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Facile and rapid synthesis of crystalline quadruply bonded Cr(II) acetate coordinated with axial ligands†

Intek Song,^a Jinyoung Koo^b and Seok Min Yoon^{*c}

A quadruple bond formed between d-block or f-block atoms is an interesting research topic due to its unique nature including a supershort bonding distance and narrow energy gap between δ and δ^* . Among various multiply bonded complexes, quadruply bonded Cr(II) acetates are considered useful to control the δ – δ^* energy gap by the Lewis basicity of additional ligands. However, the synthesis and preparation of the high-quality, large-sized crystals of Cr(II) acetates coordinated with axial ligands ($\text{Cr}_2(\text{OAc})_4\text{L}_2$) have been difficult due to their vulnerability to O_2 , a representative oxidizing agent under aerobic conditions. In this study, we report a facile synthesis of sub-millimeter-scale crystals of $\text{Cr}_2(\text{OAc})_4\text{L}_2$ by simple dissolution of $\text{Cr}_2(\text{OAc})_4$ in ligand solvents L. To obtain stably ligated $\text{Cr}_2(\text{OAc})_4\text{L}_2$, anhydrous Cr(II) acetates ($\text{Cr}_2(\text{OAc})_4$) were dissolved in the ligand solvents L, which was degassed of dissolved O_2 . Also, sub-millimeter-scale single crystals of $\text{Cr}_2(\text{OAc})_4\text{L}_2$ were produced rapidly for less than an hour by the drop-drying process. The single-crystalline phase of the synthesized Cr(II) complexes was measured by X-ray diffraction techniques, confirming the dependency of Lewis basicity of the additional axial ligands on the Cr–Cr quadruple bond distance. Further, the Raman peaks of the quadruple bonds in $\text{Cr}_2(\text{OAc})_4\text{L}_2$ were observed to be red-shifted with the increased basicity of the axial ligands.

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Introduction

There has been quite some progress in the research field on multiple bonds between transition metals since the Cotton group synthesized the quadruple bonded Cr(II) acetate ($\text{Cr}_2(\text{OAc})_4$) in the early 1970s.^{1,2} More recently the Power group reported Cr_2 quintuple bonds in addition to the quadruple bond,³ stimulating the in-depth research of the metal-to-metal (M–M) bonds.^{4–6} The multiple M–M bond, particularly the quadruple bond exists because the metals' d- or f-orbitals give rise to a delta bond (δ) as well as a sigma (σ) and two pi (π) bonds (Fig. 1a and b).^{1,2} Since the formation of quadruple bonds requires d-orbitals, they provide ultrashort (~ 2 Å) metal-to-metal bonds^{1,2} and a narrow energy gap.⁷ Also, various ligands can coordinate to the axial position of a M–M multiple bonded complex. Thus, the axial coordination to the M–M bond has been an important research topic to control the M–M bond

length and their reactivity depending on the types of ligand.³ Therefore, quadruple bonds have been used to construct a one-dimensional chain of transition metal atoms, to enable selective and reversible adsorption of O_2 , and a promising efficient catalyst.^{8,9} Besides, Cotton *et al.*⁷ reported that their magnetism can be changed at room temperature by the δ -to- δ^* transition

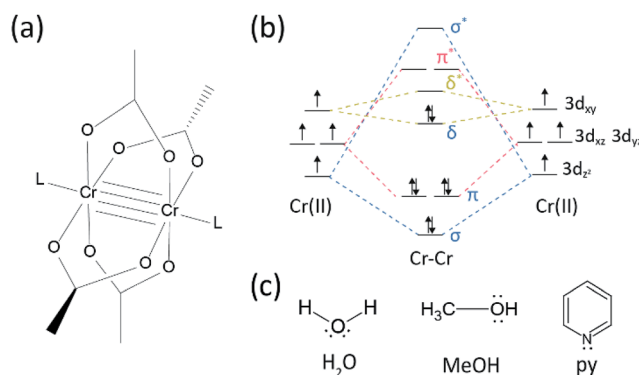


Fig. 1 (a) Molecular structure of ligated Cr–Cr acetates. The L stands for the axial ligand. The anhydrous Cr(II) acetate has the identical structure except that it lacks L. (b) Molecular orbital diagram of Cr–Cr quadruple bond. Note that non-bonding d orbitals are omitted for simplicity. (c) Molecular structure of the axial ligands used in this study. All of them have lone pair electrons.

