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CO_2 Coordination by Inorganic Polyoxoanion in Water

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Carbon dioxide has been well-recognized as one of the greenhouse gases causing global warming.[1] Although people currently are more focused toward understanding the storage of CO_2,[2,3] searching for economic methods to fix CO_2 remains a hot issue. The chemical transformation using carbon dioxide as renewable carbon resources has attracted much attention in the past decades, because of its application in the synthesis of fine chemicals and clean fuels.[4−6] However, highly thermodynamic stability and kinetic inertness of CO_2 hamper its activation in the chemical transformation. A promising route to CO_2 fixation is to bind CO_2 by a simple complex, so that the resulting complex becomes either a useful chemical or CO_2-activated reagent. So far, the number of structurally characterized CO_2-containing compounds is still limited.[7] These reported complexes represented four coordination modes of η^1-CO_2, η^2-COO, η^1-OCO, and μ-η^2, η^2-CO_2.[8,9] The reactions of these organometallic complexes strongly depend on toxic organic solvents such as benzene and tetrahydrofuran, and the remaining toxic solvents become again a new environmental problem. In addition, the expensive anhydrous solvents and raw materials make these reactions impractical for an industrially sustainable process. The development of environmentally friendly and economic methods for CO_2 fixation therefore remains a long-standing challenge. Our special attention thus focused on the chemical reaction in water to avoid the use of toxic or carcinogenic organic solvents as well as reduce solvent cost.

Polyoxometalates (POMs), as a class of large cluster polyoxoanions consisting of both metal ion (Mo, W, and V elements) and oxo ligand, have been widely used in diverse areas such as catalysis,[10] materials science,[11] and medicine.[12] The previous researches have proved that the polyoxoanions could covalently link a carboxylic or carbonato ligand in aqueous solution.[13,14] Inspired by these results, we consider that CO_2 may combine with polyoxoanions. When attempting to synthesize an imidazole-grafted polyoxoanion in aqueous solution together with in situ generated CO_2, fortuitously, we obtained an unusual CO_2-ligated compound, $(C_3H_5N_2)_3(C_3H_4N_2)[PMo_{11}CoO_{38}(CO_2)]\cdot 4H_2O$ (**1**). Compound **1** could feasibly be synthesized by an aqueous solution containing $[H_2PMo_{11}CoO_{40}]^{5-}$ polyoxoanion[15] with bubbled CO_2. Also, the analogic compound $(C_3H_5N_2)_4[SiMo_{11}CoO_{38}(CO_2)]\cdot 4H_2O$ (**2**) was isolated by the same process.[16] These two compounds, for the first time, represent the CO_2 coordination by inorganic polyoxoanions in aqueous solution. Noteworthy, the μ-η^1,η^1-**OCO** linear coordination mode is first shown among the known CO_2 complexes. The reactions depend on clean water solvent and inexpensive raw materials, and only mechanical stirring expends the electric power. Such an economic and environmentally friendly approach should be more suitable for the current industrial process of CO_2 fixation.

The single-crystal X-ray diffraction data[17] revealed the molecular structures of **1** and **2**. The skeletons of **1** and **2** are composed of $[PMo_{11}CoO_{38}(CO_2)]_n$ and $[SiMo_{11}CoO_{38}(CO_2)]_n$ polymeric chains, respectively (Figure 1). The polyoxoanion in the chain could be considered to be a mono-Co^{II}-substituted Keggin-type $[PMo_{12}O_{40}]^{3-}$ or $[SiMo_{12}O_{40}]^{3-}$ anion. The chain skeleton is bridged by the CO_2 ligand in an axial direction, showing a linear geometry. But the CO_2 groups show slightly bent arrangements with O−C−O angles of 158.7(14)° for **1** and 166.8(10)° for **2**. Two O atoms of CO_2 link Mo^{VI} and Co^{II} from two neighboring polyoxoanions, respectively. Atoms Mo(1) and Co of **1** and Mo(1), Co(1), Mo(3), and Co(2) of **2** were refined as mixed atoms (Mo(1) 50% and Co (50%) of **1**; Mo(1) (64%), Co(1) (36%), Mo(3) (86%), Co(2) (14%) of **2**). The polyanionic chains arrange each other along the *a* axis in the two complexes (Figure S1). The data of the elemental analysis and X-ray photoelectron spectra (Figure S2) well identify these atoms. The binding energies of Mo $3d_{5/2}$ (232.6 eV) and Co $2p_{3/2}$ (781.0 eV) for both **1** and **2** are in agreement with the reported data of Mo^{6+} and Co^{2+} ions.[18,19] Although the C−O distances obtained from single crystal data are not exact values due to the disorder of Mo and Co atoms in the crystal structure, the values 1.287(9) Å for **1** and 1.304(13) Å for **2** are still acceptable as compared with the values observed in other CO_2-ligated compounds.[8,9] The coordination binding of the two O atoms from CO_2 with electropositive Mo^{VI} and Co^{II} ions should reduce the electron density of O atoms in **1** and **2**, resulting in the increased C−O bond lengths.

