Inorg. Chem. **2008**, *47*, 10202−10204

Inorganic Chemistry
Communication

Control of 1D Wave versus 2D Honeycomb $Co^{III}Cd^{II}Cu^{I}$ Heterotrimetallic Architectures by $\Delta_L-\Lambda_L$ Diastereoisomerism of L-Cysteinatocobalt(III) Building Units

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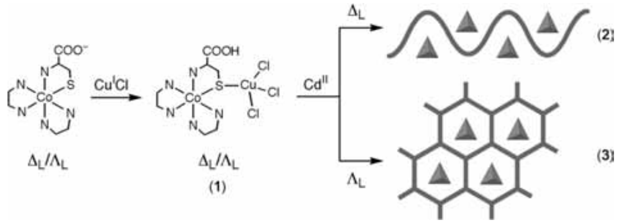
Received August 6, 2008

The reactions of the Δ_L and Λ_L isomers of $[Co(L\text{-}Hcys\text{-}N,S)(en)_2]^{2+}$ (L-H_2cys = L-cysteine) with CuCl in aqueous HCl gave $Co^{III}Cu^{I}$ dinuclear complexes with the same S-bridged structures, Δ_L-**1** and Λ_L-**1**. When Δ_L-**1** was treated with $CdCl_2$ in water, a 1D wavelike $(Co^{III}{}_2Cd^{II}Cu^{I})_n$ polymeric complex (**2**) was produced. On the other hand, similar treatment of Λ_L-**1** led to the formation of a 2D honeycomb-like $(Co^{III}{}_3Cd^{II}{}_3Cu^{I})_n$ polymeric complex (**3**), supported by the presence of counter-monoanions.

Scheme 1



Aggregation of molecular building units into metallosupramolecular structures with the use of transition-metal ions as linkers has been a subject of considerable research interest in coordination chemistry and supramolecular chemistry.[1] This is because of not only the beauty and diversity of the created structures but also their potential applications as functional materials. To date, a variety of metallosupramolecular species with different compositions and dimensional structures have been synthesized through variation of the building units and linking metal ions.[2] However, the rational creation of different metallosupramolecular structures from a single set of building units and metal ions controlled by external factors is still a challenging subject.[2d] Our interest has been directed toward this subject, employing thiolatometal complexes as building units that can be linked by transition-metal ions through S bridges.[3] Recently, we have shown that the octahedral cobalt(III) complex with N,S-chelating L-cysteinate, $[Co(L\text{-}cys\text{-}N,S)(en)_2]^+$ (L-H_2cys = L-cysteine), binds to Ag^I, Cd^{II}, or Hg^{II} ions with a d^{10} electronic configuration not only through a coordinated thiolato S atom but also through a free carboxylate O atom to afford discrete and dimensional heterobimetallic species.[4] Significantly, their structures were found to be changed by diastereoisomerism (Δ_L/Λ_L) of $[Co(L\text{-}cys\text{-}N,S)(en)_2]^+$, as well as reaction stoichiometries. From these results, it was anticipated that heterotrimetallic supramolecular species showing more attractive structures and properties are created if one can control the reactions such that thiolato and carboxylate groups in $[Co(L\text{-}cys\text{-}N,S)(en)_2]^+$ bind to different d^{10} metal ions. In this Communication, we report the stepwise reactions of $[Co(L\text{-}cys\text{-}N,S)(en)_2]^+$ with Cu^I and Cd^{II}, which successfully afforded heterotrimetallic $Co^{III}Cd^{II}Cu^{I}$ compounds by way of $Co^{III}Cu^{I}$ dinuclear complexes. Remarkably, the use of the different diastereomers (Δ_L and Λ_L) of $[Co(L\text{-}cys\text{-}N,S)(en)_2]^+$ led to the creation of heterotrimetallic architectures with different compositions and dimensionalities, although their precursory $Co^{III}Cu^{I}$ complexes possessed the same S-bridged structures (Scheme 1).

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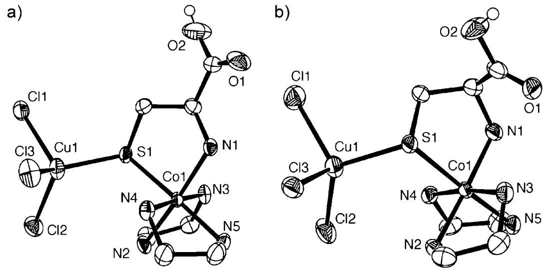

Figure 1. Perspective views of Δ_L-**1** (a) and Λ_L-**1** (b).

