

Supplementary Information

Facile and Rapid Synthesis of Crystalline Quadruply Bonded Cr(II) Acetate Coordinated with Various Ligands

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Experimental Methods

Synthesis of anhydrous $\text{Cr}_2(\text{OAc})_4$

The overall process is a modification to Levy et al.¹ 20 ml of acetic acid (Samchun, 99 %), 5 ml of acetic anhydride (Alfa Aesar, 99+ %), and 0.5 g of chromium powder (Alfa Aesar, ~325 mesh, 99 %) was mixed in a double-neck round-bottom flask (rbf) with a rotating magnetic stirrer inside. The flask was connected to a condenser, and the opposite end of the condenser was kept open. The remaining neck was closed with a septum. The reaction vessel was heated up to 120 °C, which is near the boiling point of acetic acid and acetic anhydride. When the temperature reached the target temperature, the septum was removed, and 1 ml of aqueous solution of HCl (Sigma Aldrich, 37 %) was quickly injected into the vessel through the open neck. The septum then closed the open neck. The color of the solution was gray at first due to dispersed chromium powder, and it turned green and eventually dark brown or purple. Note that reaction longer than an hour may result in a dark green solution instead of red powder shown in Figure 2a, implying excess oxidation of the product to Cr(III) state. After the reaction, the solution was filtered with a cellulose filtering paper, and the remaining red powder was rinsed with excess acetone. The powder was vacuum dried for several hours.

Synthesis of $\text{Cr}_2(\text{OAc})_4\text{L}_2$

A three-neck round bottom flask (50 ml) was used in this process. The target solvent (25 ml) and a rotating magnetic stirring bar were put in the vessel. In the case of water and pyridine (Sigma-Aldrich, ACS reagent, 99.0 %), fresh solvent was put in the flask without any pre-treatment. In the case of methanol (ACS reagent, 99.8 %), water molecules were removed by immersing fresh molecular sieve before putting in the flask. The center neck of the flask was connected to a condenser, and the opposite end of the condenser was connected to an oil bubbler to prevent inward diffusion of air. Another neck of the flask was closed with a rubber

septum, and a needle was stuck into the septum to supply Ar gas into the solvent. The other neck was closed with a septum, and it was opened only when chemicals or reagents were supplied into the flask. The reaction vessel was heated just below the boiling point of the solvent with Ar bubbles injected (i.e. 95 °C for H₂O, 60 °C for MeOH, 110 °C for py). After an hour, dried Cr₂(OAc)₄ powder (~300 mg for H₂O and ~150 mg for all other solvents) was gently dissolved into the solvent; the temperature and the Ar supply were not changed. Putting too much powder at once is not recommended, because the powder is not well dispersed in the solvent. When all the powder was put in the vessel, it was kept still (without changing the temperature, stirring rate, and Ar injection) for ten minutes for complete dissolution. Stirring was then stopped for full precipitation of remnants. For the cooling process, the clear supernatant was put in an Ar-filled vial. The solution is quite susceptible to air exposure, especially at elevated temperature, so it should be transferred as carefully as possible. The vial was then cooled down to room temperature, and small red crystallites (~10 to 20 mg) were precipitated at the bottom. For the drop-drying process, a drop of the supernatant was put on a clean substrate under the ambient condition. The drop was then dried to yield small crystallites on the substrate.

Characterization

All measurement and characterization were performed under the ambient condition. Raman spectra were measured using a WITec Alpha 300R confocal Raman spectroscopy equipped with a Nd:YAG laser (wavelength: 532 nm). Laser power was 1 mW, and the total exposure time was 100 seconds (10 accumulations times 10 seconds per each accumulation). All spectra were analyzed by a custom-made program (Python 3.7 with NumPy and SciPy package). Powder X-ray diffraction (PXRD) was measured using a Rigaku D/Max-2500 X-ray diffractometer.

The single-crystal diffraction data for $\text{Cr}_2(\text{OAc})_4\text{L}_2$ crystals were recorded on an ADSC Q210 CCD area detector with a synchrotron radiation ($\lambda = 0.70000 \text{ \AA}$) at 2D beamline in Pohang Accelerator Laboratory (PAL). The diffraction images were processed by using HKL3000.¹ Absorption correction was performed by using the program PLATON.² The structure was solved by direct methods (SHELXS-97)³ and refined by full-matrix least squares calculations on F^2 (SHELXL-97)⁴ using the WinGX⁵ program package.