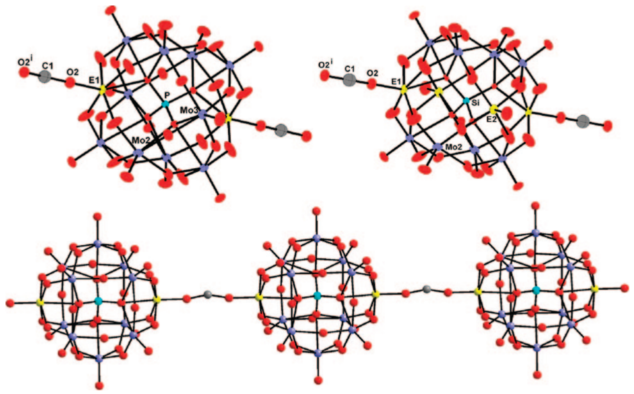

Figure 1. Thermal ellipsoid plots of polyoxoanions located in **1** (top left; Mo 50% and Co 50% for E1; symmetry code $i = -x, 1 - y, z$) and **2** (top right; Mo 60% and Co 40% for E1; Mo 90% and Co 10% for E2; symmetry code $i = 2 - x, 1 - y, z$). Ball−stick representation of polymeric chain structure of complex **1** (bottom). All imidazole and water molecules are omitted.

The infrared spectra of the crystalline samples exhibit the absorption bands at 2169 cm^{-1} for **1** and 2165 cm^{-1} for **2** (Figure S3), indicative of the coordinated CO_2 ligands. These absorption bands clearly show the red shift in comparison with $\upsilon_{asym} = 2348$ cm^{-1} of free CO_2.[8] This is in accordance with the structural features that CO_2 ligands appear in longer C−O bond distances for **1** and **2**. When **1** and **2** are prepared from the isotopically labeled $^{13}CO_2$ gas, these absorption bands show a stronger red shift (at 2108 cm^{-1}

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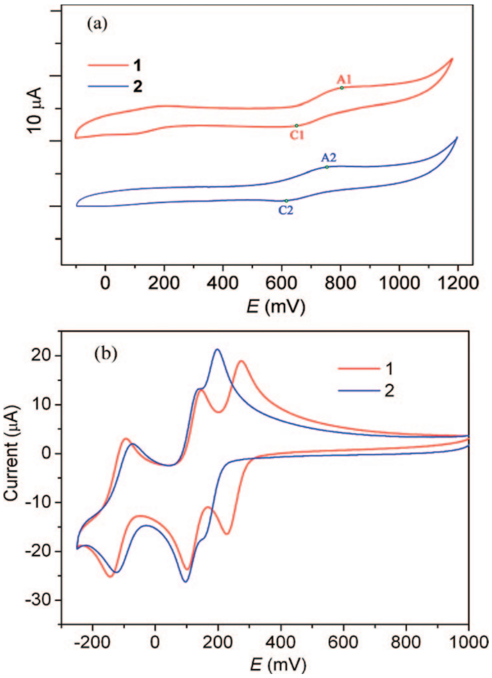

Figure 2. CV curves of 1.0×10^{-3} mol/L **1** and **2** in DMF solution using (a) 0.1 mol/L Bu_4NClO_4 and (b) addition of 30% (v/v) pH = 1.0 H_2SO_4 aqueous solution as electrolytes (scan rate 50 mV/s vs SCE).

for **1** and 2105 cm^{-1} for **2**), evidently resulting from an axial ν_{as}(OCO) vibrational mode. The electronic spectra of **1** and **2** display characteristic bands at 212 nm [p_π ($O_{terminal}$) → d_{π^*} (Mo) transitions] and 562 nm (d−d transitions of Co^{2+}) as shown in Figure S4. Such bands are very close to the reported values 214 and 565 nm for $(n\text{-}Bu_4N)_4HPMo_{11}Co^{II}(L)O_{39}$ (L = H_2O or pyridine) complexes.[20] In ^{13}C NMR spectra, the chemical shift (δ) for carbon atoms of CO_2 are 113.86 ppm for **1** and 112.50 ppm for **2** (Figure S5), appearing in distinct upfield shifts relative to free CO_2 at 125.8 ppm.[21] Further, the intensities of such resonances clearly increase when **1** and **2** are prepared using $^{13}CO_2$ (Figure S5).