Treatment of the Δ_L isomer of [Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$[5] with 1 mol equiv of CuCl in aqueous HCl gave a deep-dark-brown solution, from which black blocklike crystals (Δ_L-**1**) were isolated by the addition of aqueous NaCl.[6] X-ray fluorescence spectrometry indicated the presence of Co and Cu atoms in Δ_L-**1**, and its elemental analytical data were in agreement with the formula for a 1:1 adduct of [Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ and [CuCl$_3$]$^{2-}$. The presence of a protonated COOH group in Δ_L-**1** is indicated by its IR spectrum, which gives a relatively sharp C=O stretching at 1744 cm^{-1}.[7] The molecular structure of Δ_L-**1** was determined by single-crystal X-ray crystallography. As shown in Figure 1a, Δ_L-**1** is a discrete neutral complex consisting of an octahedral Δ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ unit and a [CuCl$_3$]$^{2-}$ moiety. A thiolato S atom in the Δ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ unit coordinates to a Cu^{I} atom in the [CuCl$_3$]$^{2-}$ moiety, forming an S-bridged Co^{III}Cu^{I} dinuclear structure in Δ_L-[CuCl$_3${Co(L-Hcys-*N*,*S*)(en)$_2$}]. The Cu^{I} atom is situated in a tetrahedral environment bound by one S and three Cl atoms [ave Cu−Cl = 2.350(2) Å, Cu−S = 2.238(1) Å, S−Cu−Cl = 111.84(6)°, Cl−Cu−Cl = 106.58(6)°]. While a number of copper(I) coordination compounds with mixed S and Cl donors have been reported,[8] to our knowledge, this is the first example of a thiolatocopper(I) complex having three nonbridging Cl$^-$ ligands. In Δ_L-**1**, the N,S-chelating ring adopts a thermodynamically favorable *lel* (λ for Δ) conformation,[9] which regulates the free COOH group to have an equatorial orientation.

A similar treatment of the Λ_L isomer of [Co(L-cys-*N*,*S*)(en)$_2$](ClO$_4$)[5] with CuCl in aqueous HCl produced black platelike crystals (Λ_L-**1**).[6] In the IR spectrum, Λ_L-**1** shows a sharp C=O stretching at 1742 cm^{-1}, indicative of the presence of a protonated COOH group. From this result, together with X-ray fluorescence and elemental analyses, Λ_L-**1** is assigned as a Co^{III}Cu^{I} dinuclear complex, analogous to Δ_L-**1**. Indeed, X-ray analysis demonstrated that Λ_L-**1** has an S-bridged Co^{III}Cu^{I} dinuclear structure, in which a thiolato group in the Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ unit binds to a [CuCl$_3$]$^{2-}$ moiety (Figure 1b). Like in Δ_L-**1**, the Cu^{I} atom in Λ_L-**1** is tetrahedrally coordinated by a thiolato S and three Cl atoms [ave Cu−Cl = 2.364(2) Å, Cu−S = 2.254(2) Å, S−Cu−Cl = 109.08(7)°, Cl−Cu−Cl = 108.83(8)°]. However, the free COOH group in Λ_L-**1** does not have an equatorial orientation but adopts an axial orientation, regulated by a favorable *lel* (δ for Λ) conformation of the N,S-chelating ring.

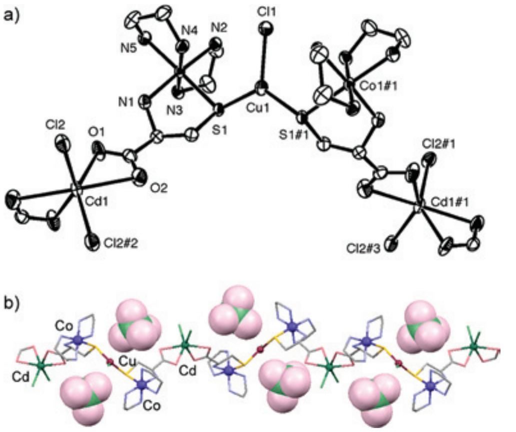

Figure 2. Perspective views of **2** (a) and its 1D structure (b).