^aDepartment of Applied Chemistry, Andong National University, 1375 Gyeongdong-ro, Andong, Gyeongbuk, 36729, Republic of Korea

^bDepartment of Chemistry, Pohang University of Science and Technology, 77 Cheongam-ro, Pohang, Gyeongbuk, 37673, Republic of Korea

^cDepartment of Bio-Nano Chemistry, Wonkwang University, 460 Iksandae-ro, Iksan, Jeonbuk, 54538, Republic of Korea. E-mail: smyoon1@wku.ac.kr

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between the diamagnetic singlet state ($\sigma^2\pi^2\delta^2$) and the paramagnetic triplet state ($\sigma^2\pi^2\delta\delta^*$).

There are various organometallic complexes having delta bonds, such as $\text{Re}_2\text{Cl}_8^{2-}$,¹⁰ $\text{Mo}_2(\text{mhp})_4$,¹¹ $\text{Cr}_2(\text{OAc})_4$,¹² etc.^{1–6} Among them, significant examples are paddle-wheel-structured anhydrous $\text{Cr}(\text{II})$ acetate ($\text{Cr}_2(\text{OAc})_4$), which lacks any axial ligands, and their derivatives that have axial ligands ($\text{Cr}_2(\text{OAc})_4\text{L}_2$, $\text{L} = \text{ligand}$) (Fig. 1a).^{1,13} Since $\text{Cr}(\text{II})$ has d^4 electronic configuration, two $\text{Cr}(\text{II})$ ions in the acetates completely fill the four bonding orbitals of a quadruple bond (bond order = 4) (Fig. 1b). $\text{Cr}(\text{II})$ acetates are thus moderately air-stable unlike other $\text{Cr}(\text{II})$ compounds such as CrCl_2 ; as dictated by the Pourbaix diagram,¹⁴ most $\text{Cr}(\text{II})$ compounds are very hygroscopic and quite easily oxidized to $\text{Cr}(\text{III})$. In addition, $\text{Cr}(\text{II})$ acetates are good Lewis acids that accept electron pairs at their axial positions. These electron donors contribute to the empty δ^* antibonding orbitals (LUMO), so the Lewis basicity of the ligands affects the physicochemical properties by modulating the narrow energy gap between δ and δ^* orbitals.^{1,12,13,15} Therefore, the synthesis of $\text{Cr}(\text{II})$ acetates with various axial ligands L ($\text{Cr}_2(\text{OAc})_4\text{L}_2$) would facilitate fundamental study on the nature of the unique delta bonds.

Traditionally $\text{Cr}_2(\text{OAc})_4\text{L}_2$ have been prepared by ligand exchange of the hydrate; for example, layering pyridine (py) on top of an aqueous solution of the hydrate ($\text{L} = \text{H}_2\text{O}$) precipitates small crystals of $\text{Cr}_2(\text{OAc})_4(\text{py})_2$.¹⁶ Such interfacial diffusion, however, may yield crystals of $\text{Cr}_2(\text{OAc})_4(\text{H}_2\text{O})_2$ as by-products (Fig. S1†). A rather straight forward way to coordinate the desired ligands is to dissolve $\text{Cr}_2(\text{OAc})_4$ in the target ligand solvent, as pointed out by Cotton *et al.*¹ However, this method has been restricted to few kinds of ligands, such as CH_3OH .⁷

The $\text{Cr}(\text{II})$ acetates should be handled with care to prevent the oxidation of $\text{Cr}(\text{II})$ to $\text{Cr}(\text{III})$, since even the quadruple bonds are not strong enough to altogether avoid the oxidation;¹⁷ they instead expedite the oxidation process to some extent. This is because O_2 in the air is such a good oxidizing agent that it effectively breaks the quadruple bond. Therefore, dissolved oxygen in the solvent should be removed, or degassed, before dissolving $\text{Cr}(\text{II})$ acetate. Nevertheless, the degassing process has not been explicitly mentioned or reported, to the best of our knowledge.^{1,7,12,16}