Cyclic voltammetry (CV) curves of **1** and **2** indicate a quasi-reversible one-electron Co^{3+}/Co^{2+} redox process with ΔE_p of 155 and 156 mV, respectively (Figure 2a). The couloumetric detection confirmed the electron transfer number of 0.93 and 0.95 for the reduced processes of **1** and **2**, respectively. The Co^{3+}/Co^{2+} redox couples disappeared in *N*,*N*-dimethylformamide (DMF)/H_2SO_4 (pH = 1.0) mixed solvent (Figure 2b), suggesting that **1** and **2** are stable in organic solvent but easily transformed into the absent-Co^{2+} Keggin-type structures by acidification.[22] When the solid samples of **1** or **2** were dissolved in H_2SO_4 aqueous solution (pH = 0.5), CO_2 bubbles could be observed. By the gas chromatographic analysis (Figure S6), the generated CO_2 in **1** and **2** (**1**, 1.692%; **2**, 1.715%) are close to the calculated values (**1**, 1.815%; **2**, 1.816%). This result strongly demonstrates the existence of CO_2 ligands in the two compounds and indicates the structural decomposition of **1** or **2** in acidic solution. Thus, a quantifiable control of CO_2 release could be performed by the dissolution of **1** or **2** in acidic solution.

The electrospray ion mass spectra in the negative mode for **1** and **2** present several peaks in the region $m/z = 200-1000$ (Figure S7). These peaks at $m/z = 456.2$ and 512.6 for **1** and 512.1, 901.8, and 921.3 for **2** indicated the presence of CO_2-bearing ion clusters $[(PMo_{11}CoO_{39})_2(CO_2)(Him)H]^{8-}$ (calcd $m/z = 456.7$; Him = protonated imidazole) and $[(PMo_{11}CoO_{39})_2(CO_2)H_3]^{7-}$ (calcd $m/z = 512.2$) for **1** and $[(SiMo_{11}CoO_{39})_2(CO_2)H_5]^{7-}$ (calcd $m/z =$ 511.8), $[(CO_2)(SiMo_{11}O_{38})(CO_2)(SiMo_{11}O_{39})H_6]^{4-}$ (calcd $m/z =$ 902.6), and $[(CO_2)SiMo_{11}CoO_{38}(CO_2)H_2]^{2-}$ (calcd $m/z = 919.8$) for **2**. These results also suggest the occurrence of a C−O bond break in the polymeric chains.[23]

The successful syntheses of **1** and **2** provide a promising route to capture CO_2 by simple inorganic polyoxoanions in aqueous medium. The linear pattern of the CO_2 ligand in **1** and **2** should become a significant structural and functional model for catalytic conversion of CO_2 into useful chemicals. In particular, most of the current CO_2 reactions depend on organic solvent.[24] Thus, **1** and **2** represent a green chemical approach to CO_2 coordination chemistry.

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Supporting Information Available: Experimental details, structural figures, IR, UV−vis, NMR, XPS, ESI-MS spectra, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Experimental details are available as Supporting Information. Complex **1** can be prepared typically by the following procedure: $Co(CH_3COO)_2 \cdot 4H_2O$ (0.4 mmol), $Na_2MoO_4 \cdot 2H_2O$ (4.4 mmol), $Na_2HPO_4 \cdot 12H_2O$ (0.4 mmol), and $C_3H_4N_2$ (1.8 mmol) were dissolved in 20 mL of distilled water. After the pH was adjusted to 3.5 by 4 $mol \cdot L^{-1}$ HCl, an excess of CO_2 was bubbled through the stirred red mixture for 4 h. The resulting filtrate was transferred into a beaker of 50 mL. Evaporation of the solvent at room temperature generates the crystals of **1** (yield 33% based on Mo).

(17) Data collection were performed at 293(2) K on a Bruker SMART APEX(II) diffractometer with a charge-coupled device (CCD) area detector, with graphite-monochromated Mo Kα radiation (λ = 0.710 73). Molecular structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques. For **1**: *Orthorhombic*, *Fmmm*, $a = 13.055(1)$, $b = 21.179(2)$ Å, $c = 21.966(2)$ Å, $V = 6073.4(9)$ Å^3, $Z = 4$, $R1 = 0.0466$ and $wR2 = 0.1097$ for all data. For **2**: *Orthorhombic*, *Fmmm*, $a = 13.039(1)$ Å, $b = 21.333(2)$ Å, $c = 21.889(2)$ Å, $V = 6088.7(9)$ Å^3, $Z = 4$, $R1 = 0.0621$ and $wR2 = 0.1383$ for all data. CCDC number (**1**, 669695; **2**, 669696).

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