

Cobalt Complexes Appended with *p*- and *m*-Carboxylates: Two Unique {Co³⁺–Cd²⁺} Networks and Their Regioselective and Size-Selective Heterogeneous Catalysis

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Supporting Information

ABSTRACT: Co³⁺ complexes appended with arylcarboxylate groups act as molecular building blocks to afford {Co³⁺–Cd²⁺} networks. These networks function as the heterogeneous and reusable catalysts for regio- and stereoselective ring opening of epoxides and size-selective cyanation of aldehydes.

Crystalline extended networks are unique materials with multidimensional topologies¹ and applications in sorption,² sensing,³ separation,⁴ and catalysis.⁵ The important features of these networks are strong metal–ligand interactions that provide stability and the existence of porosity for substrate accessibility.^{2–5} Such materials are typically synthesized by the reaction of a suitable organic ligand with a metal ion. In particular, carboxylic acid based ligands have been quite successful in generating assorted networks.⁶ The major drawbacks with this approach are limited structural diversity of the resultant material and catenation,⁷ which prevents accessibility to the substrates or analyte. Catenation is often observed because of the flexible nature of the ligands used for the construction of such networks.⁷ One way to circumvent catenation is to utilize either geometrically rigid ligands or metalloligands, which will direct the functional groups to limited orientations. While the design of geometrically rigid ligands may involve multiple synthetic steps, a suitable metalloligand takes advantage of the placement of appended functional groups in desirable orientations because of the geometrical preference of a metal ion.

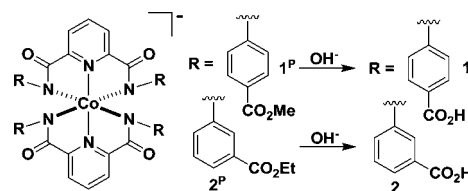
In addition to sorption properties,² extended networks have also provided a tunable platform for the design of heterogeneous catalysts.⁵ The most remarkable features that extended networks as catalysts offer are the easy recovery and reusability and architecture-dependent catalysis. Although a good number of networks have been examined as heterogeneous catalysts,⁵ most of these studies focus on proof-of-concept transformations. However, recently a few networks are shown to act as next-generation catalysts with unique active site structures and porous nature for shape- and size-selective and regio- and enantioselective reactions.⁵

Our group is working on Lewis acid based homogeneous as well as heterogeneous catalysts.⁸ These catalysts have been synthesized utilizing coordination complexes as the building blocks. This approach offers precise control of the placement of molecular components with an identical chemical environment because of the material's crystalline nature and also avoids

catenation.⁷ These points have helped us to achieve substrate-specific^{8a,b} and regioselective^{8b,d} catalysis including heterogeneous and solvent-free examples.^{8e,f} Herein we report the construction of two {Co³⁺–Cd²⁺} networks starting from Co³⁺ complexes appended with *p*- or *m*-carboxylates and their application in regio- and stereoselective ring-opening reactions (RORs) and size-selective cyanation reactions (CRs).

Complexes **1^P** and **2^P** were synthesized starting with ligands H₂L^{*p*}-COOMe and H₂L^{*m*}-COOEt containing protected carboxylic acid esters.⁹ These complexes on base-assisted deprotection afforded [Co(L^{*p*}-COOH)₂][–] (**1**) and [Co(L^{*m*}-COOH)₂][–] (**2**) with free carboxylic acid groups (Scheme 1; Figures S1–S6,