Herein, we unveil a simple solvent degassing process for the various ligation of the anhydrous $\text{Cr}(\text{II})$ acetate at the axial position, to prepare crystalline $\text{Cr}_2(\text{OAc})_4\text{L}_2$ ($\text{L} = \text{H}_2\text{O}$, CH_3OH (MeOH), and pyridine (py)) (Fig. 1c). Then, the target crystals are obtained by lowering the temperature of the solution or drop-drying process (Fig. 3a). The whole process takes less than a day to yield sub-millimeters scale crystals, while the conventional synthetic methods took several days according to previous literatures.^{15,18} Our findings would contribute to promoting the exploration of quadruple bonds between metal atoms, the extension of metal-to-metal (M–M) multiple bonds-based networks to form coordination polymers^{19,20} or metal–organic frameworks^{8,21} as well as the study of their unique physical and chemical properties of the quadruple bonds.

Results and discussion

1. Synthesis of Anhydrous $\text{Cr}_2(\text{OAc})_4$

Anhydrous $\text{Cr}_2(\text{OAc})_4$, the precursor of the $\text{Cr}_2(\text{OAc})_4\text{L}_2$ has been prepared by annealing the hydrate or ethanolate ($\text{L} = \text{EtOH}$) in a vacuum. However, this process yields amorphous powder, which is easily oxidized.^{12,17} An altered approach to preparing $\text{Cr}_2(\text{OAc})_4$ by a direct chemical reaction between acetic acid and chromocene ($\text{Cr}(\text{C}_2\text{H}_5)_2$), but the chromocene is air-sensitive and flammable complex.^{18,22} Therefore, both methods are not suitable for preparing $\text{Cr}_2(\text{OAc})_4$ that is stable in air.

Recently, Levy *et al.*²² reported another synthetic method to prepare the crystalline $\text{Cr}_2(\text{OAc})_4$, using such air-stable precursors as $\text{Cr}(\text{0})$ powder, acetic acid, acetic anhydride, and HBr . In addition, the product is stable in the air up to several hours, unlike that of the predecessors. Therefore, we adapted Levy *et al.*'s manner for the preparation of the high-purity crystals of $\text{Cr}_2(\text{OAc})_4$ with slight modification (refer to Experimental section for details in ESI†).

In our synthetic process, concentrated (37%) HCl (aq) was used instead of HBr or KBr , and the Cr powder was halved in the amount of the reference. The total reaction time was less than an hour to prevent oxidation to $\text{Cr}(\text{III})$. Such modifications are to guarantee the exclusion of by-products or unreacted reactants (e.g. $\text{Cr}(\text{III})$ acetate and $\text{Cr}(\text{0})$ powder, respectively) in the final product. Therefore, red crystalline powder was prepared after simply filtering the product and washing it with excess acetone to remove $\text{Cr}(\text{III})$ acetates (Fig. 2a).

The powder was then dried in a vacuum at room temperature for a few hours. As shown in Fig. 2b, powder X-ray diffraction (PXRD) revealed that the red powder is $\text{Cr}_2(\text{OAc})_4$ having a triclinic unit cell ($P\bar{1}$, $a = 7.583 \text{ \AA}$, $b = 8.688 \text{ \AA}$, $c = 5.178 \text{ \AA}$, $\alpha = 111.16^\circ$, $\beta = 95.77^\circ$, $\gamma = 98.16^\circ$, $V = 310.626 \text{ \AA}^3$); the pattern is identical to a pattern calculated from previously reported crystallographic information of $\text{Cr}_2(\text{OAc})_4$ (CCDC#: TACETC).

Note that the obtained powder was used without further purification, since it was very difficult to purify. When vapor-phase recrystallization of $\text{Cr}_2(\text{OAc})_4$ was attempted for the purification, nothing was evaporated below 270°C under Ar flow. Only a small portion of the red powder evaporated at temperature above 270°C and below 300°C , and the remnant was decomposed into black powder (Fig. S2†). The evaporated powder was recrystallized into reddish thin film, but it was so quickly decomposed into green-implicating oxidation to $\text{Cr}(\text{III})$ —that it could not be retrieved for further reactions. At temperature above 300°C the powder was fully decomposed without evaporation. Such difficulty in vapor-phase recrystallization is consistent with previous reports.^{1,13,15}

