Gram-scale Synthesis of Quadruply Bonded Chromium (II) Acetate with Axial Ligands by Ligand Vapor Diffusion

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ABSTRACT

Quadruply bonded chromium (II) acetate coordinated with axial ligands was synthesized in gram scale by ligand vapor diffusion, where vapor-phase ligands diffuse onto the surface of anhydrous chromium (II) acetate crystals without dissolution. The product was obtained in gram scale with nearly 100 % yield, with the size of each crystal being comparable to previous reports. Powder X-ray diffraction studies confirmed the high purity of the product. The reaction mechanism was scrutinized by changing the amount of ligand inside the reaction vessel and the reaction time. As a new, simple route for ligand coordination by simple diffusion of vapor, this new method would contribute to fundamental studies and application of various complexes and materials with desired ligand coordination.

Keywords: Chromium, Quadruple bond, Synthesis, Interfacial diffusion, Ligand coordination

1. Introduction

Quadruple bonds between transition metals are one of the most intriguing topics in chemistry [1]. This unique type of bond contains δ bonds that are formed by the overlap of d orbitals of adjacent transition metal centers. Because the overlap of the d orbitals are not as significant as s or p orbitals, it requires an ultrashort distance between the metal atoms that results in a very narrow energy gap between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). Also, these quadruply bonded complexes prefer an eclipsed configuration of the ligands because of angle sensitive δ bonds. Therefore, they often leave room for the coordination of additional ligands at their “axial” positions, which significantly affects the chemical nature of quadruple bonds [2-4].

Among various compounds with quadruple bonds, anhydrous chromium (II) acetate ($\text{Cr}_2(\text{OAc})_4$) and chromium (II) acetate with axial ligands ($\text{Cr}_2(\text{OAc})_4\text{L}_2$; L=axial ligands) are unique [Fig. 1(a)]. First synthesized in 1844, the molecule was later revealed to have a quadruple bond between chromium (II) nuclei [5,6]. An important characteristic of chromium (II) acetate is the unavoidable coordination of ligands at their axial positions; even the anhydrous molecule, which lacks any axial ligands, has weak coordination interaction at its axial position with the acetoxy moiety of adjacent molecule. Such axial coordination alters the properties of the whole complex depending on the Lewis basicity of the axial ligands. For example, chromium (II) acetates exhibit diamagnetism-paramagnetism transition due to the excitation of electrons between d and d^* orbitals, and the energy required for the transition is reduced by the increased Lewis basicity of the ligands [7,8]. In addition, intermetallic vibrations are weakened

by the increasing basicity of the ligands, as observed by Raman spectroscopy [9]. That is, coordinating a desired ligand at the axial position changes the energy gap between the HOMO and the LUMO, which will in turn provides a new way to utilize chromium (II) acetate as a novel material with tunable band gap.

Synthesis of axially coordinated chromium (II) acetates has been usually achieved by the direct dissolution of anhydrous chromium (II)

Figure 1. (a) Molecular structure of anhydrous chromium (II) acetate. The arrows represent the reaction site where the ligands are coordinated. (b) Photograph of as-synthesized anhydrous chromium (II) acetate. (c) Powder X-ray diffraction pattern of as-synthesized chromium acetate. The blue line represents the measured data and the red line represents a pattern calculated from single crystal diffraction data (CCDC Number: 1265080). (d) Scheme for ligand vapor diffusion process.

acetate in the target solvent because the dissolution of anhydrous chromium (II) acetates in certain solvents always accompanies the coordination of the solvent molecule to the anhydrous molecule. Recently, we reported a versatile method to prepare crystalline forms of axially coordinated chromium (II) acetates by dissolution; anhydrous chromium (II) acetate was first dissolved in an anoxic target ligand solvent, and the crystals were later precipitated by lowering the temperature of the solution or by a simple drop-drying process [9]. While this method enabled the synthesis of high-quality complex, it was still impractical to prepare the products in large amount because of very low yield (~10 %). Such poor yield is attributed to the low solubility of anhydrous chromium (II) acetate in solvents. In addition, the high sensitivity of the solution toward oxygen requires proper removal of oxygen dissolved in the solvent during the reaction; otherwise, chromium (II) complexes are oxidized before precipitation. Therefore, any solution-based approach has an intrinsic limitation in obtaining high yield of the complex without oxidation.

