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A New Redox-Active Coordination Polymer with Cobalticinium Dicarboxylate

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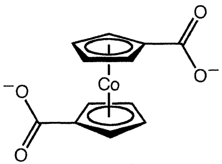
A new two-dimensional coordination polymer with cobalticinium 1,1′-dicarboxylate (ccdc) incorporated in the framework has been prepared, the ccdc functioning as unique monoanionic dicarboxylate ligands. The compound shows a high redox activity based on the ccdc units.

Scheme 1



ccdc

Coordination polymers with metallocene units in the framework have attracted intense interest for the development of new redox-active crystalline solids,[1−9] with ferrocene moieties having mainly been utilized as the redox-active units. While ferrocene shows a redox potential due to the Fe(III)/Fe(II) couple at about 0.6 V ($E_{1/2}$) versus SCE, cobaltocene shows the Co(III)/Co(II) couple at a quite different potential, about −0.9 V.[10,11] This large difference in the M(III)/M(II) redox potentials results in the different oxidation states for these units that are generally observed at ambient conditions.[12,13] That is, Fe(II) and Co(III) states are the most convenient oxidation states for ferrocene and cobaltocene units, respectively.[11,12] Although coordination polymers with cobaltocene or cobalticinium units in the framework are promising compounds that show different redox properties compared with those for ferrocene units, the coordination polymers constructed by cobaltocene units are still unexplored. We have selected cobalticinium 1,1′-dicarboxylate (ccdc; Scheme 1) as a bridging ligand toward the synthesis of new redox-active crystalline materials. Here we report the synthesis and structural characterization of a new coordination polymer, $[\mathrm{Cu(ccdc)_2}]\cdot 2\mathrm{MeOH}$ (**1**). An additional unique feature of this type of network is the creation of coordination frameworks with mixed metal ions, studies of which are still rare.

The Hccdc was prepared by oxidation of 1,1′-dimethylcobalticinium hexafluorophosphate with potassium permanganate according to the literature.[12] Compound **1** was isolated as green plate crystals by diffusion of a methanol solution of $\mathrm{Cu(CH_3COO)_2\cdot H_2O}$ into a DMF solution of Hccdc. (One of the single crystals was used for single X-ray analysis. The residual sample was used for other measurements. Anal. Calcd for $\mathrm{C_{26}H_{30}Co_2CuO_{13}}$ (**1**$\cdot 3\mathrm{H_2O}$): C, 42.67; H, 4.13. Found: C, 43.15; H, 3.58%.)

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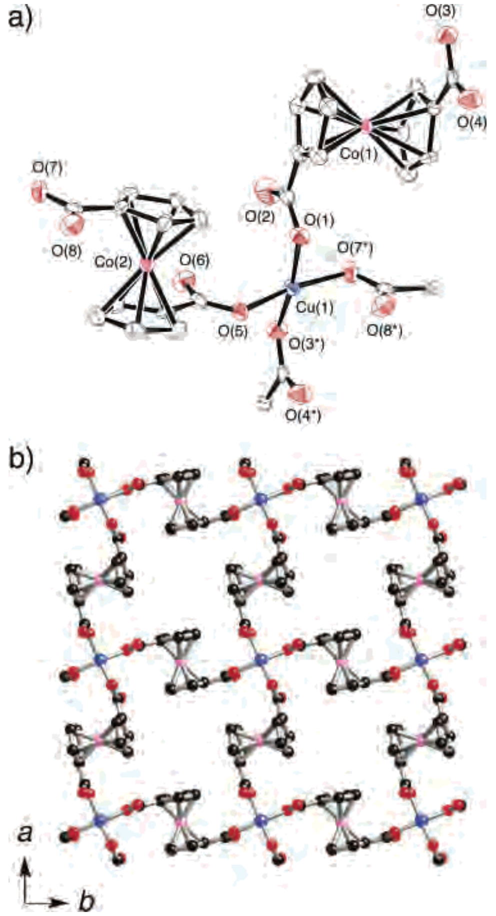


Figure 1. ORTEP view of the crystal structure of **1** (a) (30% probability level) and views of the two-dimensional structure (b). Hydrogen atoms and methanol molecules are omitted for clarity.

