is assigned to be a 1:1 adduct of [Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ and [CdCl$_4$]$^{2-}$ that are linked through a Cd−S bond. Indeed, X-ray crystallography established that $\mathbf{1_{Cl}}$ has an S-bridged Co^{III}Cd^{II} dinuclear structure in Λ_L-[CdCl$_4${Co(L-Hcys-*N*,*S*)(en)$_2$}] (vide infra). In the solid-state CD spectrum, $\mathbf{1_{Cl}}$ gives a major negative CD band at 494 nm in the d−d absorption band region, which differs markedly from the CD spectral feature for the mononuclear Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ (Figure 1). The additional chirality (*S* configuration) due to the bridging S atom in $\mathbf{1_{Cl}}$, together with the difference in the conformational chirality of L-Hcys chelate ring between $\mathbf{1_{Cl}}$ (δ conformation) and Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ (λ conformation),[20] seems to be responsible for this CD spectral difference.

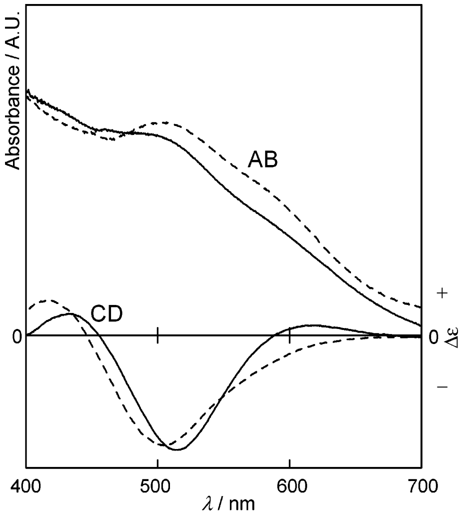

Figure 2. Absorption (AB) and circular dichroic (CD) spectra of $(\Lambda_L)_2$-[CdBr$_3${Co(L-Hcys-*N*,*S*)(en)$_2$}{Co(L-cys-*N*,*S*)(en)$_2$}][CdBr$_4$] (**2**) (—) and Λ_L-[CdBr$_4${Co(L-Hcys-*N*,*S*)(en)$_2$}] ($\mathbf{1_{Br}}$) (---) in the solid state.

Similar treatment of Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ with CdBr$_2$ in a 1:1 ratio, followed by the addition of NaBr, produced dark brown block crystals (**2**). The absorption spectral feature of **2** in the solid state is not similar to that of $\mathbf{1_{Cl}}$, showing an ill-defined d−d absorption peak at ca. 495 nm (Figure 2). Furthermore, in the solid-state CD spectrum, **2** gives a positive CD band at 616 nm, which is not observed in the spectrum of $\mathbf{1_{Cl}}$. Thus, it is assumed that **2** has a solid-state structure different from that of $\mathbf{1_{Cl}}$. The elemental analytical data of **2** do not match with the formula of [Co(L-Hcys-*N*,*S*)(en)$_2$][CdBr$_4$] that corresponds to the formula of $\mathbf{1_{Cl}}$, but with the formula of [Co(L-H$_{0.5}$cys-*N*,*S*)(en)$_2$][CdBr$_{3.5}$] having a semiprotonated carboxyl group. The presence of a semiprotonated carboxyl group in **2** is evidenced by its IR spectrum that exhibits a rather weak C=O stretching band at 1715 cm^{-1} (Figure S2). X-ray crystallography indicated that **2** is an S-bridged Co^{III}Cd^{II}Co^{III} trinuclear complex salt consisting of a $(\Lambda_L)_2$-[CdBr$_3${Co(L-Hcys-*N*,*S*)(en)$_2$}{Co(L-cys-*N*,*S*)(en)$_2$}]$^{2+}$ complex cation and a [CdBr$_4$]$^{2-}$ counteranion (vide infra).

When excess HBr was added to the reaction mixture of Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ and CdBr$_2$, dark brown plate crystals of $\mathbf{1_{Br}}$, the elemental analytical data of which are consistent with the formula of [Co(L-Hcys-*N*,*S*)(en)$_2$][CdBr$_4$], were isolated. The absorption and CD spectral

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(18) CrystalStructure Analysis Package, Rigaku and MSC, 2001.

(19) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1997.

(20) Aridomi, T.; Igashira-Kamiyama, A.; Kawamoto, T.; Konno, T. *Acta Crystallogr.* **2006**, *E62*, m1838−m1840.

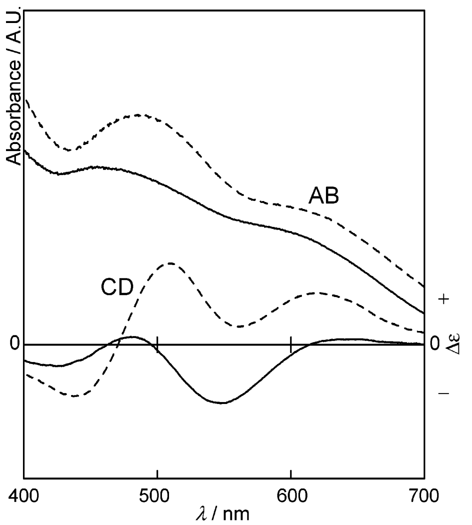

Figure 3. Absorption (AB) and circular dichroic (CD) spectra of Λ_{L}-[Co(L-Hcys-*N*,*S*)(en)$_2$][CdI$_4$] (**3**) (—) and Λ_{L}-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ (---) in the solid state.

features of $\mathbf{1}_{\mathrm{Br}}$ in the solid state resemble those of $\mathbf{1}_{\mathrm{Cl}}$, although its d−d absorption band is located at the longer wavelength side of 500 nm (Figure 2). In the IR spectrum, $\mathbf{1}_{\mathrm{Br}}$ gives a strong C=O stretching band at 1705 cm^{-1} due to the COOH group, as does $\mathbf{1}_{\mathrm{Cl}}$ (Figure S2, Supporting Information). Judging from these results, $\mathbf{1}_{\mathrm{Br}}$ is assigned to have an S-bridged Co$^{\mathrm{III}}$Cd$^{\mathrm{II}}$ dinuclear structure in Λ_{L}-[CdBr$_4${Co(L-Hcys-*N*,*S*)(en)$_2$}], which was unambiguously confirmed by X-ray crystallography (vide infra).

