Chem. Mater. **2004,** *16,* 2981−2983

Hydrothermal Synthesis of Single-Crystalline Zinc Glutarate and Its Structural Determination

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Received December 21, 2003
Revised Manuscript Received June 20, 2004

Carbon dioxide (CO_2) is currently regarded not only as a major greenhouse gas causing global warming but also as the cheapest and most abundant raw material source of carbon.[1] The polymerization of CO_2 with alkylene oxide to produce poly(alkylene carbonate) (PAC), a biocompatible material that undergoes complete thermal decomposition, has come to be widely regarded as one of the most effective methods for utilizing CO_2.[2−12] Considerable effort has been expended on developing organometallic catalysts with high catalytic performance for this CO_2 polymerization process.[2−12] Of the catalysts reported to date, zinc dicarboxylates are among the most effective for preparing PAC with a reasonably high molecular weight,[3−5] and among the zinc dicarboxylates, zinc glutarate (ZnGA) gives the highest yield in the polymerization of CO_2 with propylene oxide (PO).[3−5] ZnGA is currently considered the most effective and economically viable catalyst for the large-scale conversion of CO_2 resources into PAC materials. However, to date no structural information has been reported for this catalyst, and such information is essential if we are to understand its catalytic mechanism and activity. This lack of structural information is due in part to the difficulty of preparing single crystals of ZnGA, which results from its extremely low solubility in all common solvents [with the exception of strong acidic solutions (pH < 2), in which it dissociates]. Here, we present the first report of the synthesis of single-crystalline ZnGA and of the determination of its structure.

Single-crystalline ZnGA (*sc*-ZnGA) was first successfully synthesized with an average size of 1 mm × 1 mm × 10 μm (see the inset of Figure 1) by the hydrothermal reaction of zinc perchlorate hexahydrate [$Zn(ClO_4)_2 \cdot 6H_2O$] and glutaronitrile [$NC(CH_2)_3CN$] at 160 °C, as shown in the following:[13]

$$n\mathrm{Zn(ClO_4)_2{\cdot}6H_2O} + n\mathrm{NC(CH_2)_3CN} \xrightarrow[\mathrm{H_2O}]{160\ °\mathrm{C}/40\ \mathrm{h}} [\mathrm{Zn(O_2C(CH_2)_3CO_2)}]_n$$

This hydrothermal synthesis approach only gave *sc*-ZnGA when the zinc metal ion and glutarate ligand sources were zinc perchlorate hexahydrate and glutaronitrile, respectively. However, attempts to produce *sc*-ZnGA by hydrothermal reaction of glutaronitrile with other zinc ion sources (e.g., zinc chloride, zinc oxide, zinc nitrate, and zinc acetate) failed. Attempts to synthesize *sc*-ZnGA by hydrothermal reaction of glutaric acid with all the zinc ion sources including zinc perchlorate hexahydrate also failed.

The infrared spectrum of *sc*-ZnGA resembles that of the powdery ZnGA commonly prepared from zinc oxide and glutaric acid.[5] In particular, the spectrum exhibits a doublet band with peaks at 1585 and 1539 cm^{-1} due to the antisymmetric C═O stretching vibration and a singlet band at 1405 cm^{-1} due to the symmetric C═O stretching vibration, which indicates that glutarate ligands with two carboxyl end groups were successfully produced by the hydrolysis of glutaronitrile. Furthermore, the wavenumber differences of the antisymmetric bands with respect to the symmetric band are 180 and 134 cm^{-1}, respectively, suggesting that the carboxyl end groups of the glutarate ligand are in bridging coordination with the zinc metal ion, as reported previously.[5,14,15] The chemical formula of *sc*-ZnGA was confirmed by elemental analysis.[13] The synthesis of *sc*-ZnGA was found to be highly reproducible. Evidence of the stability of *sc*-ZnGA was obtained by thermogravimetric analysis, which showed that *sc*-ZnGA begins to decompose at 471 °C.