Scheme 1. Synthesis of Building Blocks **1** and **2**



Supporting Information, SI). The preliminary crystal structures of **1** and **2** reveal that the Co³⁺ ion is coordinated by two tridentate ligands, whereas the appended arylcarboxylic acids remain uncoordinated.¹⁰ Building blocks **1** and **2** upon reaction with Cd(OAc)₂·2H₂O afforded {Co³⁺–Cd²⁺} heterobimetallic networks [(**1**)Cd_{2.5}(OH₂)₁₀·24H₂O]_n (**3**) and [(**2**)Cd_{2.5}(OH₂)₁₅·9H₂O]_n (**4**).⁹ The Fourier transform infrared (FTIR) spectra of **3** and **4** exhibited strong but significantly red-shifted bands between 1560 and 1585 cm^{–1} due to the coordinated carboxylate groups in their anionic form. In addition, broad features at ca. 3400 cm^{–1} suggest the presence of water molecules in these networks. Thermogravimetric analysis and differential scanning calorimetry (DSC) studies for **3** and **4** show weight loss between 25 and 160 °C for the release of 34 and 24 water molecules, respectively (Figures S7, SI).¹¹ This observation is strongly supported by the microanalysis results as well as crystallography. Both networks are stable up to ca. 320 °C and, above this temperature, systematically decompose by the loss of CO₂ and Cd²⁺ ions. The powder X-ray diffraction (PXRD) patterns for both networks activated at 300 °C were quite similar to those of

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freshly prepared samples, thus justifying their thermal stability (Figure S8, SI). Further, for both networks, the PXRD patterns closely match the one simulated from single-crystal data, thereby proving that a homogeneous and single-crystalline phase has resulted during synthesis (Figures S9, SI).

The molecular structure of network **3**⁹ shows that the Co³⁺-based building blocks are connected through Cd²⁺ ions (Figures 1 and S10, SI). Every building block offers four

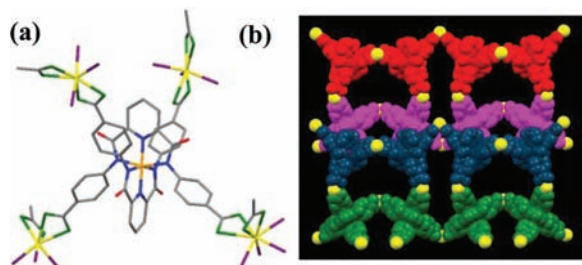


Figure 1. (a) Stick representation of a selected part of the crystal structure of network **3**. Color code: orange, Co; yellow, Cd; blue, N; green, O_{carboxylate}; purple, O_{water}; red, O_{amide}; gray, C. (b) Space-filling view along the *a* axis showing pores and channels in the structure of network **3**. The coordinated water molecules are omitted for clarity to show accessible Lewis acidic Cd²⁺ ions (yellow spheres).

arylcarboxylate fragments and thus coordinates four different Cd²⁺ ions. Interestingly, out of four Cd²⁺ ions, three are seven-coordinate, whereas the fourth one is eight-coordinate. While every Cd²⁺ ion is coordinated by two bidentate carboxylate moieties, the remaining sites are occupied by the water molecules. In the building block, the Co³⁺ ion is coordinated by two tridentate ligands, maintaining a N₆-based octahedral core. The building block has a structural role in the resulting network, where it orients the carboxylic acid fragments to different yet limited directions.

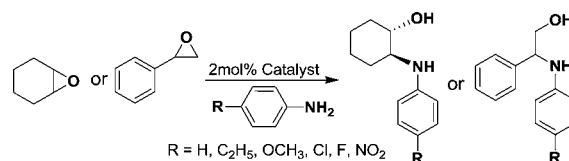
The crystal structure of network **4**⁹ is quite complex yet unique and shows the presence of two different individual networks (discussed as networks **4a** and **4b** hereafter) (Figures S11 and S12, SI). As noted for **3**, in this case also, the network is generated via coordination between the Cd²⁺ ions and arylcarboxylate fragments that originated from different building blocks. For network **4a**, every carboxylate group connects a group of three Cd²⁺ ions. As a result, Cd²⁺ ions in the resultant Cd₃ cluster are coordinated by four different carboxylate groups from four different building blocks. In a Cd₃ cluster, two Cd²⁺ ions are seven-coordinate, with four and three coordination sites being occupied by O_{carboxylate} and water molecules, respectively. The third Cd ion is six-coordinate and respectively receives two coordination sites from O_{carboxylate} and four from the water molecules. The network **4b** is generated by the unique binding mode of carboxylate groups to the Cd²⁺ ions. The pairs of Cd²⁺ ions are bridged by two carboxylate groups, individually further coordinated by a bidentate carboxylate group, and ligated to two or three water molecules. The networks **4a** and **4b** are connected to each other via an array of hydrogen bonds involving O_{carboxylate}, O_{amide}, and coordinated and uncoordinated water molecules (Figure S13, SI).