Treatment of Λ_{L}-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ with CdI$_2$ was also carried out under similar conditions, which gave dark brown block crystals (**3**) after the addition of NaI. The elemental analysis implies that **3** is a 1:1 adduct of [Co(L-Hcys)(en)$_2$]$^{2+}$ and [CdI$_4$]$^{2-}$, which is analogous to $\mathbf{1}_{\mathrm{Cl}}$ and $\mathbf{1}_{\mathrm{Br}}$. However, the absorption spectrum of **3** is similar to that of the mononuclear Λ_{L}-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$, rather than the spectra of $\mathbf{1}_{\mathrm{Cl}}$ and $\mathbf{1}_{\mathrm{Br}}$, showing a d−d absorption peak at 460 nm with a clear shoulder at ca. 600 nm (Figure 3). Thus, **3** is considered to be a monomeric Co$^{\mathrm{III}}$ species, in which a thiolato group does not bind with a Cd$^{\mathrm{II}}$ center. X-ray analysis revealed that **3** is a mononuclear Λ_{L}-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ having [CdI$_4$]$^{2-}$ as a counteranion (vide infra). It is interesting to note that the CD spectrum of **3** in the solid state differs significantly from that of the starting Λ_{L}-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ (Figure 3). The CD spectral difference between **3** and Λ_{L}-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ is likely due to the difference in the conformational chirality of the L-Hcys chelate ring; it was shown by X-ray analysis that the L-Hcys chelate ring in **3** has the δ conformation with an axially oriented COOH group, while that in Λ_{L}-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ has the λ conformation with an equatorially oriented COOH group (vide infra).[20]

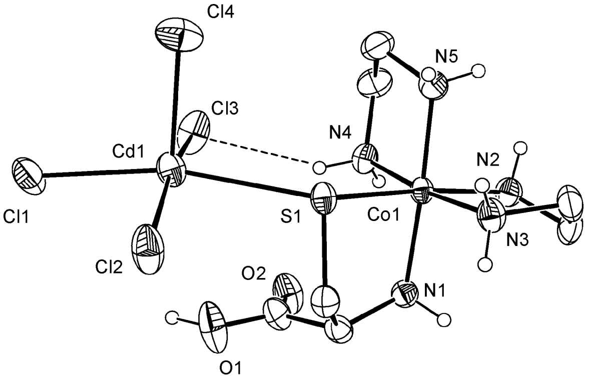

Figure 4. ORTEP drawing (30% probability ellipsoids) of Λ_{L}-[CdCl$_4${Co(L-Hcys-*N*,*S*)(en)$_2$}] ($\mathbf{1}_{\mathrm{Cl}}$) with the atomic labeling scheme. H atoms bonded to C atoms are omitted for clarity.

Table 2. Selected Bond Distances and Angles for Λ_{L}-[CdCl$_4${Co(L-Hcys-*N*,*S*)(en)$_2$}]·H$_2$O ($\mathbf{1}_{\mathrm{Cl}}$·H$_2$O)

	Distances (Å)		
Cd1−S1	2.7753(9)	Co1−S1	2.2652(9)
Cd1−Cl1	2.611(1)	Co1−N1	1.993(3)
Cd1−Cl2	2.486(1)	Co1−N2	1.958(3)
Cd1−Cl3	2.536(1)	Co1−N3	1.994(3)
Cd1−Cl4	2.530(1)	Co1−N4	1.972(3)
		Co1−N5	1.964(3)
	Angles (deg)		
S1−Cd1−Cl1	166.76(3)	Cl2−Cd1−Cl4	100.32(5)
S1−Cd1−Cl2	83.72(3)	Cl3−Cd1−Cl4	95.99(4)
S1−Cd1−Cl3	94.41(3)	S1−Co1−N1	87.43(9)
S1−Cd1−Cl4	92.20(4)	S1−Co1−N3	173.0(1)
Cl1−Cd1−Cl2	89.79(4)	S1−Co1−N5	95.33(9)
Cl1−Cd1−Cl3	88.56(4)	N2−Co1−N3	84.8(1)
Cl1−Cd1−Cl4	100.33(4)	N3−Co1−N5	91.2(1)
Cl2−Cd1−Cl3	163.64(5)	N4−Co1−N5	84.8(1)

Crystal Structures of $\mathbf{1}_{\mathrm{Cl}}$, $\mathbf{1}_{\mathrm{Br}}$, 2, and 3. X-ray structural analysis of $\mathbf{1}_{\mathrm{Cl}}$·H$_2$O revealed the presence of a discrete complex molecule ($\mathbf{1}_{\mathrm{Cl}}$) and a solvated water molecule. The structure of the complex molecule is shown in Figure 4, and its selected bond distances and angles are listed in Table 2. The complex molecule $\mathbf{1}_{\mathrm{Cl}}$ consists of an approximately octahedral [Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ unit and a [CdCl$_4$]$^{2-}$ moiety. The thiolato S atom in the [Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ unit coordinates to a Cd$^{\mathrm{II}}$ center of the [CdCl$_4$]$^{2-}$ moiety, forming an S-bridged Co$^{\mathrm{III}}$Cd$^{\mathrm{II}}$ dinuclear structure in Λ_{L}-[CdCl$_4${Co(L-Hcys-*N*,*S*)(en)$_2$}]. The coordination environment about the Cd$^{\mathrm{II}}$ atom in $\mathbf{1}_{\mathrm{Cl}}$ is best described as a slightly distorted square-pyramid, based on an angular structural parameter $\tau = 0.05$[21] or $\chi = 0.20$,[10c,13] in which the basal plane is occupied by three Cl and one S atoms and the apical site is coordinated by one Cl atom. While a number of crystal structures of tetrahalocadmate(II) anions, [CdX$_4$]$^{2-}$ (X=Cl,[22] Br,[23] I[24]), have been presented, to our knowledge, five-coordinated cadmium(II) species with one S and four X atoms have not been reported so far. As expected, the chiral configuration about the [Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ unit in $\mathbf{1}_{\mathrm{Cl}}$ is Λ, like the starting mononuclear Λ_{L}-[Co(L-Hcys-*N*,*S*)-

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(21) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.

(22) For example: (a) Doudin, B.; Chapuis, G. *Acta Crystallogr.* **1992**, *C48*, 1218−1220. (b) Zompa, L. J.; Haidar, R. *Acta Crystallogr.* **1996**, *C52*, 1188−1190. (c) Mahoui, A.; Lapasset, J.; Moret, J.; Grégoire, P. S. *Acta Crystallogr.* **1996**, *C52*, 2671−2674. (d) Exarchos, G.; Robinson, S. D.; Steed, J. W. *Polyhedron* **2001**, *20*, 2951−2963.

(23) For example: (a) Geselle, M.; Fuess, H. *Acta Crystallogr.* **1994**, *C50*, 1582−1585. (b) Ravikumar, K.; Lakshmi, N. V.; Swamy, G. Y. S. K.; Mohan, K. C. *Acta Crystallogr.* **1995**, *C51*, 1556−1558. (c) Buvaylo, E. A.; Kokozay, V. N.; Vassilyeva, O. Y.; Skelton, B. W.; Jezierska, J.; Brunel, L. C.; Ozarowski, A. *Inorg. Chem.* **2005**, *44*, 206−216. (d) Zhang, H.; Fang, L. *Acta Crystallogr.* **2005**, *E61*, m101−m102. (e) Kropidłowska, A.; Chojnacki, J.; Becker, B. *Acta Crystallogr.* **2006**, *E62*, m457−m459.