The crystal structure was determined by X-ray diffraction studies. (Crystallographic data for **1**: $C_{26}H_{24}Co_2CuO_{10}$, $M = 677.9$, tetragonal, space group $P4_3$ (No. 78), $a = b = 10.550(5)$ Å, $c = 23.15(1)$ Å, $V = 2576(2)$ Å^3, $Z = 4$, $D_c = 1.747$ g cm^{-3}, μ(Mo Kα) = 2.419 mm^{-1}, $F(000) = 1372$, $T = 293$ K, $\lambda = 0.7107$ Å, ω scan, $R = 0.058$, $wR = 0.060$ for 3057 unique reflections ($R_{\text{int}} = 0.047$) with $I > 2\sigma(I)$ and 332 parameters. The data collection was performed on a Rigaku CCD Mercury system. The structure was solved by direct methods using SIR-92.[18] All non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included but not refined. See Supporting Information for crystallographic data in CIF format.) Compound **1** crystallizes in the asymmetric space group $P4_3$. Figure 1 shows the coordination center and crystal structure of **1**, which contains two crystallographically independent ccdc units and a copper ion. Four oxygen atoms of the carboxylate groups from ccdc bind to the copper(II) center to form a distorted square planar geometry. Each ccdc connects two copper(II) centers to yield a two-dimensional structure with small square cavities (about 4 × 4 Å^2) in the *ab* plane (Figure 1b).

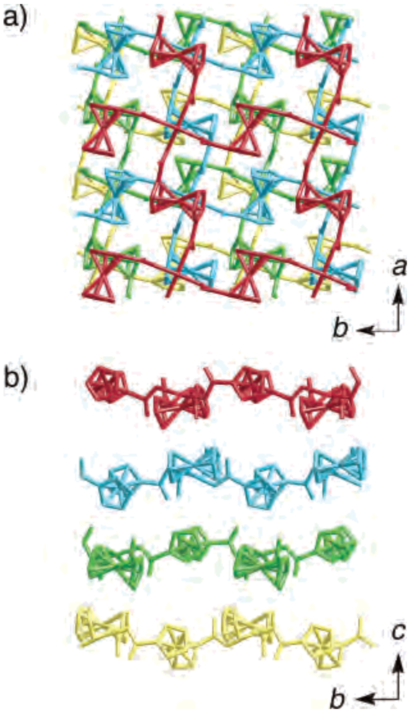
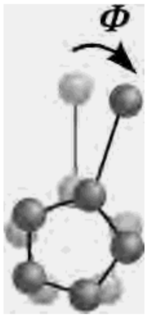


Figure 2. Stacking aspect showing the ABCD pattern along the *a* axis (a) and the *c* axis (b), in which each layer is shown by different colors. Hydrogen atoms and methanol molecules are omitted for clarity.

Scheme 2



Because the two cp rings of ccdc can rotate, this ligand acts as a flexible connector between the metal ions. When the torsion angle Φ of the two carboxylate groups of ccdc is defined as in Scheme 2, the steric configurations are generally classified following six patterns:[9] synperiplanar (0°), synclinal-staggered (36°), synclinal-eclipsed (72°), anticlinal-staggered (108°), anticlinal-eclipsed (144°), and antiperiplanar (180°). For **1**, the Φ values are about 162° and 157° for the two crystallographically independent ccdc units with Co(1) and Co(2) centers, respectively. That is, both carboxylate groups of ccdc show a conformation between anticlinal-eclipsed and antiperiplanar. As a result, ccdc connects between two copper(II) centers with slightly bent angles from 180°.