There are several structural novelties in networks **3** and **4**. For example, both networks **3** and **4** show the presence of pores and channels with cross sections of 17.9 × 16.3/21.5 × 7.5 and 13.6 × 10.4/11.1 × 10.9 Å², respectively. In addition,

both networks contain accessible Lewis acidic Cd²⁺ sites located in an orderly way in the networks (cf. Figure 1b). Another unique feature is the observation that Cd²⁺ ions are coordinated by a large number of labile water molecules. These structural features encouraged us to explore possible organic transformations.^{5,8} It was presumed that the suitable O-based substrates are likely to replace the labile water molecules coordinated to the Cd²⁺ ions without altering the network topology. We thus reasoned to select transformations where substrates are O-based and the reactions are known to be catalyzed by Lewis acids. The RORs of epoxides and CRs of aldehydes were deemed fit considering these points. Both of these reactions provide important synthetic tools for the preparation of several fine chemicals.¹² While a variety of catalysts have been successfully utilized for such reactions,¹² the use of designed networks, including metal–organic frameworks, as heterogeneous catalysts has recently shown promising results.^{5,8}

The networks **3** and **4** were successful as heterogeneous catalysts for the aminolysis reaction of various epoxides under solvent-free conditions. For example, when an equimolar mixture of cyclohexene oxide (or styrene oxide) and aniline was stirred for 4 h with only 2 mol % catalyst, a smooth reaction took place that produced the respective β-amino alcohol in nearly quantitative yield (Scheme 2 and Table S6,

Scheme 2. RORs of Epoxides



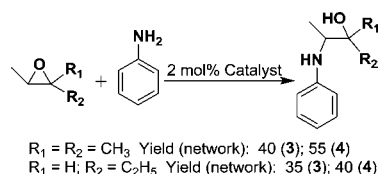
SI). Without the network (**3** or **4**) or with only building blocks (**1** or **2**), the reaction did not proceed at all, whereas the use of Cd(OAc)₂ resulted in little conversion.¹³ Further, when the catalyst was filtered off, the reaction was no longer promoted. These control experiments strongly suggest that the soluble and catalytically active species are not leached out from both networks. Thus, the reaction proceeded by heterogeneous catalysis of networks **3** and **4**. Notably, both networks can be recovered by simple filtration and reused several times (tested four consecutive times) without much loss of activity (~2% drop in the fourth run). The recovered networks were characterized by recording FTIR spectra and PXRD patterns that were superimposable on those of fresh ones (Figures S15 and S16, SI). To explore the functional group tolerance as well as the effect of electronic substituents on catalysis, several para-substituted anilines with e⁻-donating or e⁻-withdrawing groups were tested. The catalytic results are general; however, the yields were higher with the electron-rich anilines.^{8b,d,f}

Importantly, in the case of cyclohexene oxide, the stereoselective trans product was exclusively formed without any observation of the cis product. More importantly, with styrene oxide as a model asymmetrical substrate, perfect regioselectivity was observed. This selectivity resulted in only a single product in all cases for both networks **3** and **4**. Out of two possible products due to nucleophilic attack at either benzylic or a less hindered site of the epoxide ring, in all cases, nucleophilic attack exclusively took place at the former position. Such an observation suggests that the epoxide has interacted with the Cd²⁺ ion through the less hindered face, possibly because of

confinement of the Cd^{2+} ions within the microporous network (Scheme S1, SI).