Table 3. Selected Bond Distances and Angles for Λ_{L}-[$CdBr_4${Co(L-Hcys-*N*,*S*)$(en)_2$}]·H_2O ($\mathbf{1}_{\mathbf{Br}}$·H_2O)

	Distances (Å)		
Cd1−S1	2.876(2)	Co1−S1	2.272(2)
Cd1−Br1	2.644(1)	Co1−N1	2.001(6)
Cd1−Br2	2.598(1)	Co1−N2	1.999(5)
Cd1−Br3	2.637(1)	Co1−N3	1.959(6)
Cd1−Br4	2.780(1)	Co1−N4	1.958(6)
		Co1−N5	1.968(6)
	Angles (deg)		
S1−Cd1−Br1	91.21(5)	Br2−Cd1−Br4	91.46(4)
S1−Cd1−Br2	83.84(5)	Br3−Cd1−Br4	88.13(4)
S1−Cd1−Br3	92.85(5)	S1−Co1−N1	87.6(2)
S1−Cd1−Br4	169.29(5)	S1−Co1−N2	172.5(2)
Br1−Cd1−Br2	103.63(4)	S1−Co1−N4	90.1(2)
Br1−Cd1−Br3	96.96(4)	N2−Co1−N3	84.5(3)
Br1−Cd1−Br4	99.27(4)	N2−Co1−N4	93.3(2)
Br2−Cd1−Br3	159.19(4)	N4−Co1−N5	84.9(3)

$(en)_2]^{2+}$. In $\mathbf{1}_{\mathbf{Cl}}$, the *N*,*S*-chelate ring of the L-Hcys ligand adopts a δ conformation, which regulates the free COOH group to an axial orientation so as to cover the sixth coordination site of the Cd^{II} center with the Cd···O separation of 3.273(4) Å. This is distinct from the fact that the COOH group in the mononuclear Λ_{L}-[Co(L-Hcys-*N*,*S*)$(en)_2]^{2+}$ has an equatorial orientation with a λ configurational *N*,*S*-chelate ring,[20] although its deprotonated form, Λ_{L}-[Co(L-cys-*N*,*S*)-$(en)_2]^{+}$, possesses an axially oriented COO^- group with a δ configurational *N*,*S*-chelate ring.[16] The Cd−S distance in $\mathbf{1}_{\mathbf{Cl}}$ is 2.7753(9) Å (Table 2), which is much longer than those found in S-bridged polycadmium(II) complexes with related aliphatic thiolate ligands (2.51−2.57 Å).[25] Furthermore, this distance is still longer than those in the related S-bridged $Co^{III}Cd^{II}$ complexes composed of $[Co(aet)(en)_2]^{2+}$ units, ΔΛ-$[CdCl_4\{Co(aet)(en)_2\}_2]^{2+}$ (Cd−S = 2.716(1) Å) and ΛΛ-$[Cd_2Cl_7\{Co(aet)(en)_2\}_2]^{+}$ (Cd−S =2.589(1), 2.656(1) Å).[12] It has been shown that there exists a multiple intramolecular hydrogen bonding between Cl and amine N atoms in ΔΛ-$[CdCl_4\{Co(aet)(en)_2\}_2]^{2+}$ and ΛΛ-$[Cd_2Cl_7\{Co(aet)(en)_2\}_2]^{+}$, which sustains their S-bridged $Co^{III}Cd^{II}$ structures. On the other hand, only a weak intramolecular NH···Cl hydrogen bond is found in $\mathbf{1}_{\mathbf{Cl}}$ (N5···Cl3 = 3.318(3) Å). Thus, the inherent weak binding ability of a thiolato group in a Co^{III} octahedron, together with the absence of effective intramolecular hydrogen bonds, seems to be responsible for the elongated Cd−S bond in $\mathbf{1}_{\mathbf{Cl}}$. The Cd−Cl distance *trans* to the S atom (2.611(1) Å) is longer than the Cd−Cl distances *cis* to the S atom (average 2.517(1) Å), indicative of a greater *trans* influence due to a thiolato donor relative to that due to a Cl donor.

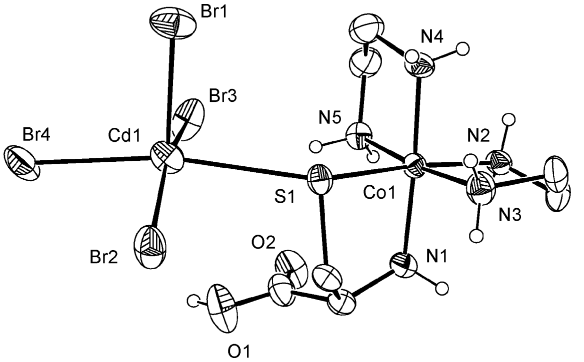

Figure 5. ORTEP drawing (30% probability ellipsoids) of Λ_{L}-[$CdBr_4$-{Co(L-Hcys-*N*,*S*)$(en)_2$}] ($\mathbf{1}_{\mathbf{Br}}$) with the atomic labeling scheme. Hydrogen atoms bonded to C atoms are omitted for clarity.

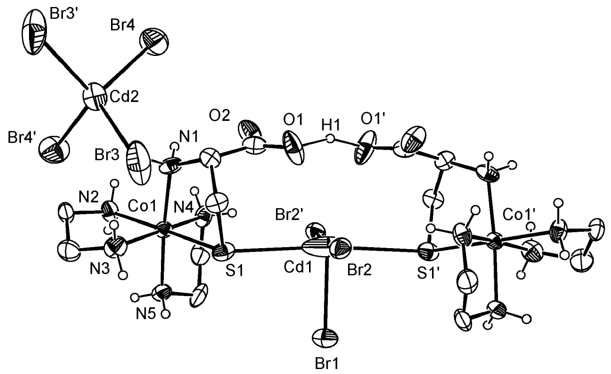

Figure 6. ORTEP drawing (30% probability ellipsoids) of $(\Lambda_{\mathrm{L}})_2$-[$CdBr_3$-{Co(L-Hcys-*N*,*S*)$(en)_2$}{Co(L-cys-*N*,*S*)$(en)_2$}][$CdBr_4$] (**2**) with the atomic labeling scheme. Hydrogen atoms bonded to C atoms are omitted for clarity.

X-ray analysis indicated that $\mathbf{1}_{\mathbf{Br}}$·H_2O is isomorphous with $\mathbf{1}_{\mathbf{Cl}}$·H_2O, and thus the overall structure of $\mathbf{1}_{\mathbf{Br}}$·H_2O is essentially the same as that of $\mathbf{1}_{\mathbf{Cl}}$·H_2O (Table 3). In the complex molecule $\mathbf{1}_{\mathbf{Br}}$, a Λ configurational [Co(L-Hcys-*N*,*S*)-$(en)_2]^{2+}$ unit is linked with a $[CdBr_4]^{2-}$ moiety through a Cd−S bond, forming an S-bridged $Co^{III}Cd^{II}$ dinuclear structure in Λ_{L}-[$CdBr_4${Co(L-Hcys-*N*,*S*)$(en)_2$}] (Figure 5). The Cd^{II} atom in $\mathbf{1}_{\mathbf{Br}}$ adopts a distorted square-pyramidal geometry ($\tau = 0.18$, $\chi = 0.29$), coordinated by one thiolato S and four Br atoms, and its sixth coordination site is covered with an axially oriented COOH group of the Λ_{L}-[Co(L-Hcys-*N*,*S*)$(en)_2]^{2+}$ unit (Cd···O = 3.403(8) Å). The Cd−S distance (2.876(2) Å) in $\mathbf{1}_{\mathbf{Br}}$ is ca. 0.10 Å longer than that in $\mathbf{1}_{\mathbf{Cl}}$, indicative of the much weaker binding of the thiolato S atom of the Λ_{L}-[Co(L-Hcys-*N*,*S*)$(en)_2]^{2+}$ unit in $\mathbf{1}_{\mathbf{Br}}$ to a Cd^{II} center. The averaged Cd−Br distance in $\mathbf{1}_{\mathbf{Br}}$ (2.665(1) Å) is ca. 0.12 Å longer than the averaged Cd−Cl distance in $\mathbf{1}_{\mathbf{Cl}}$ (2.541(1) Å). This value is appreciably smaller than the difference in ionic radius between Cl^- and Br^- (0.15 Å).[26] Thus, it is considered that Br^- anions coordinate to a Cd^{II} center more strongly than do Cl^- anions, which results in the weaker binding of the thiolato S atom in $\mathbf{1}_{\mathbf{Br}}$ to the Cd^{II} center.

