Reversible Single Crystal to Single Crystal Transformation through Fe−O(H)Me/Fe−OH₂ Bond Formation/Bond Breaking in a Gas−Solid Reaction at an Ambient Condition

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In recent times, reversible single crystal to single crystal transformations driven by a gas−solid reaction have received great attention because of their potential applications in modern science, especially in obtaining functional materials, such as chemical sensors for toxic gases or volatile organic compounds.[1] Examples of single crystalline reactants that retain the single crystallinity in the corresponding product, even after crystalline state reactions, are limited;[2−7] loss of single crystallinity is a common phenomenon in this sort of solid-state reaction.[2] Best known reversible single crystal to single crystal transformations are mostly driven by light[3] or temperature.[4] The porous crystalline compounds comprise the major category exhibiting crystal to crystal transformations (including the gas−solid reactions),[5−7] since this type of reactions involves the cooperative movement of atoms in solid state.[4f] Metal−organic coordination complexes display unique structural changes induced by the removal/reabsorptions of an ancillary molecule in a crystal to crystal transformation.[8] A crystalline solid, that does not contain pores, but facilitates the diffusion of gaseous guest species in a reversible manner retaining its single crystallinity at an ambient condition, is rarely seen. We report here a gas−solid reaction based on a nonporous crystalline compound that operates not only in a reversible fashion but also maintains single crystallinity even after a solid-state rearrangement of atoms. A single crystal of a trinuclear iron compound [Fe₃(μ_3-O)(μ_2-CH₃COO)₆(C₅H₅NO)₂(H₂O)]ClO₄·3H₂O (1) containing a Fe−OH₂ covalent bond, on exposure with MeOH vapor, goes to a single crystal with the formation of a Fe−O(H)Me covalent bond in compound [Fe₃(μ_3-O)(μ_2-CH₃COO)₆-(C₅H₅NO)₂(MeOH)]ClO₄·3H₂O (2), retaining the lattice water molecules.

Original water coordinated compound 1 can be regenerated from MeOH-coordinated complex 2 by "atmospheric water vapor" at ambient conditions in a single crystal to single crystal transformation (Scheme 1).

Scheme 1
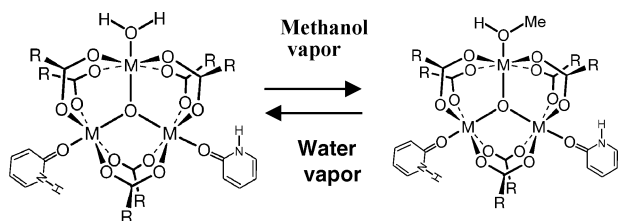
Unlike a symmetric basic carboxylate, the present {Fe₃} cluster has an unusual water coordination at one of three iron centers with two other irons, each coordinating one organic ligand, namely, 2-pyridone (see Scheme 1 and Figure 1, left). When the single crystals of compound 1 are exposed to methanol (MeOH) vapor at room temperature for 25 h, crystals of compound 1 get moistened

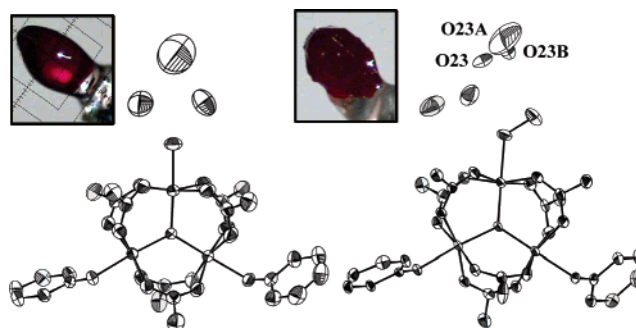**Figure 1.** Thermal ellipsoidal plots with 50% probability: left, compound 1; right, compound 2. The pictures of the relevant single crystals are shown in respective insets. In compound 2, one of the lattice waters (O23) is disordered over three positions (see section 1C2 in Supporting information for details).

without their dissolution. The color of the crystals remained the same to that of compound 1 (Figure 1).