These layers stack along the *c* axis in an ABCD pattern with 90° rotation (Figure 2), in which the four crystallographic screw axes run through the cavities of the layer. Each square cavity is capped from above and below by ccdc units in the adjacent layers, creating closed cavities with dimensions of about 4 × 4 × 6 Å^3 in the crystal. These spaces are connected by small crevices with sizes of about 2 × 1 Å^2. As a result, each cavity, which traps methanol molecules, is well isolated from the outside. To the best of our knowledge, this is the first example of a coordination polymer with cobalticinium units incorporated in the framework.

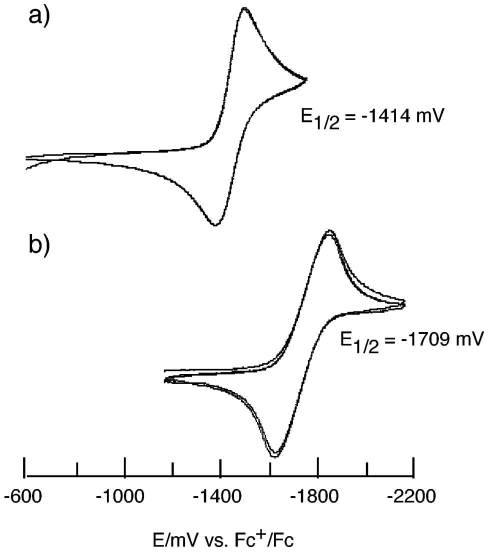


Figure 3. Cyclic voltammograms of ccdc in DMF solution in the presence of triethylamine (a) and **1** in the solid state (b).

The unique feature of the ccdc ligand compared with other general organic dicarboxylate ligands is the difference of the charge.[14] When the neutral coordination frameworks are constructed by combination of dianionic dicarboxylate ligands with divalent metal ions, the ratio of the ligand to metal ions of the frameworks would be 1:1 because of the charge balance. That is, when the dicarboxylate groups simply connect metal ions as bis-monodentate ligands, a one-dimensional framework is formed. For example, 1,1′-ferrocenedicarboxylate (fcdc) produces a 1:1 salt with Cd(II) ion to yield [Cd(fcdc)(dmf)$_2$(H$_2$O)] with a zigzag chain framework.[3] In contrast to this case, **1** creates a two-dimensional framework, which consists of a 2:1 ratio of ccdc with Cu(II) ion. This result implies that the charge of the dicarboxylate ligands, which is controlled by the oxidation states of the metal ions of the metallocene units, has a large effect on the network motifs of the coordination frameworks.

The construction of this new coordination network with cobalticinium units prompted us to study the redox properties of **1**. When the cyclic voltammogram (CV) of ccdc was measured in a DMF solution, the quasireversible couple was observed at −1414 mV (vs Fc$^+$/Fc), as shown in Figure 3a, in which the ccdc was prepared in a DMF solution by addition of an equivalent amount of triethylamine. The corresponding redox couple based on the cobalticinium units of **1** was observed at −1709 mV by a solid-state CV measurement (Figure 3b). The solid-state CV measurement of ccdc was difficult in water or general organic media because of the high solubility of either ccdc or the reducing product. The negative shift (295 mV) of the redox potential of **1** from that of ccdc is not negligible since our previous studies indicate that the solid-state redox potentials of the sulfide or ferrocene groups incorporated in the coordination frameworks reveal similar redox potentials compared to the free ligands in the solution.[8,15] The negative shift of the redox potential of **1** is in contrast to the expectation of an electron-withdrawing effect by the dipositive charge of the copper(II) ions. This could be the result of donation from the dπ orbital of Cu(II) ions to the antibonding orbital of ccdc. A similar negative shift is observed in Ag complexes with ferrocene units.[16]

Redox-active bridging ligands do not always produce redox-active coordination networks. For example, redox-active azopyridines do not show any redox properties when they are incorporated in coordination networks.[17] On the other hand, the network system described here shows a high redox property based on the ccdc units, demonstrating that the metallocene is an effective bridging unit for creation of new redox-active network materials. The redox potential is remarkably more negative than that of the coordination compounds with ferrocene units. Further characterization and synthetic studies with ccdc are currently underway.

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Supporting Information Available: X-ray crystallographic file for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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