As shown in Figure 6, **2** was found to be a 1:1 complex salt consisting of a discrete $(\Lambda_{\mathrm{L}})_2$-[$CdBr_3${Co(L-Hcys-*N*,*S*)-

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(24) For example: (a) Bailey, R. D.; Pennington, W. T. *Acta Crystallogr.* **1995**, *C51*, 226−229. (b) Bengtsson-Kloo, L.; Berglund, J.; Stegemann, H.; Svensson, C.; Svensson, P. H. *Acta Crystallogr.* **1996**, *C52*, 3045−3047. (c) Wu, D.-D.; Mak, T. C. W. *Inorg. Chim. Acta* **1996**, *245*, 123−128. (d) Nesterova, O. V.; Petrusenko, S. R.; Dyakonenko, V. V.; Shishkin, O. V.; Linert, W. *Acta Crystallogr.* **2006**, *C62*, m281−m283.

(25) (a) Freeman, H. C.; Huq, F.; Stevens, G. N. *J. Chem. Soc., Chem. Commun.* **1976**, 90−91. (b) Fawcett, T. G.; Ou, C.-C.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 2058−2062. (c) Casals, I.; González-Duarte, P.; Sola, J.; Font-Bardia, M.; Solans, J.; Solans, X. *J. Chem. Soc. Dalton, Trans.* **1987**, 2391−2395. (d) Casals, I.; González-Duarte, P.; Clegg, W.; Foces-Foces, C.; Cano, F. H.; Martinez-Ripoll, M.; Gómez, M.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1991**, 2511−2518. (e) Clegg, W.; Casals, I.; González-Duarte, P. *Acta Crystallogr.* **1993**, *C49*, 129−130. (f) Mikuriya, M.; Jian, X.; Ikemi, S.; Kawahashi, T.; Tsutsumi, H.; Nakasone, A.; Lim, J.-W. *Inorg. Chim. Acta* **2001**, *312*, 183−187.

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Table 4. Selected Bond Distances and Angles for $(\Lambda_L)_2$-[$CdBr_3${Co(L-Hcys-*N*,*S*)$(en)_2$}{Co(L-cys-*N*,*S*)$(en)_2$}][$CdBr_4$] (**2**)

Distances (Å)			
Cd1−S1	3.046(3)	Co1−S1	2.259(3)
Cd1−Br1	2.646(2)	Co1−N1	1.991(9)
Cd1−Br2	2.574(1)	Co1−N2	1.999(8)
Cd2−Br3	2.578(2)	Co1−N3	1.954(9)
Cd2−Br4	2.582(2)	Co1−N4	1.961(9)
		Co1−N5	1.976(9)
Angles (deg)			
S1−Cd1−S1	174.9(1)	Br4−Cd2−Br4	102.5(1)
S1−Cd1−Br1	87.46(6)	S1−Co1−N1	86.5(3)
S1−Cd1−Br2	97.41(6)	S1−Co1−N2	176.3(3)
Br1−Cd1−Br2	94.55(5)	S1−Co1−N4	94.3(3)
Br2−Cd1−Br2	170.91(9)	N2−Co1−N3	84.1(4)
Br3−Cd2−Br3	112.9(1)	N2−Co1−N4	89.4(4)
Br3−Cd2−Br4	116.16(5)	N4−Co1−N5	85.7(4)
Br3−Cd2−Br4	104.52(9)		

$(en)_2$}{Co(L-cys-*N*,*S*)$(en)_2$}]$^{2+}$ complex cation and a tetrahedral [$CdBr_4$]$^{2-}$ anion. In the complex cation of **2**, two octahedral Λ_L-[Co(L-cys-*N*,*S*)$(en)_2$]$^+$ units are linked by a T-shaped [$CdBr_3$]$^-$ moiety to give a $Co^{III}Cd^{II}Co^{III}$ trinuclear structure. The Cd^{II} atom in the complex cation of **2** is surrounded by two thiolato S atoms from two Λ_L-[Co(L-cys-*N*,*S*)$(en)_2$]$^+$ units and three Br^- anions to form a *trans*-[$CdBr_3S_2$] coordination environment with a distorted square pyramid ($\tau = 0.07$, $\chi = 0.12$). The averaged Cd−Br distance (2.598(2) Å) in the complex cation of **2** is shorter than that in $\mathbf{1_{Br}}$ (2.665(1) Å), while the Cd−S bonds (3.046(3) Å) are much elongated compared with that in $\mathbf{1_{Br}}$ (2.876(2) Å) (Table 4). This is ascribed to the nearly linear S−Cd−S arrangement in $\mathbf{1_{Br}}$ (S1−Cd−S1′ = 174.9(1)°), which induces a mutual *trans* influence between two thiolato donors. The striking structural feature of **2** is that the axially oriented COO^- groups from two Λ_L-[Co(L-cys-*N*,*S*)$(en)_2$]$^+$ units are bridged by a proton to form a strong intramolecular hydrogen bond with an O···O distance of 2.50(2) Å.[27] The bond distances of the tetrahedral [$CdBr_4$]$^{2-}$ anion in **2** (average Cd−Br = 2.580(2) Å) are within the range observed for the previously reported [$CdBr_4$]$^{2-}$ anions (2.56−2.60 Å).[23]

From the X-ray analysis, it was demonstrated that **3** is a 1:1 complex salt consisting of a mononuclear Λ_L-[Co(L-Hcys-*N*,*S*)$(en)_2$]$^{2+}$ cation and a [CdI_4]$^{2-}$ counteranion (Figure 7). The bond distances and angles around the Co^{III} center in **3** are very similar to those in Λ_L-[Co(L-Hcys-*N*,*S*)$(en)_2$]$(ClO_4)_2$.[20] However, the COOH group in **3** adopts an axial orientation with the δ conformational *N*,*S*-chelate ring, which is in contrast to the equatorial orientation of the COOH group with the λ conformational *N*,*S*-chelate ring in Λ_L-[Co(L-Hcys-*N*,*S*)$(en)_2$]$(ClO_4)_2$. This may be due to the difference in the number of counteranions between **3** (one [CdI_4]$^{2-}$ anion) and Λ_L-[Co(L-Hcys-*N*,*S*)$(en)_2$]$(ClO_4)_2$ (two ClO_4^- anions), which could cause the difference in a packing effect. The Cd−I distances in the tetrahedral [CdI_4]$^{2-}$ anion of **3** (average 2.783(1) Å, Table 5) are similar to those found in the previously reported [CdI_4]$^{2-}$ anions (2.73−2.81 Å).[24]

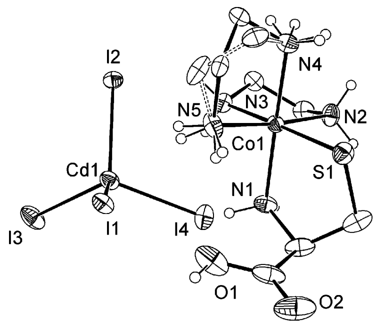

Figure 7. ORTEP drawing (30% probability ellipsoids) of Λ_L-[Co(L-Hcys-*N*,*S*)$(en)_2$][CdI_4] (**3**) with the atomic labeling scheme. One of the disorder components of en (C6A−C7A) and hydrogen atoms bonded to C atoms are omitted for clarity.