The crystallographic analysis of the MeOH-vapor-treated crystal confirmed that iron coordinated water in compound 1 had been substituted by a MeOH molecule and excluded from the crystal resulting in the formation of a MeOH coordinated complex 2 (Scheme 1 and Figure 1, right). The methanol coordinated complex 2, on exposure to atmospheric water vapor at room temperature, reverts to water coordinated complex 1 (**regenerated 1**, Scheme 1), as confirmed by crystallography and IR spectroscopy (vide infra). The regeneration of parent compound 1, retaining single crystallinity, from compound 2 at normal atmospheric condition is unprecedented (see Figures S4 and S7 and sections 1C3 and 2B3 in Supporting Information). The crystal structure determinations[9] (see also sections 1A through 1D and S3 in Supporting Information) of compounds 1, 2, and **regenerated 1** provide us an unequivocal evidence for the reversibility of these quantitative crystalline state reactions, driven alternatively by MeOH and water vapors. The reversibility of this system can also be elucidated by infrared (IR) spectroscopic studies.

The IR spectrum of compound 2 remained overall similar to that of compound 1 except for the appearance of a new peak at 2841 cm⁻¹ (shown in the circle, Figure 2) that corresponds to C−H stretching vibrations of coordinated MeOH. The characteristic IR bands of the {Fe₃} complex (iron basic carboxylate) obscure the O−H stretching vibrations of MeOH. The system was, therefore, monitored by infrared spectral studies using CD₃OD-vapor exposed compound 1 (the isotope effect would result in the shifting of concerned IR bands). The infrared bands responsible for C−D and O−D stretching vibrations (of iron coordinated CD₃OD) are clearly visible in the region of 2000 to 2600 cm⁻¹ (2400, 2250, and 2080 cm⁻¹, Figure 2) in the infrared spectrum of the compound, that was obtained by exposing the crystals of compound 1 to CD₃OD vapor for 25 h at room temperature; fortunately, this region is

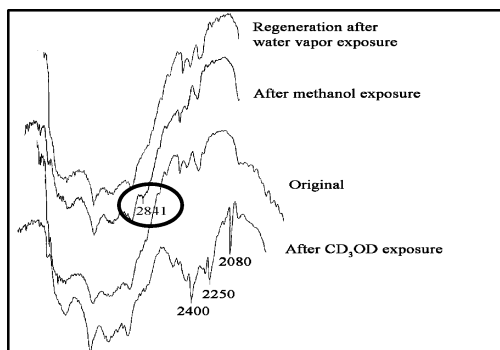**Figure 2.** From bottom to top: first, infrared spectrum of CD$_3$OD analogue of compound **2**, [{Fe$_3$(μ_3-O)(μ_2-CH$_3$COO)$_6$(C$_5$H$_5$NO)$_2$(CD$_3$OD)}]ClO$_4\cdot$3H$_2$O that was obtained by exposing crystals of **1** to CD$_3$OD vapor for 25 h; second, infrared spectrum of compound [{Fe$_3$(μ_3-O)(μ_2-CH$_3$COO)$_6$-(C$_5$H$_5$NO)$_2$(H$_2$O)}]ClO$_4\cdot$3H$_2$O (**1**); third, infrared spectrum of compound of [{Fe$_3$(μ_3-O)(μ_2-CH$_3$COO)$_6$(C$_5$H$_5$NO)$_2$(MeOH)}]ClO$_4\cdot$3H$_2$O (**2**); fourth, infrared spectrum of **regenerated 1**.