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(13) Synthesis of *sc*-ZnGA: A mixture of 0.5 g (1.34 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ and 0.126 g (1.34 mmol) of $NC(CH_2)_3CN$ was dissolved in 12 mL of purified water in a Teflon-lined reaction vessel, which was then sealed and maintained at 160 °C. After 2 days, the vessel was cooled to room temperature over a period of 5 h. Colorless platelike crystals of *sc*-ZnGA were collected by filtration, washed with water, and dried in air. Yield: 0.39 g, 75%. Elemental analysis, calcd. (observed) for $ZnC_5H_6O_4$ (%): C, 30.72 (30.72); H, 3.09 (3.08); O, 32.74 (32.52).

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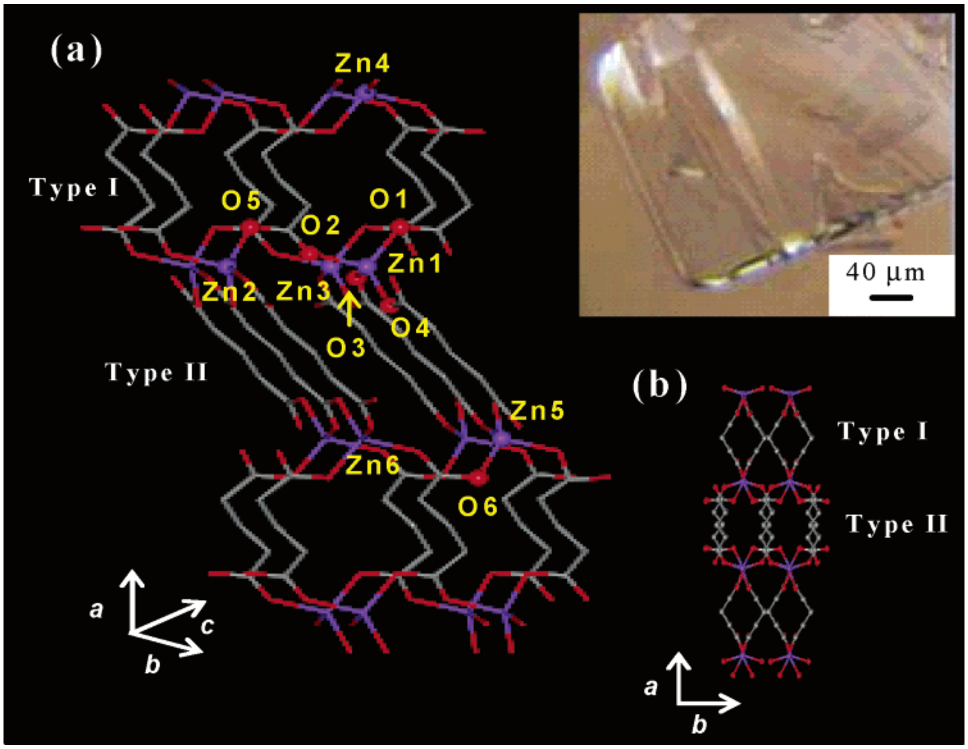

Figure 1. (a) Coordination geometry around the Zn^{II} centers in *sc*-ZnGA. The atoms are distinguished as the following: Zn, violet; O, red; C, gray. Selected bond distances (Å): Zn(1)···Zn(2), 4.639; Zn(1)···Zn(3), 4.784; Zn(1)···O(1), 1.968; Zn(1)···O(2), 1.961; Zn(1)···O(3), 1.954; Zn(1)···O(4), 1.961. (b) View down the crystallographic *c*-axis. Inset: Optical microscopy of *sc*-ZnGA; the crystallographic *a*-axis is parallel to the thickness direction of the single-crystal plate.