Table 5. Selected Bond Distances and Angles for Λ_L-[Co(L-Hcys-*N*,*S*)$(en)_2$][CdI_4]·H_2O (**3**·H_2O)

Distances (Å)			
Cd1−I1	2.8035(8)	Co1−S1	2.234(2)
Cd1−I2	2.7788(8)	Co1−N1	2.000(6)
Cd1−I3	2.7635(9)	Co1−N2	1.965(6)
Cd1−I4	2.787(1)	Co1−N3	2.024(7)
		Co1−N4	1.974(7)
		Co1−N5	1.968(7)
Angles (deg)			
I1−Cd1−I2	114.28(3)	S1−Co1−N1	86.9(2)
I1−Cd1−I3	114.38(3)	S1−Co1−N3	175.7(2)
I1−Cd1−I4	99.66(3)	S1−Co1−N5	91.0(3)
I2−Cd1−I3	105.38(3)	N2−Co1−N3	84.5(3)
I2−Cd1−I4	105.92(3)	N3−Co1−N5	92.6(3)
I3−Cd1−I4	117.24(4)	N4−Co1−N5	85.0(3)

Reactions of Λ_L-[Co(L-cys-*N*,*S*)$(en)_2$]$^+$ with CdX_2 (X = Cl, SCN). To investigate the binding behavior of Λ_L-[Co(L-cys-*N*,*S*)$(en)_2$]$^+$ having a deprotonated COO^- group toward a Cd^{II} center, the 1:1 reaction of Λ_L-[Co(L-cys-*N*,*S*)$(en)_2$]ClO_4 with $CdCl_2$ in water was carried out. When excess NaCl was added to the dark brown reaction mixture, followed by allowing the mixture to stand at room temperature, dark red needle crystals ($\mathbf{4_{Cl}}$) were isolated. X-ray fluorescence spectrometry indicated that $\mathbf{4_{Cl}}$ contains Co and Cd atoms, and its elemental analytical data were consistent with the 1:1 adduct of [Co(L-cys-*N*,*S*)$(en)_2$]$^+$ and [$CdCl_3$]$^-$. The presence of a deprotonated carboxyl group in $\mathbf{4_{Cl}}$ is confirmed by the IR spectrum that gives a broad, intense C═O stretching band at 1613 cm^{-1} (Figure S3),[19] and the formation of a Cd−S bond is indicated by the lack of the absorption shoulder at ca. 600 nm in the solid-state spectrum (Figure 8). X-ray structural determination revealed that $\mathbf{4_{Cl}}$ does not have a discrete dinuclear structure but possesses a helical $(Co^{III}Cd^{II})_n$ chain structure in $(\Lambda_L)_n$-[$CdCl_3${Co(L-cys-*N*,*S*)$(en)_2$}$]_n$ (vide infra). Although the absorption spectrum of $\mathbf{4_{Cl}}$ in the solid state is very similar to that of $\mathbf{1_{Cl}}$, an appreciable difference is observed in the CD spectra (Figures 1 and 8). That is, a major negative CD band observed for $\mathbf{1_{Cl}}$ (494 nm) turns to a positive and a negative CD bands from the longer wavelength side for $\mathbf{4_{Cl}}$. The difference in the chiral configurations of bridging thiolato S atoms (*R* for $\mathbf{4_{Cl}}$ and *S* for $\mathbf{1_{Cl}}$), which was shown by X-ray analyses, besides the difference in the overall structures, seems to be related to this CD spectral difference.

When excess NaSCN was added to the 1:1 mixture of Λ_L-

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(27) (a) Braga, D.; Grepioni, F.; Sabatino, P.; Desiraju, G. R. *Organometallics* **1994**, *13*, 3532−3543. (b) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311−2327. (c) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375−1405. (d) Desiraju, G. R. *Acc. Chem. Res.* **2002**, *35*, 565−573.

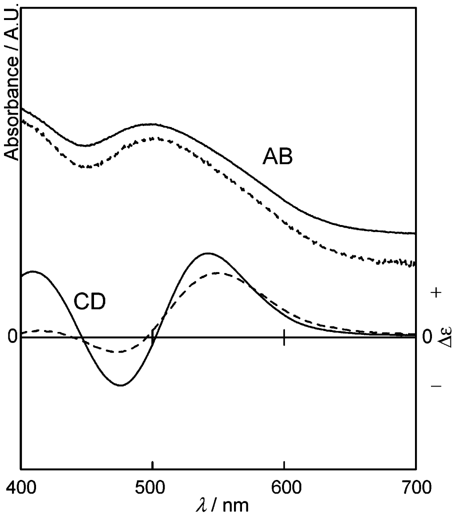

Figure 8. Absorption (AB) and circular dichroic (CD) spectra of $(\Lambda_L)_n$-$[CdCl_3\{Co(\text{L-cys-}N,S)(en)_2\}]_n$ ($\mathbf{4_{Cl}}$) (—) and $(\Lambda_L)_n$-$[Cd(NCS\text{-}N)_3\{Co(\text{L-cys-}N,S)(en)_2\}]_n$ ($\mathbf{4_{NCS}}$) (---) in the solid state.

$[Co(\text{L-cys-}N,S)(en)_2]ClO_4$ and $Cd(ClO_4)_2$ in water, dark red stick crystals of $\mathbf{4_{NCS}}$, the elemental analytical result of which is consistent with the formula of $[Co(\text{L-cys-}N,S)(en)_2][Cd(SCN)_3]$, were isolated. The absorption and CD spectral features of $\mathbf{4_{NCS}}$ in the solid state are very similar to those of $\mathbf{4_{Cl}}$ (Figure 8), and X-ray analysis indicated that $\mathbf{4_{NCS}}$ has a chain $(Co^{III}Cd^{II})_n$ structure in $[Cd(NCS\text{-}N)_3\{Co(\text{L-cys-}N,S)(en)_2\}]_n$, which is analogous to the structure in $\mathbf{4_{Cl}}$ (vide infra). In the IR spectrum, $\mathbf{4_{NCS}}$ gives two C═N stretching bands at 2070 and 2096 cm^{-1}, corresponding to two types of N-bonded NCS^- ions that are *trans* and *cis* to a thiolato S atom,[19] besides a broad C═O stretching band due to deprotonated COO^- group at 1620 cm^{-1} (Figure S3, Supporting Information).