We propose a new, gram-scale synthesis method called ligand vapor diffusion (LVD) to synthesize high-quality chromium (II) acetate with axial ligands, where anhydrous chromium (II) acetate crystals are exposed to vapor-phase ligand without dissolution. LVD achieves gram-scale synthesis of the compound within 6 h without degassing of the solvent with nearly 100 % yield. This makes LVD more convenient and less time-consuming than the previous method, which requires degassing of the solvent and anaerobic conditions for the crystallization. The quality of the product obtained by LVD is still comparable to that of the previous method, with high crystallinity and purity as shown by powder X-ray diffraction (PXRD).

2. Experimental details

Anhydrous chromium (II) acetate was prepared according to literature [10]. For LVD, a small cylindrical vessel (4 ml) was placed inside a large cylindrical vessel (20 ml). The inner vessel was filled with 3 ml of target ligand (such as water, methanol, and pyridine). It was then kept open without any cover during the reaction [Fig. 1(d)]. Note that while water and pyridine can be used with pre-treatment, methanol should first be dehydrated with a molecular sieve. Anhydrous chromium (II) acetate was placed in the outer vessel. The outer vessel was then sealed with a cap and connected to a Schlenk line. It was first evacuated and then filled with Ar, and this process was repeated at least three times to completely remove redundant gas. Then, Ar gas was continuously supplied into the vessel during the reaction. The whole vessel was immersed in a heating bath, and the temperature was maintained just below the boiling point of each target ligand. After 5 h for other ligands and 4 h for methanol, the vessel was slowly cooled to room temperature. The cap of the outer vessel was then removed, and the inner vessel was taken out. The powder in the outer vessel was carefully collected and dried. The specimen was kept in Ar (for L = methanol) or in vacuum (otherwise) for storage. All the measurements were performed in ambient conditions. A Powder X-ray diffractometer (Rigaku Ultima IV) was used to analyze the crystal structure of the specimen, using CuK α radiation. The diffraction study was conducted in ambient conditions without any evacuation or sealing process.

3. Results and discussion

Anhydrous chromium (II) acetate was prepared according to

literature [Fig. 1(b)] [10]. As shown by the powder X-ray diffraction pattern, the quality of anhydrous chromium (II) acetate is comparable to the literature [Fig. 1(c)]. The configuration of the reaction vessel for LVD is shown in Fig. 1(d). Water, methanol, and pyridine were used as the target ligands for LVD. After cooling the reaction vessel, the samples were collected and dried to remove condensed ligand vapor formed during the cooling process. The color of each specimen is different from that of anhydrous chromium (II) acetate [Fig. 1(b), Figs. 2(a)-(c)]. Note that unlike the water-coordinated or pyridine-coordinated complexes, the methanol-coordinated complex was susceptible to air exposure and prolonged evacuation but was stable in an Ar environment.

To analyze the morphology of the products, optical microscopy was used as shown in Figs. 2(d)-(f). The size of the specimens was roughly 50 to 100 μm in diameter, which is comparable to the previous report. Powder X-ray diffraction was used to analyze the crystal structure and the composition of the product, as shown in Fig. 3. The measured diffraction patterns were identical to those of the previous reports. There were no signs of byproducts or contaminants, such as oxidized forms of the compound or metallic chromium. This shows that even without degassing of the ligand solvents prior to LVD, all the reactions were properly completed without contamination or oxidation. This overcomes the limitation of the previous solution-based method, because even a small amount of oxygen dissolved in the solvent easily oxidized the whole solution [9]. The estimated yields

Figure 2. Photographs ((a) to (c)) and optical microscopy images ((d) to (f)) of specimens prepared by LVD. (a) and (d): L = water, (b) and (e): L = methanol, (c) and (f): L = pyridine. Molecular structure of each ligand is depicted at the topmost row. All scale bars in (d) to (f) represent 50 μm .

Figure 3. Powder X-ray diffraction patterns of specimens with (a) L = water, (b) L = methanol, (c) L = pyridine. Note that blue lines represent the measured XRD patterns of each specimen, and red lines show powder XRD patterns calculated from single crystal diffraction data (Reference: (a) CCDC Number: 1131602, (b) Ref. 9, (c) CCDC Number: 1100915).