It is expected that the free COOH group in Δ_L-**1** or Λ_L-**1** can coordinate to another metal center triggered by deprotonation, converting the S-bridged Co^{III}Cu^{I} dinuclear structures into higher-order heterotrimetallic structures. Thus, Δ_L-**1** and Λ_L-**1** were treated with CdCl$_2$ in water under neutral conditions, followed by the addition of aqueous NaClO$_4$, which produced black rodlike crystals (**2**) and black sticklike crystals (**3**), respectively.[6,10] The presence of deprotonated carboxyl groups in **2** and **3** is indicated by their IR spectra, which exhibit a C=O stretching at ca. 1620 cm^{-1}.[7] While X-ray fluorescence spectrometry implied that both of the compounds contain Co, Cu, and Cd atoms, their elemental analytical data were quite different. Single-crystal X-ray analyses demonstrated that **2** and **3** contain Cu^{I}, Cd^{II}, and [Co(L-cys-*N*,*S*)(en)$_2$]$^+$ in 1:1:2 and 1:3:3 ratios, respectively.[11]

In **2**, two Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units are linked by a Cu^{I}Cl moiety through S atoms to form an S-bridged Co^{III}Cu^{I}Co^{III} trinuclear unit, [CuCl{Co(L-cys-*N*,*S*)(en)$_2$}$_2$]$^{2+}$ (Figure 2). Two COO$^-$ groups in each Co^{III}Cu^{I}Co^{III} unit bind to two adjacent Cd^{II}Cl$_2$ moieties in a chelating mode, completing a 1D wavelike chain structure in {[(CdCl$_2$)(CuCl){Co(L-cys-*N*,*S*)(en)$_2$}$_2$]$^{2+}$}$_n$. Each Cu^{I} atom is situated in a trigonal-planar environment, coordinated by two thiolato S and one Cl atoms [Cu−S = 2.225(1) Å, Cu−Cl = 2.327(2) Å, S−Cu−Cl = 116.76(3)°, S−Cu−S = 126.48(7)°]. Two ClO$_4$$^-$ anions approach each Cu^{I} center with an averaged Cu···O distance of 2.809(5) Å, and thus the geometry about the Cu^{I} center may be described as an axially elongated trigonal bipyramid. On the other hand, each Cd^{II} atom is in a distorted octahedral environment, coordinated by four O atoms from two COO$^-$ groups [2.318(3) and 2.438(3) Å]

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(10) These compounds were also obtained by the direct reactions of Δ_L- or Λ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$, CuCl, and CdCl$_2$ in water.

(11) Complexes **2** and **3** are formulated as {(Δ_L)$_2$-[(CuCl)(CdCl$_2$){Co(L-cys-*N*,*S*)(en)$_2$}$_2$](ClO$_4$)$_2$}$_n$ and {(Λ_L)$_3$-[(CuCl)(Cd$_3$Cl$_8$){Co(L-cys-*N*,*S*)(en)$_2$}$_3$](ClO$_4$)}$_n$, respectively.

and two trans Cl atoms [2.518(1) Å]. Note that the carboxyl group in each Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ unit in **2** has an equatorial orientation with the *lel* conformational N,S-chelating ring, which is consistent with that in the precursory Δ_L-**1**.

In **3**, three Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units are linked by a Cu^{I}Cl moiety through S atoms. A COO$^-$ group in each Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ unit bridges two Cd^{II} atoms in a [Cd$_3$Cl$_8$]$^{2-}$ moiety that contains six terminal and two μ_3-bridging Cl atoms.[12] As a result, Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units are connected alternately by Cu^I atoms and [Cd$_3$Cl$_8$]$^{2-}$ moieties to construct a 2D honeycomb-like layer structure. In this structure, three Cu^I atoms and three [Cd$_3$Cl$_8$]$^{2-}$ moieties are located at the apexes of a honeycomb hexagon with a side of 8.31 Å. Each Cu^I atom has a tetrahedral geometry with an S$_3$Cl donor set [Cu−S = 2.328(2) Å, Cu−Cl = 2.350(4) Å, S−Cu−Cl = 110.20(7)°, S−Cu−S = 108.74(7)°], while each Cd^{II} atom has a severely distorted octahedral geometry with a *trans*-O$_2$Cl$_4$ donor set [Cd1−O1 = 2.299(6) Å, Cd1−O1′ = 2.575(6) Å, Cd−Cl$_{\text{terminal}}$ = 2.471(3) Å, 2.531(2) Å, Cd−Cl$_{\text{bridging}}$ = 2.680(3) Å, 2.782(3) Å, trans O−Cd−O = 140.1(2)°, trans Cl−Cd−Cl = 162.71(9)°]. Like in the precursory Λ_L-**1**, the COO$^-$ group in each Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ unit in **3** adopts an axial orientation with the *lel* conformational N,S-chelating ring. It is interesting to note that a ClO$_4$$^-$ ion, together with three water molecules, is accommodated in each hexagon cavity by forming $O_{ClO_4}\cdots O_w$ [3.03(2) Å], $O_w\cdots$Cl [3.243(8) Å], and $O_w\cdots$N [3.06(1) Å] hydrogen bonds. This appears to sustain the unique honeycomb-like structure in **3**.