Crystal Structures of $\mathbf{4_{Cl}}$ and $\mathbf{4_{NCS}}$. X-ray structural analysis of $\mathbf{4_{Cl}}\cdot 0.25NaCl\cdot 3H_2O$ revealed the presence of an infinite complex molecule ($\mathbf{4_{Cl}}$), besides Na^+ and Cl^- ions and water molecules. The structure of the complex molecule is shown in Figure 9, and its selected bond distances and angles are listed in Table 6. The complex molecule $\mathbf{4_{Cl}}$ contains Λ_L-$[Co(\text{L-cys-}N,S)(en)_2]^+$ octahedral units and T-shaped $[CdCl_3]^-$ moieties in a 1:1 ratio. The thiolato S atom in each Λ_L-$[Co(\text{L-cys-}N,S)(en)_2]^+$ unit is bound to a Cd^{II} center of each $[CdCl_3]^-$ moiety to form an S-bridged Co^{III}-Cd^{II} repeating unit, Λ_L-$[CdCl_3\{Co(\text{L-cys-}N,S)(en)_2\}]$. The $Co^{III}Cd^{II}$ units are linked with one another through the chelation of a COO^- group of each Λ_L-$[Co(\text{L-cys-}N,S)(en)_2]^+$ unit toward an adjacent Cd^{II} center, completing a helical $(Co^{III}Cd^{II})_n$ chain structure. As a result, each Cd^{II} atom in $\mathbf{4_{Cl}}$ has a quasi-octahedral geometry, coordinated by one thiolato S and two carboxylate O atoms, besides three Cl^- anions. The COO^- group of each Λ_L-$[Co(\text{L-cys-}N,S)(en)_2]^+$ unit in $\mathbf{4_{Cl}}$ has an axial orientation with a δ conformational *N,S*-chelate ring, as has the COOH group in the dinuclear $\mathbf{1_{Cl}}$. However, each bridging S atom adopts an *R* configuration, which is opposite to the *S* configurational S atom in $\mathbf{1_{Cl}}$. The averaged Cd−Cl bond distance in $\mathbf{4_{Cl}}$ (2.616(7) Å) is slightly longer than that in $\mathbf{1_{Cl}}$ (2.541 (1) Å), as expected from the difference in the coordination number about a Cd^{II} center. In contrast, the Cd−S distances in $\mathbf{4_{Cl}}$ (average 2.597(5) Å) are considerably shorter than that in $\mathbf{1_{Cl}}$ (2.7953(9) Å). In $\mathbf{4_{Cl}}$, the *trans* position of the thiolato S atom is occupied by a carboxylate O atom with the S−Cd−O angle (average 150.1(4)°) considerably deviated from 180°. Thus, no effective *trans* influence would exist in $\mathbf{4_{Cl}}$, which results in the shorter Cd−S bond. The presence of an N−H···Cl [average (3.38(2) Å)] and two N−H···O (average 2.93(2) and 3.04(2) Å) hydrogen bonds between each S-bridged Co^{III}-Cd^{II} repeating unit in $\mathbf{4_{Cl}}$ seems to contribute in part to this observation. The Cd−O distances in $\mathbf{4_{Cl}}$ (average 2.41(1) Å) are within the range normally observed for Cd^{II} compounds with chelating carboxylate groups (2.33−2.50 Å).[28]

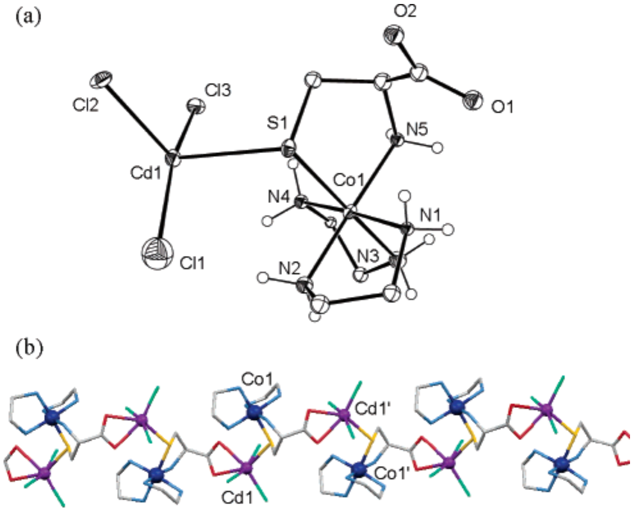

Figure 9. (a) ORTEP drawing (30% probability ellipsoids) of the asymmetric unit of $(\Lambda_L)_n$-$[CdCl_3\{Co(\text{L-cys-}N,S)(en)_2\}]_n$ ($\mathbf{4_{Cl}}$) with the atomic labeling scheme. Hydrogen atoms bonded to C atoms are omitted for clarity. (b) Helical $(Co^{III}Cd^{II})_n$ chain structure of $\mathbf{4_{Cl}}$. Hydrogen atoms are omitted for clarity.

Table 6. Selected Bond Distances and Angles for $(\Lambda_L)_n$-$[CdCl_3\{Co(\text{L-cys-}N,S)(en)_2\}]_n\cdot 0.25NaCl\cdot 3H_2O$ ($\mathbf{4_{Cl}}\cdot 0.25NaCl\cdot 3H_2O$)

	Distances (Å)		
Cd1−S1	2.590(5)	Co1−S1	2.253(5)
Cd1−O1	2.42(1)	Co1−N1	1.96(2)
Cd1−O2	2.42(1)	Co1−N2	1.97(1)
Cd1−Cl1	2.797(7)	Co1−N3	1.97(2)
Cd1−Cl2	2.441(5)	Co1−N4	1.98(2)
Cd1−Cl3	2.578(5)	Co1−N5	1.97(1)
	Averaged Distances (Å)		
Cd−S	2.597(5)	Cd−Cl	2.616(7)
Cd−O	2.41(1)	Co−S	2.271(6)
	Angles (deg)		
S1−Cd1−O1	149.2(3)	O1−Cd1−Cl2	99.3(3)
S1−Cd1−O2	94.3(3)	O1−Cd1−Cl3	88.5(3)
S1−Cd1−Cl1	84.5(2)	O2−Cd1−Cl1	74.4(4)
S1−Cd1−Cl2	110.3(2)	O2−Cd1−Cl2	151.2(3)
S1−Cd1−Cl3	93.6(2)	O2−Cd1−Cl3	91.0(3)
O1−Cd1−Cl1	85.7(4)		

X-ray analysis demonstrated that $\mathbf{4_{NCS}}$ has a helical $(Co^{III}$-$Cd^{II})_n$ structure analogous to that of $\mathbf{4_{Cl}}$, consisting of Λ_L-

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(28) (a) Li, X.; Cao, R.; Bi, W.; Wang, Y.; Wang, Y.; Li, X.; Guo, Z. *Cryst. Growth Des.* **2005**, *5*, 1651−1656. (b) Gao, S.; Liu, J.-W.; Huo, L.-H.; Zhao, J.-G. *Acta Crystallogr.* **2005**, *E61*, m1092−m1094. (c) Zhao, H.; Huo, L.-H.; Gao, S.; Zhao, J.-G. *Acta Crystallogr.* **2005**, *E61*, m2686−m2688. (d) Liu, C.-S.; Shi, X.-S.; Li, J.-R.; Wang, J.-J.; Bu, X.-H. *Cryst. Growth Des.* **2006**, *6*, 656−663.