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

In order to synthesize the $\text{Cr}(\text{II})$ acetates coordinated with axial ligands ($\text{Cr}_2(\text{OAc})_4\text{L}_2$), we first selected target ligand solvents as follows: MeOH, H_2O , and py (Fig. 1c). These ligands have electron lone pairs to form a stable coordination bond to $\text{Cr}_2(\text{OAc})_4$. They have different Lewis basicity ($\text{MeOH} < \text{H}_2\text{O} < \text{py}$), and accordingly the internuclear distance of the quadruple bond in



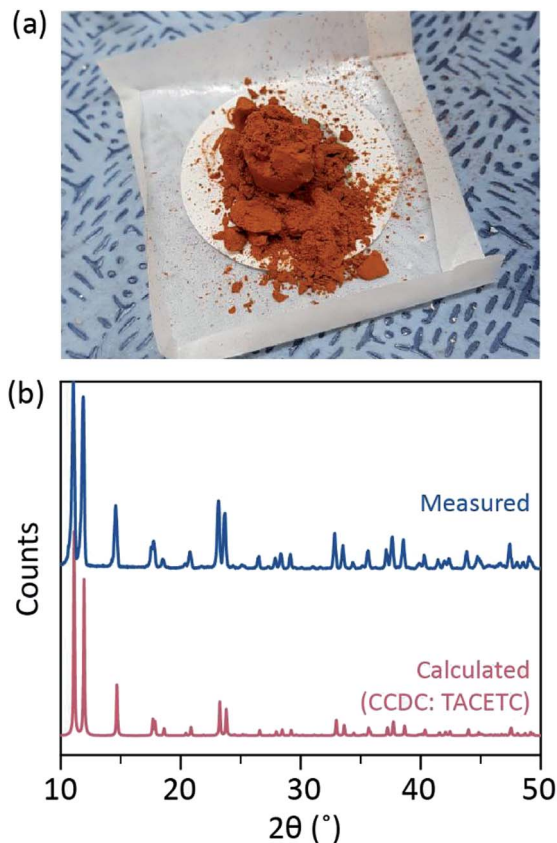


Fig. 2 (a) Photograph of the as-prepared $\text{Cr}_2(\text{OAc})_4$ powder. The image was taken in air. (b) X-ray diffraction of the powder (blue). The red graph is an estimated diffraction pattern based on the crystallographic information of $\text{Cr}_2(\text{OAc})_4$ registered in the CCDC database.

the ligated complex is known to span from 2.288 Å (anhydrous), 2.329 Å (MeOH), 2.362 Å (H_2O), and to 2.369 Å (py), according to the Lewis basicity of the axial ligands.^{7,12,16,23}

The ligand solvents were degassed by heating it just below its boiling point with an injection of Ar gas (Fig. 3a). This degassing process is prerequisite for the dissolution of $\text{Cr}_2(\text{OAc})_4$ in the target solvent for preventing degradation of the quadruple bonds, as obstructing vigorous oxidation by the dissolved O_2 . When $\text{Cr}_2(\text{OAc})_4$ was dissolved into a degassed solvent, the color of the solution instantly changed to red like $\text{Cr}_2(\text{OAc})_4$ (Fig. 3b). Note that dissolution in degassed H_2O is not instantaneous; when a small amount of $\text{Cr}_2(\text{OAc})_4$ was put in degassed H_2O , it was blue at first, and then adding an extra amount of the solute eventually turned it reddish brown. Such two-step dissolution may be attributed to the equilibrium between $\text{Cr}_2(\text{OAc})_4$ (aq) and Cr^{2+} (aq), as follows:^{1,24} (i) $\text{Cr}_2(\text{OAc})_4 \rightleftharpoons 2\text{Cr}(\text{OAc})_2$, (ii) $\text{Cr}(\text{OAc})_2 \rightleftharpoons \text{Cr}(\text{OAc})^+ + \text{OAc}^-$, (iii) $\text{Cr}(\text{OAc})^+ \rightleftharpoons \text{Cr}^{2+} + \text{OAc}^-$.