Figure 4. Powder X-ray diffraction patterns of water-coordinated chromium (II) acetate ($L=H_2O$) prepared by changing the amount of the ligand in the inner vessel with fixing the reaction time of 5 h (a) and the reaction time with fixing the water amount of 3 ml (b). Black lines at the bottom of both graphs represent the calculated diffraction pattern of anhydrous chromium (II) acetate (CCDC Number: 1265080) and purple lines at the top show that of water-coordinated chromium (II) acetate (CCDC Number: 1131602).

were near unity (i.e., 97 % for water, 95 % for methanol, and 97.1 % for pyridine), and these values are substantially higher than the previous report, which is approximately 10 % [9]. Considering the unnecessary of any degassing process as well as the high yield of the products, we believe that this process is a remarkable improvement on the previous solution-based process.

To understand the mechanism of LVD, the amount of the ligand liquid in the inner vessel was reduced. At first, the amount of evaporated ligand during the reaction was estimated by performing an experiment without anhydrous chromium (II) acetate in the outer vessel. As a proof of concept, water was selected as a model ligand. After the reaction, the decreased amount of water was 0.87 ml. This implies that if the amount of water in the inner vessel is less than 0.87 ml, then the water would mostly exist as vapor phase and can also serve as the limiting reagent during the reaction. Therefore, 0.1, 0.3, and 0.5 ml of water were put in the inner vessel to determine which kinds of products were formed after the reaction under water-deficient condition. Figure 4(a) shows powder X-ray diffraction patterns of the specimens; anhydrous chromium (II) acetate and water-coordinated chromium (II) acetate have significantly different PXRD patterns, so it is very useful to observe the changes in the composition of the product. As shown in the graph, 0.1 ml of water did not produce any significant amount of water-coordinated chromium (II) acetate, but the portion of the water-coordinated complex increased as the amount of water in the inner vessel increased. This shows that ligand as vapor can indeed react with anhydrous chromium (II) acetate to trigger the coordination reaction without dissolution.

Time evolution of the ligand coordination reaction between water vapor and anhydrous chromium (II) acetate was also studied by PXRD [Fig. 4(b)]. The diffraction patterns show a gradual change from anhydrous chromium (II) acetate to water-coordinated chromium (II) acetate as the reaction time increased. This shows that at least 4 h of reaction is required for complete coordination. In addition, the lack of intermediates or byproducts in the XRD patterns clearly shows that the axial coordination occurs without any side-reaction or formation of intermediates. In addition, 5 h of reaction resulted in sharper peaks in the XRD pattern, showing the high quality of the product. Nonetheless, too much reaction time (such as more than 12 h) is not desired, because it eventually resulted in complete soaking of anhydrous chromium (II) acetate with the condensed ligand vapor, which made the specimen easily oxidized.

Based on the observations described above, we propose the

Figure 5. Scheme of reaction mechanism. When ligand vapor L is supplied onto the surface of anhydrous chromium (II) acetate, it forms coordinated chromium (II) acetate without dissolution process.

mechanism of LVD as follows Fig. 5. When the reaction vessel is heated, the ligand liquid in the inner vessel is slowly evaporated. The ligand vapor then diffuses out to the outer vessel and encounters the surface of anhydrous chromium (II) acetate powder located in the outer vessel. Upon contact, the ligand molecules are coordinated to anhydrous chromium (II) acetate to form coordinated complex, rather than forming separate, condensed liquid phase. The coordination reaction is mainly driven by diffusion of the ligands at the interface of the ligand vapor and anhydrous chromium (II) acetate crystal, rather than dissolution.

4. Conclusions

We synthesized chromium (II) acetate with ligands by LVD method. This new method features degassing-free, high-yield, gram-scale synthesis of chromium (II) acetates coordinated with various ligands. This proves that this new method is superior to the previous solution-based method, which requires a degassing process and has poor yield. This gram-scale preparation of chromium (II) acetate with diverse ligands can be expanded to other complexes and ligands, which will contribute to fundamental studies and applications of ligand-dependent tuning of materials. We believe that our findings would contribute to various fields of science and engineering by illuminating a new way to control the properties of solid-state materials by simple surface treatment with diffusion of ligand vapor.

Acknowledgements

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