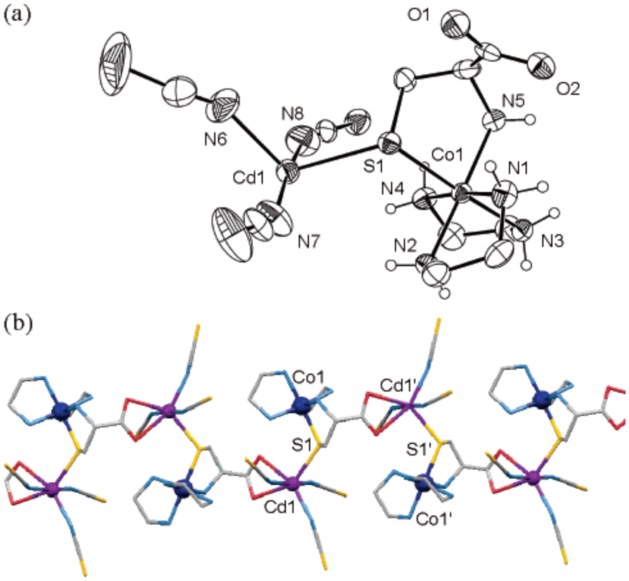

Figure 10. (a) ORTEP drawing (30% probability ellipsoids) of the asymmetric unit of $(\Lambda_\mathrm{L})_n$-[Cd(NCS-*N*)$_3${Co(L-cys-*N*,*S*)(en)$_2$}]$_n$ ($\mathbf{4_{NCS}}$) with the atomic labeling scheme. Hydrogen atoms bonded to C atoms are omitted for clarity. (b) Helical $(\mathrm{Co^{III}Cd^{II}})_n$ chain structure of $\mathbf{4_{NCS}}$. Hydrogen atoms are omitted for clarity.

Table 7. Selected Bond Distances and Angles for $(\Lambda_\mathrm{L})_n$-[Cd(NCS-*N*)$_3${Co(L-cys-*N*,*S*)(en)$_2$}]$_n$·2H$_2$O ($\mathbf{4_{NCS}}$·2H$_2$O)

	Distances (Å)		
Cd1−S1	2.603(3)	Co1−S1	2.271(3)
Cd1−O1	2.428(8)	Co1−N1	1.973(7)
Cd1−O2	2.392(7)	Co1−N2	1.981(7)
Cd1−N6	2.22(1)	Co1−N3	2.001(7)
Cd1−N7	2.34(1)	Co1−N4	1.963(7)
Cd1−N8	2.34(1)	Co1−N5	1.993(7)
	Angles (deg)		
S1−Cd1−O1	90.6(2)	S1−Co1−N1	90.2(2)
S1−Cd1−O2	145.1(2)	S1−Co1−N3	175.4(3)
S1−Cd1−N6	112.5(3)	S1−Co1−N5	86.3(2)
S1−Cd1−N7	87.0(3)	N2−Co1−N3	93.0(3)
S1−Cd1−N8	93.7(3)	N3−Co1−N5	90.1(3)
O1−Cd1−N6	156.9(4)	N4−Co1−N5	92.6(3)
O1−Cd1−N7	86.8(3)	Cd1−S1−Co1	118.7(2)
O1−Cd1−N8	85.7(3)	Cd1−N6−C8	152(1)
O2−Cd1−N6	102.4(4)	Cd1−N7−C9	156(1)
O2−Cd1−N7	90.4(3)	Cd1−N8−C10	157(1)
O2−Cd1−N8	84.8(3)		

[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units and [Cd(NCS)$_3$]$^-$ moieties in a 1:1 ratio (Figure 10). The Cd$^\mathrm{II}$ atom in $\mathbf{4_{NCS}}$ is situated in a quasi-octahedral geometry, surrounded by one thiolato S, two carboxylate O atoms, and three NCS$^-$ anions. Each NCS$^-$ ion coordinates to a Cd$^\mathrm{II}$ center via N atom with an average Cd−N distance of 2.30(1) Å (Table 7). This κN coordination mode is not rare for SCN$^-$ [29,30] but is relatively limited in number compared with μ_2-$\kappa N,S$ and μ_3-$\kappa N,S,S$ modes.[31] The Cd−S (2.603(3) Å) and Cd−O (2.428(8) and 2.392(7) Å) bond distances in $\mathbf{4_{NCS}}$ are very similar to those found in $\mathbf{4_{Cl}}$.

Construction of Co$^\mathrm{III}$Cd$^\mathrm{II}$ Structures. The chiral S-bridged Co$^\mathrm{III}$Cd$^\mathrm{II}$ dinuclear structure in Λ_L-[CdCl$_4${Co(L-Hcys-*N*,*S*)(en)$_2$}] ($\mathbf{1_{Cl}}$) was successfully obtained by treatment of Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ with CdCl$_2$ in a 1:1 ratio in water, assisted by the addition of NaCl (Scheme 1). The pH of the reaction solution was ca. 1.5, which permits the free carboxyl group to exist as a protonated form. The presence of extra Cl$^-$ ions in solution is required for the formation of [CdCl$_4$]$^{2-}$ that associates with the doubly charged Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ cation to precipitate the less soluble, neutral Λ_L-[CdCl$_4${Co(L-Hcys-*N*,*S*)(en)$_2$}] molecule. Similar treatment of Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ with CdBr$_2$ in water, followed by the addition of NaBr, did not give the analogous dinuclear complex, Λ_L-[CdBr$_4${Co(L-Hcys-*N*,*S*)(en)$_2$}] ($\mathbf{1_{Br}}$), but led to the construction of the S-bridged Co$^\mathrm{III}$Cd$^\mathrm{II}$Co$^\mathrm{III}$ trinuclear structure in $(\Lambda_\mathrm{L})_2$-[CdBr$_3${Co(L-Hcys-*N*,*S*)(en)$_2$}{Co(L-cys-*N*,*S*)(en)$_2$}][CdBr$_4$] (**2**). The preparation of $\mathbf{1_{Br}}$ was achieved by the addition of HBr to the reaction mixture, instead of NaBr. Comparison of the crystal structures of $\mathbf{1_{Cl}}$ and $\mathbf{1_{Br}}$ points out that the Cd−S bond in $\mathbf{1_{Br}}$ is much weaker than that in $\mathbf{1_{Cl}}$, affected by the stronger Cd−Br bonds relative to the Cd−Cl bonds. Thus, it is considered that under moderate acidic conditions (pH ∼1.5) Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ reacts with [CdBr$_4$]$^{2-}$ so as to construct the Co$^\mathrm{III}$Cd$^\mathrm{II}$Co$^\mathrm{III}$ trinuclear structure in **2** stabilized by a strong intramolecular COOH···OOC hydrogen bond, rather than the Co$^\mathrm{III}$Cd$^\mathrm{II}$ dinuclear structure in $\mathbf{1_{Br}}$ connected by a weak Cd−S bond. On the other hand, S-bridged species were not obtained by similar treatment of Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ with CdI$_2$ in water (pH ∼ 1.5), followed by the addition of NaI; the 1:1 complex salt consisting of Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ and [CdI$_4$]$^{2-}$, Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$][CdI$_4$] (**3**), was isolated. This is understood by the bulkiness of [CdI$_4$]$^{2-}$ formed in solution, which makes it hard to permit the coordination of the thiolato group in Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$. The stronger Cd−I bond, which in turn weakens the Cd−S bond, may also be account for this result. In addition to the choice of halide anions employed in the reactions, the change of solution pH affects the Co$^\mathrm{III}$Cd$^\mathrm{II}$ structures constructed. That is, treatment of the isolated **2** with aqueous HBr gave $\mathbf{1_{Br}}$, while $\mathbf{1_{Br}}$ was converted to **2** by its recrystallization from aqueous NaBr (Scheme 2). This can be ascribed to the degree of protonation on the carboxyl group in Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$, which dominates the formation of the intramolecular COOH···OOC bond that stabilizes the trinuclear structure in **2**.