X-ray single-crystal structure determinations[16] revealed that the unit cell of *sc*-ZnGA is monoclinic with a $P2/c$ space group and lattice parameters of a = 13.934(3) Å, b = 4.7842(11) Å, c = 9.276(2) Å, and β = 90.628(5)°, and its Zn^{II} centers have a coordination of four. Each Zn^{II} center coordinates to four different carboxyl oxygen atoms via η^1,η'^1−bridging; for example, Zn(1) coordinates to four oxygen atoms, O(1), O(2), O(3), and O(4). All Zn^{II} centers of *sc*-ZnGA thus coordinate to four carboxyl oxygen atoms on different glutarate ligands via four syn−anti bridges, forming a distorted tetrahedral geometry (see Figure 1a). This coordination pattern is very different from the structures commonly reported for zinc monocarboxylates, in which two zinc atoms are linked by three syn−syn and one syn−anti bridging carboxylate ligands to produce a linear(3,1) polymer.[15]

In the crystal structure of *sc*-ZnGA, the glutarate ligands take on either a bent (type-**I**) or a fully extended (type-**II**) conformation, depending on their location in the crystal structure. Type-**I** glutarate ligands coordinate to two Zn^{II} ions on the *c*-axis [e.g., see the type-**I** ligand linked to Zn(1) and Zn(2) separated by an interatomic distance of 4.639 Å on the *c*-axis in Figure 1a]; the bent direction of the ligand alternately crosses along to the *c*-axis, as shown in Figure 1b. In contrast, type-**II** glutarate ligands coordinate to two Zn^{II} ions on the *b*-axis [e.g., see the type-**II** ligand linked to Zn(1) and Zn(3) separated by an interatomic distance of 4.784 Å on the *b*-axis in Figure 1a]. Consequently, each Zn^{II} center in *sc*-ZnGA coordinates with two carboxyl oxygen atoms from type-**I** glutarate ligands and two from type-**II** glutarate ligands, generating a three-dimensional network.

Figure 2a shows a view down the crystallographic *a*-axis (in fact, the crystallographic *a*-axis in the single-crystal plate of the inset of Figure 1 is parallel to the thickness direction of the crystal plate), while Figures 2b and 1b display views down the crystallographic *b*- and *c*-axis, respectively. As seen in Figures 1 and 2b, two types of metallacycles are formed, which are distinguished by the conformations (type-**I** and type-**II**) of the glutarate ligands coordinated to the Zn^{II} ions. One type is a 16-membered metallacycle (**A**) composed of two Zn^{II} ions [e.g., Zn(1) and Zn(4) with an interatomic distance of 6.990 Å] and two glutarate ligands in the type-**I** conformation. The other type is a 24-membered metallacycle (**B**) composed of four Zn^{II} ions [e.g., Zn(1), Zn(2), Zn(5), and Zn(6)] and two glutarate ligands in the type-**II** conformation as well as two carboxyl groups on two glutarate ligands in the type-**I** conformation; in this case, the interatomic distance of O(5) and O(6) is 12.895 Å, which is the longest interatomic distance in the metallacycle.

Metallacycles **A** and **B** are arranged in alternating layers along the *a*-axis (mean separation = 6.968 Å) and make eclipsed stacks along the *b*-axis, forming their own channel structures (Figure 2b). In the case of metalla-

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[16] Crystallographic data of *sc*-ZnGA: M_r = 195.47, monoclinic, $P2/c$, a = 13.934(3) Å, b = 4.7842(11) Å, c = 9.276(2) Å, β = (90.628(5))°, V = 618.3(2) Å^3, Z = 4, ρ_{cald} = 2.10 g cm^{-3}, T = 296 K, Siemens SMART CCD diffractometer, Mo Kα (λ = 0.71073 Å), μ = 6.33 cm^{-1}. The structure was solved by the Patterson method (SHELXS-86). The positions of all nonhydrogen atoms were refined anisotropically (SHELXL-93). Final block-diagonal matrix least-squares refinement on F^2 with all 1516 reflections and 92 variables converged to R1 ($I > 2\sigma(I)$) = 0.0733, wR2(all data) = 0.2182, and GOF = 1.134. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-166386.