To investigate the effect of steric crowding on the reactivity and selectivity, we performed the aminolysis of 2,3-epoxypentane (A) and 2,3-epoxy-2-methylbutane (B) with aniline (Scheme 3 and Table S7, SI). Interestingly, for both A

Scheme 3. RORs of Hindered Epoxides



and B, nucleophilic attack predominantly occurred on the less hindered C atom. The results indicate that the catalytic Cd^{2+} ion is capable of distinguishing between a methyl and an ethyl substituent with high selectivity.^{8f} Notably, the poor product yield even after prolonged reaction time can be correlated to the hindered accessibility of epoxides A and B due to sterically demanding substituents. To further establish the accessibility issue, when nonplanar nucleophile cyclohexylamine was used, poor conversion ($\sim 50\%$) was noticed compared to RORs with aniline (yield $\sim 99\%$). Collectively, these results substantiate that poor yield is related to the restricted accessibility of the substrate or nucleophile to the catalytic Cd^{2+} ions that are confined within the interior of the microporous network.

We finally targeted CRs of aldehydes to primarily understand the size selectivity because it does constitute good circumstantial evidence for heterogeneous catalysis within the pores and channels of a network and not only on the surface.¹⁴ Notably, both networks 3 and 4 were able to catalyze the CRs within 4 h (Scheme 4 and Table S8, SI). Benzaldehyde as well

Scheme 4. CR of Assorted Aldehydes



as several functionalized analogues provided the corresponding cyanohydrins in high yield (70–92%). The observed catalysis is presumably occurring via displacement of the labile water by aldehyde before its activation and reaction (Scheme S2, SI). Importantly, both networks function as heterogeneous catalysts, while the recyclability and control experiments yielded results similar to those noted for RORs.¹³ More importantly, the reaction yield systematically depends on the molecular size of the substrate. For example, when cyanation of sterically demanding aldehydes, such as 1-naphthaldehyde (1N), 2-naphthaldehyde (2N), and 9-anthraldehyde (9A), was attempted, substrate-size-dependent catalysis was observed. For network 3, the conversion decreased in the order of benzaldehyde (86%) > 1N (68%) > 2N (60%) > 9A (38%), in line with their sizes of $8.21 \times 5.83 \text{ \AA}^2$ (benzaldehyde), $9.69 \times 8.29 \text{ \AA}^2$ (1N), $10.67 \times 7.49 \text{ \AA}^2$ (2N), and $10.88 \times 8.60 \text{ \AA}^2$ (9A).⁹ A similar trend was observed for network 4. Therefore, it could be concluded that the conversions are inversely proportional to the molecular size of aldehydes and the substrate accessibility to the Cd^{2+} sites controls the catalysis outcome.

In summary, we showed that the building blocks appended with *p*- and *m*-carboxylates generate $\{\text{Co}^{3+}-\text{Cd}^{2+}\}$ networks with a unique arrangement of Cd^{2+} ions. The Lewis acidic Cd^{2+} ions in the resultant networks carry out the regio- and stereoselective RORs of epoxides and size-selective CRs of aldehydes. The observed selectivities imply that catalysis exclusively takes place within the microporous network. Work is under progress to explore a few challenging reactions and to extend the chemistry to other Lewis acidic metals.

■ ASSOCIATED CONTENT

📄 Supporting Information

Details for all experiments, crystallography, tables, figures, schemes, and a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (9) See the SI for full experimental details.
- (10) See Table S1a, SI.
- (11) Network 3 (34 H₂O; obsd/calcd weight loss (%): 21.11/21.26); Network 4 (24 H₂O; obsd/calcd weight loss (%): 15.44/15.79).
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- (13) Cd(OAc)₂-catalyzed RORs of cyclohexene oxide and styrene oxide with aniline resulted in only 6% and 3% product yield, respectively. For CRs, there was no reaction. See Table S9 (SI).
- (14) FTIR spectra of networks 3 and 4 impregnated with a CH₂Cl₂ solution of (CH₃)₃SiCN exhibited ν_{CN} stretching at 2185 and 2180 cm⁻¹ that was red-shifted by 21–26 cm⁻¹, suggesting its activation within the microporous network (Figures S17 and S18, SI).