Supplementary Figures

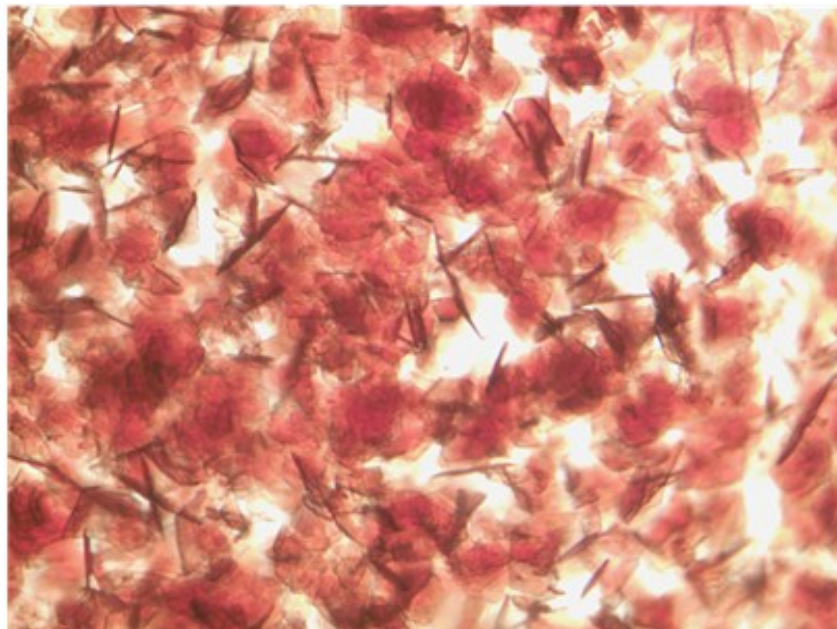


Figure S1 Crystals obtained by layering pyridine on top of an aqueous solution of Cr(II) acetate hydrate. A mixture of $\text{Cr}_2(\text{OAc})_4(\text{H}_2\text{O})_2$ and $\text{Cr}_2(\text{OAc})_4(\text{py})_2$, which have different morphologies, were obtained.

(a)



(b)



Figure S2 Evaporation of anhydrous Cr(II) acetate. (a) Evaporation at $270\text{ }^{\circ}\text{C} < T < 300\text{ }^{\circ}\text{C}$ yields reddish thin film that easily decomposes. (b) Most of the powder was decomposed to black powder after the evaporation process.

(a)



(b)

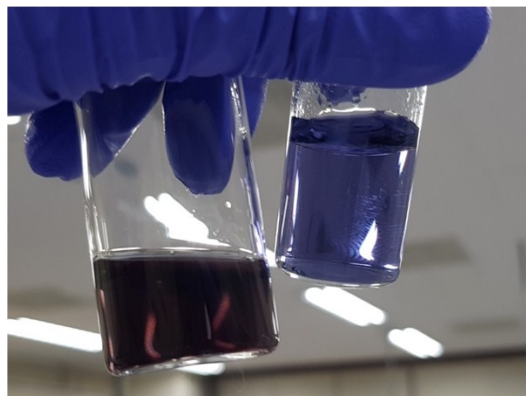


Figure S3 (a) The anhydrous $\text{Cr}_2(\text{OAc})_4$ dissolved into non-degassed methanol (left) was filtered to obtain the right solution. (b) The anhydrous $\text{Cr}_2(\text{OAc})_4$ dissolved into degassed deionized (DI) water (left) and non-degassed DI water (right).

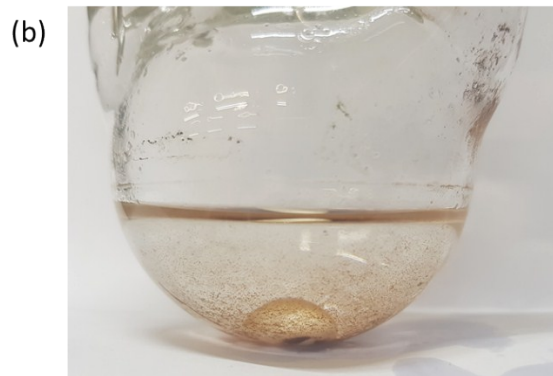
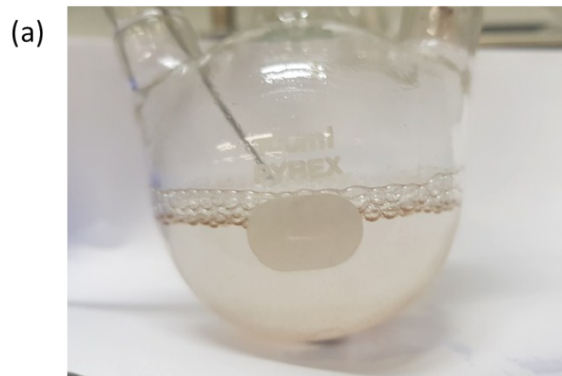


Figure S4 Photographs of $\text{Cr}_2(\text{OAc})_4$ put into degassed toluene (a) and hexane (b).

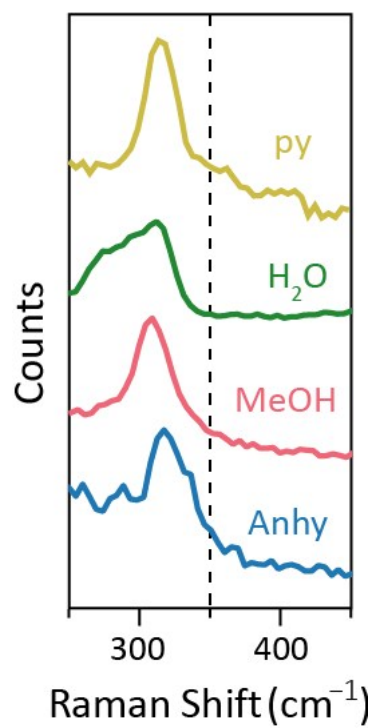


Figure S5. Detailed Raman spectra of Figure 4a at 350 cm⁻¹

References

- 1 O. Levy, B. Bogoslavsky and A. Bino, *Inorganica Chim. Acta*, 2012, **391**, 179–181.