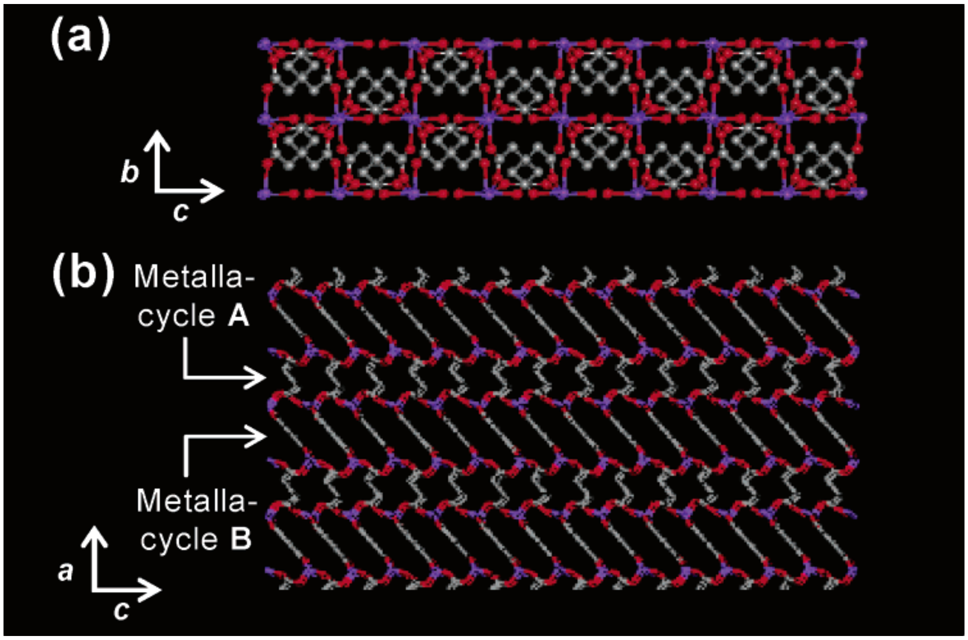

Figure 2. Three-dimensional molecular network structure in *sc*-ZnGA. (a) View down the crystallographic *a*-axis. (b) View down the crystallographic *b*-axis showing the packing order of two types of metallacycles resulting from the coordinations of the glutarate ligands in the bent and fully extended conformations to Zn^{II} ions: **A**, 16-membered metallacycle; **B**, 24-membered metallacycle.

cycle **B** channel, a small fraction of free volume is generated when the van der Waals radii of the constituent atoms are accounted for. The distance between ZnO_4 layers in the metallacycle **A** channel is similar to that in the metallacycle **B** channel, but channel **A** is almost completely filled by the van der Waals radii of the constituent atoms due to the alkylenyl units of the ligands in the bent conformation. Due to these limited spaces, the carbon dioxide and alkylene oxide monomers cannot diffuse through the channels; however, the channels do give rise to a surface topology on which the monomers adsorb favorably.

In a previous study of ZnGA catalysts prepared from a variety of zinc precursors, we found that the catalyst with the highest crystallinity gave the highest polymer yield in the polymerization of CO_2.[3,4,12] That finding indicates that the catalytic activity of ZnGA is primarily determined by its morphological characteristics, including the size and quality of its crystals. In addition, polycarbonate products obtained from the copolymerization of CO_2 and PO in the presence of a zinc carboxylate catalyst were found to be terminated with a carboxylate group originating from the catalyst.[7] Moreover, in a recent near-edge X-ray absorption fine structure spectroscopy study of polycrystalline ZnGA catalyst, we found that the ZnGA catalyst reversibly reacts with CO_2 and readily reacts with PO via adsorption onto the catalyst surface and insertion into the Zn−O bond.[11] These results collectively suggest that the Zn^{II} centers positioned at the surface function as active sites in the copolymerization of CO_2 and alkylene oxide.

The present results show that the crystal structure of ZnGA features two distinct metallacycle channel structures that alternate along the *a*-axis, providing a thermally stable framework. The structural information obtained in the present study is crucial to understanding of the catalytic active sites of ZnGA that facilitate the copolymerization of CO_2 and alkylene oxide. This understanding of the link between structure and catalytic activity can be used to guide the design of more effective catalysts.

Acknowledgment. This research work was supported by the KOSEF via the Center for Integrated Molecular Systems. We thank Dr. K. Park of Gyeongsang University for X-ray data collection.

CM035358J