In contrast, when $\text{Cr}_2(\text{OAc})_4$ was dissolved in non-degassed solvents, the solution was blue for H_2O and MeOH and orange for pyridine, which are attributed to the decomposition of $\text{Cr}_2(\text{OAc})_4$ (Fig. S3†).¹ Note that there are also certain solvents that do not dissolve $\text{Cr}_2(\text{OAc})_4$ even after the degassing process. When $\text{Cr}_2(\text{OAc})_4$ was put in hexane or toluene, which does not have any electron lone pairs to donate, neither dissolution nor

coordination was observed; all the powder sank to the bottom of the reaction vessel (Fig. S4†). Such selective solubility shows that the coordination of the ligands accompanies the dissolution of $\text{Cr}_2(\text{OAc})_4$, and *vice versa*.¹

3. Crystallization of $\text{Cr}_2(\text{OAc})_4\text{L}_2$

When the ligation in anoxic condition was finished, stirring was stopped for precipitation of remaining reactants like Cr powder or undissolved $\text{Cr}_2(\text{OAc})_4$ powder. The temperature was kept identical to the degassing and dissolution process (*i.e.*, just below the boiling point of the ligand solvent). To obtain the crystals of the ligated complexes ($\text{Cr}_2(\text{OAc})_4\text{L}_2$), clear supernatant was carefully put in an Ar-filled vial for cooling under anoxic condition at room temperature, since the solution is very air-sensitive; only a brief exposure changes the color from red to blue or green, implying the oxidation of the complex. Small red crystals in the Ar-filled vial had been grown at the bottom of the vial less than 24 hours (crystallization process (i) in Fig. 3a). The crystals can also be obtained very rapidly by even drop-drying the supernatant onto a substrate, and it takes less than an hour under the ambient condition (crystallization process (ii) in Fig. 3a). The crystalline products by both methods are identical; they are sub-millimeter-scale, reddish crystals, of which colors are subtly different depending on the ligands (Fig. 3b–d).

4. Characterization of $\text{Cr}_2(\text{OAc})_4\text{L}_2$

Further, single-crystal X-ray diffraction (SCXRD) studies confirmed that the crystallographic structure of the obtained $\text{Cr}_2(\text{OAc})_4\text{L}_2$ crystals are matched with those of previously reported crystals (Table 1).^{7,12,16} Note that SCXRD was attempted for structural confirmation of the large sized single crystal instead of PXRD, since the yield of the crystals were not high (7.94% for $\text{L} = \text{H}_2\text{O}$, 11.26% for $\text{L} = \text{MeOH}$, and 3.70% for $\text{L} = \text{py}$). Such low yield is attributed to that the solubility of $\text{Cr}_2(\text{OAc})_4$ in the ligand solvents is poor,¹ and also that most of the ligated complex molecules remain as the solute even after the crystallization. Moreover, through the SCXRD studies, it is confirmed that the internuclear distance between M–M is elongated depending on the Lewis basicity of the additional axial ligands (Lewis basicity: $\text{MeOH} < \text{H}_2\text{O} < \text{py}$). Thus, the order of M–M distances of the $\text{Cr}_2(\text{OAc})_4\text{L}_2$ are disclosed by the SCXRD as follows: $\text{Cr}_2(\text{OAc})_4 < \text{Cr}_2(\text{OAc})_4(\text{MeOH})_2 < \text{Cr}_2(\text{OAc})_4(\text{H}_2\text{O})_2 < \text{Cr}_2(\text{OAc})_4(\text{py})_2$. Besides, the rapidly synthesized ligated crystals were also stable in the air for, but not limited by, 12 hours just as the original $\text{Cr}_2(\text{OAc})_4$ crystals. A probable reason would be the packing of the molecules in the crystals, which can hinder the attack by certain oxidizing agents like O_2 . These shreds of evidence tell us that our simple crystallization method makes the diverse ligands readily attach to the axial position of the Cr–Cr quadruple bond with increased stability.