When NaNO$_3$, NH$_4$PF$_6$, NH$_4$ReO$_4$, or NaCl was added to the reaction mixture of Λ_L-**1** and CdCl$_2$, instead of NaClO$_4$, a series of 2D honeycomb-like (Co$^{III}_3$Cd$^{II}_3$Cu^I)$_n$ compounds ($\mathbf{3_{NO_3}}$, $\mathbf{3_{PF_6}}$, $\mathbf{3_{ReO_4}}$, and $\mathbf{3_{Cl}}$) were produced. These compounds were identified by their IR spectra, which are essentially the same as the spectrum of **3** except for the bands due to counteranions, besides X-ray fluorescence and elemental analyses.[6] In addition, the 2D structures that accommodate a ReO$_4$$^-$ or Cl$^-$ ion in each hexagon cavity were unambiguously determined by single-crystal X-ray analyses for $\mathbf{3_{ReO_4}}$ and $\mathbf{3_{Cl}}$.[6] On the other hand, the addition of Na$_2$SO$_4$ or Na$_3$PO$_4$ did not afford any solids that contain Co, Cd, and Cu atoms. Thus, it is considered that the presence of an appropriate counterion bearing a monoanionic charge, which balances the monocationic charge of the (Co$^{III}_3$Cd$^{II}_3$Cu^I)$_n$ framework, {[(Cd$_3$Cl$_8$)(CuCl){Co(L-cys-*N*,*S*)(en)$_2$}$_3$]$^+$}$_n$, is essential for the formation of the honeycomb-like structure in **3**.

In summary, we showed that both Δ_L and Λ_L isomers of [Co(L-Hcys-*N*,*S*)(en)$_2$]$^{2+}$ react with CuCl under acidic conditions to produce the same S-bridged Co^{III}Cu^I dinuclear structures (Δ_L-**1** and Λ_L-**1**), which are converted into the Co^{III}Cd^{II}Cu^I heterotrimetallic structures (**2** and **3**) by treatment with CdCl$_2$. Notably, the heterotrimetallic structures in **2** and **3** are different from each other not only in their compositions (Co:Cu:Cd = 2:1:1 vs 3:1:3) but also in their dimensionalities (1D vs 2D). This originates from the difference in L-cys carboxyl orientations (equatorial vs axial), which are regulated by the opposite chiral configurations (Δ vs Λ) of the Co^{III} center. Thus, a local chirality existing in molecular building units plays a crucial role in the control and determination of highly organized dimensional supramolecular structures, even when it does not affect low-nuclearity structures. Finally, the present results would provide insight not only into the creation of chiral heterometallic supramolecular architectures using simple chiral ligands such as L-cys but also into the development of copper thiolate chemistry, which is relevant to copper-containing metalloenzymes.[13]

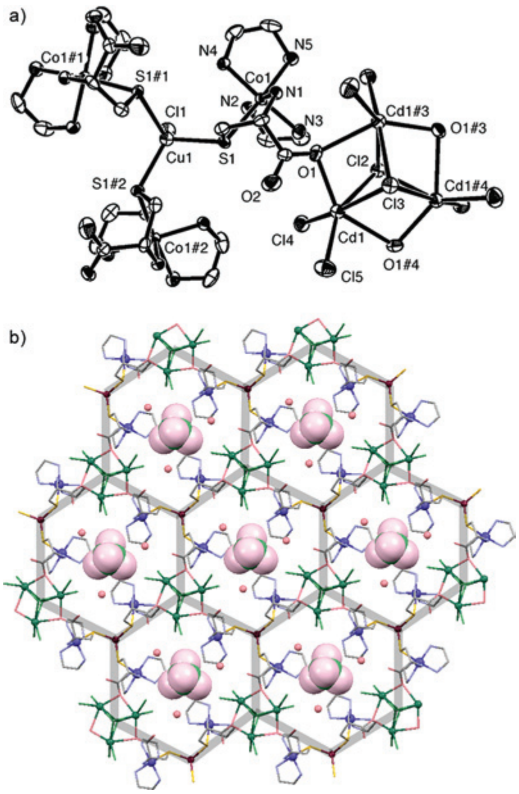

Figure 3. Perspective views of **3** (a) and its 2D structure (b).

Acknowledgment. This work was supported by Grants-in Aid for Scientific Research (Grant 20750047) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information Available: Crystallographic data in CIF format and detailed experimental and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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