Scheme 2
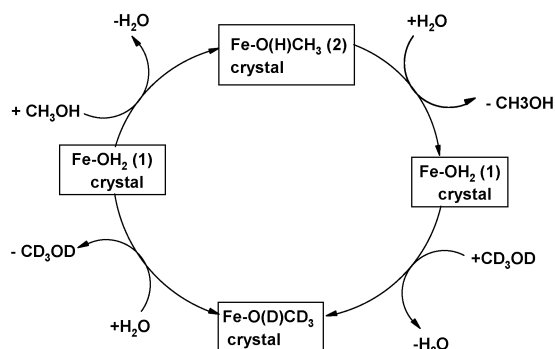
transparent in the infrared spectrum of compound **1**. The full reversibility of the crystalline state Fe−O(H)Me bond formation and Fe−OH$_2$ bond breaking (and vice versa) is demonstrated by exposing the crystals of **regenerated 1** to MeOH/CD$_3$OD vapor and H$_2$O vapor with the appearance and disappearance of these IR bands alternately. No loss in signal intensities is observed even after several repeated cycles (Scheme 2).

In conclusion, we have characterized all three states/stages of the reversible gas−solid reaction, namely, compound **1** (water coordinated), compound **2** (MeOH coordinated), and **regenerated 1** by single-crystal X-ray crystallography. This is not only a reversible single-crystal-to-single-crystal transformation through Fe−O(H)Me bond formation and Fe−OH$_2$ bond breaking (and vice versa) in a gas−solid reaction, it is selective toward methanol the molecule as well, which is evidenced from the following facts. When the single crystals of compound **1** were exposed to a mixture of different alcohols, for example, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, etc. (in the case of a high-boiling alcohol, the setup was warmed up in order to initialize the vaporization), the exposed crystals of **1** remained unreacted with all alcohols except methanol vapor (see section 2D in Supporting Information for details). It is important to note that, both H$_2$O and MeOH molecules are the competitors for the iron center, and the system needs water vapor to regenerate compound **1** in maintaining the cycle (e.g., Scheme 2). Thus, the forward reaction (compound **1**

→ compound **2**) is inhibited/retarded by the presence of water molecules in MeOH solvent. However, it has been observed that the present system (compound **1**) can recognize MeOH vapor from a 95% MeOH solvent (95% MeOH and 5% H$_2$O).

Supporting Information Available: Experimental details including syntheses and characterization data, IR spectral studies, and crystallographic details and data (CIF) for **1**, **2**, and **regenerated 1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Crystal data: (**1**) C$_{22}$H$_{36}$ClFe$_3$N$_2$O$_{23}$, *M* = 899.53 g mol^{-1}; orthorhombic, space group *Pbca*, *a* = 16.6883(9) Å, *b* = 17.5685(9) Å, *c* = 24.2830(13) Å; *V* = 7156.0(7) Å^3; *Z* = 8; ρ_{calcd} = 1.670 g cm^{-3}, μ = 1.365 mm^{-1}; 79173 reflections measured with 8856 independent reflections; R_{int} = 0.0646; R_1 = 0.0443, wR_2 = 0.1181 (observed data) and R_1 = 0.0629, wR_2 = 0.1253 (all data). (**2**) C$_{23}$H$_{38}$ClFe$_3$N$_2$O$_{23}$, *M* = 913.55 g mol^{-1}; orthorhombic, space group *Pbca*, *a* = 17.0064(12) Å, *b* = 17.4079(12) Å, *c* = 23.9382(17) Å; *V* = 7086.8(9) Å^3; *Z* = 8; ρ_{calc} = 1.712 g cm^{-3}, μ = 1.380 mm^{-1}; 47744 reflections measured with 6246 independent reflections; R_{int} = 0.0603; R_1 = 0.0481, wR_2 = 0.1199 (observed data), R_1 = 0.0765, wR_2 = 0.1449 (all data). (**regenerated 1**) C$_{22}$H$_{36}$ClFe$_3$N$_2$O$_{23}$, *M* = 899.53 g mol^{-1}; orthorhombic, space group *Pbca*, *a* = 16.6966(10) Å, *b* = 17.6462(11) Å, *c* = 24.2991(15) Å; *V* = 7159.3(8) Å^3; *Z* = 8; ρ_{calcd} = 1.669 g cm^{-3}, μ = 1.364 mm^{-1}; 34926 measured reflections with 6295 independent reflections; R_{int} = 0.1334; R_1 = 0.0575, wR_2 = 0.1374 (observed data), R_1 = 0.1276, wR_2 = 0.1771 (all data).

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