It should be mentioned that the absorption spectra of $\mathbf{1_{Cl}}$, $\mathbf{1_{Br}}$, and **2** in water are essentially the same as the spectrum of the mononuclear Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ in water, indicative of the facile cleavage of the Cd−S bonds

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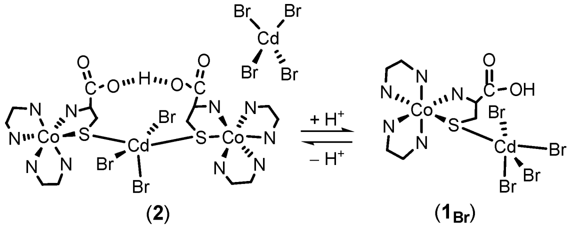
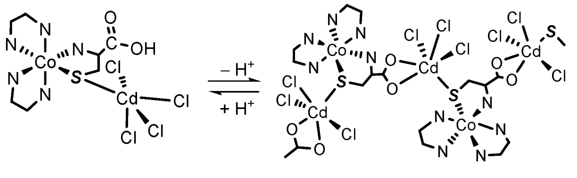
Scheme 2



(**2**) (**1**$_{Br}$)

Scheme 3



(**1**$_{Cl}$) (**4**$_{Cl}$)

in solution. On the other hand, it has been recognized that the Ag−S bonds in the related L-cysteinato $Co^{III}Ag^{I}$ polynuclear complexes are at least in part maintained in water, judging from the absence of the characteristic absorption shoulder at ca. 600 nm in the absorption spectra.[15] Thus, the thiolato group in Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ coordinates to a Cd^{II} center more weakly than to a Ag^{I} center. In parallel with this, the Cd−S bond distances in **1**$_{Cl}$, **1**$_{Br}$, and **2** are considerably longer than the Ag−S distances in the related L-cysteinato $Co^{III}Ag^{I}$ complexes (Ag−S = 2.38−2.55 Å),[15] despite the smaller ionic radius of Cd^{2+} (0.95 Å) relative to that of Ag^{+} (1.00 Å).[26] According to the HSAB rule introduced by Pearson,[32] the smaller, less polar Cd^{2+} ion would be a Lewis acid bearing a poorer softness, and therefore, the thiolato group classified as a soft Lewis base has a tendency to form a weaker bond with Cd^{2+}. The poorer softness of Cd^{2+} compared with Ag^{+} is also assumed from the hardness parameter for Lewis acids, H_a, reported by Hancock; [33a] the value for Cd^{2+} ($H_a = 3.31$) is appreciably larger than that for Ag^{+} ($H_a = -1.21$).

Notably, the 1:1 reaction of Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^{+}$ having a deprotonated COO$^-$ group with $CdCl_2$ in water (pH ∼ 6) produced a helical coordination polymer, $(\Lambda_L)_n$-[CdCl$_3$-{Co(L-cys-*N*,*S*)(en)$_2$}]$_n$ (**4**$_{Cl}$), thanks to the coordination of the COO$^-$ group in Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^{+}$ to a Cd^{II} center, together with the coordination of the thiolato group. When the isolated **4**$_{Cl}$ was treated with aqueous HCl, dark red crystals of **1**$_{Cl}$ were obtained (Scheme 3). On the other hand, **1**$_{Cl}$ was reverted back to **4**$_{Cl}$ by treatment with NaOH, followed by the addition of NaCl. Thus, the self-assembly/disassembly of the S-bridged $Co^{III}Cd^{II}$ dinuclear unit is rationally controlled by the protonation/deprotonation of the carboxylate group in Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^{+}$, which causes the formation/cleavage of Cd−O bonds with the concomitant cleavage/formation of Cd−Cl bonds (Scheme 3). An analogous $(Co^{III}Cd^{II})_n$ structure was not produced by the corresponding reaction of Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]ClO$_4$ with $CdBr_2$, resulting in the isolation of the starting Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]ClO$_4$. It is likely that the Cd−Br bonds of the [CdBr$_4$]$^{2-}$ species presented in solution are stable enough to prevent both the carboxylate and thiolato groups in Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^{+}$ from coordinating to a Cd^{II} center. However, the use of SCN$^-$ as a coexisting anion led to the production of the $(Co^{III}Cd^{II})_n$ coordination polymer, $(\Lambda_L)_n$-[Cd(NCS-*N*)$_3${Co(L-cys-*N*,*S*)(en)$_2$}]$_n$, (**4**$_{NCS}$), which is analogous to **4**$_{Cl}$. Of two possible coordination sites (N and S), each SCN$^-$ ion in **4**$_{NCS}$ binds with a Cd^{II} center through the N atom. This result is understood by considering the hardness parameter for Lewis bases, H_b, the values of which decrease in the order SCN$^-$-κN (−0.082) > Cl$^-$ (−0.100) > Br$^-$ (−0.108) > I$^-$ (−0.122) > NCS$^-$-κS (−0.128), showing the increase of covalency in this order.[33b] The coordination of SCN$^-$ via S atom would be too strong in covalency to accept the coordination of the thiolato donor in Λ_L-[Co(l-cys-*N*,*S*)(en)$_2$]$^{+}$.

Conclusion

In this study, we showed that the thiolato group of L-cysteinate bound to a Co^{III} center does coordinate, yet only weakly, to a Cd^{II} center to form S-bridged $Co^{III}Cd^{II}$ structures. Note that the chiral environment around a Co^{III} center is an important factor to construct S-bridged structures; no S-bridged $Co^{III}Cd^{II}$ species were isolated when the Δ_L isomer of [Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ was used instead of its Λ_L isomer. The $Co^{III}Cd^{II}$ structures constructed were found to vary according to the halide anions involved in the reactions, which affect the coordination of the thiolato group to a Cd^{II} center. In addition, it was shown that the degree of protonation on the pendent COO$^-$ group, which is dominated by the pH of reaction solutions, is also an important factor to determine the $Co^{III}Cd^{II}$ structures. Thus, the binding ability of L-cysteinate in a metal compound toward a Cd^{II} center is controlled by the choice of halide ions and the pH of solutions owing to the lability of Cd−S and Cd−O bonds, which allows one to rationally construct dinuclear, trinuclear, and even polymeric heterometallic Cd^{II} compounds with L-cysteinate.

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Supporting Information Available: X-ray crystallographic files (CIF), figures of IR spectra, and tables of absorption and CD spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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