Raman spectroscopy has been used as a powerful tool for studying vibration modes of multiply-bonded binuclear complexes containing Cr, Mo, W, or Re and a correlation between the M–M bond strength and distance according to various ligands.^{1,25–27} As shown in Fig. 4, confocal Raman spectroscopy (Alpha 300R, WITec) revealed vibration modes of



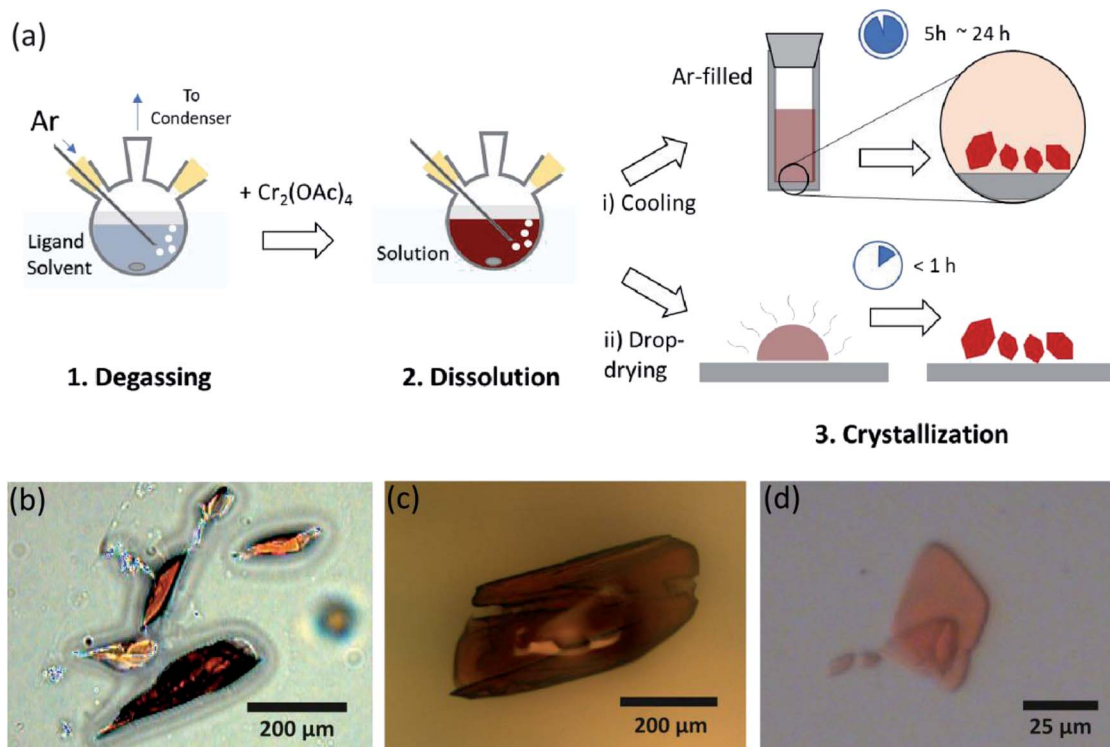


Fig. 3 (a) Scheme of the ligand coordination process. (b–d) Microscope images of obtained crystals of $\text{Cr}_2(\text{OAc})_4\text{L}_2$, where $\text{L} = \text{H}_2\text{O}$ (b), MeOH (c), py (d).

the crystals of $\text{Cr}(\text{II})$ acetates. The Raman spectral data of $\text{Cr}(\text{II})$ acetates were collected less than a few minutes, to prevent degradation of the complexes while the crystals were irradiated by laser excitation source (532 nm, 0.5 mW, Nd:YAG) under the ambient condition.

In our experiment, the measured Raman spectrum of $\text{Cr}_2(\text{OAc})_4(\text{H}_2\text{O})_2$ is identical to a previous report,²⁵ but the Raman spectra of the other synthesized complexes including anhydrous $\text{Cr}_2(\text{OAc})_4$ are not reported, to the best of our knowledge. The $\text{Cr}-\text{Cr}$ quadruply bonded complexes are shown in Fig. 4 have a similar pattern of the Raman spectrum of the $\text{Cr}_2(\text{OAc})_4(\text{H}_2\text{O})_2$, possibly due to the similarity of the molecular structures. In the Raman spectra, bands around 550 cm^{-1} and 350 cm^{-1} have been assigned to $\text{Cr}-\text{Cr}$ stretching and twisting/bending modes of $\text{Cr}(\text{II})$ acetates, respectively.^{25,28,29} Nonetheless, the exact band positions are barely distinguished from the measured Raman spectra of all $\text{Cr}(\text{II})$ acetates due to their low intensity¹⁸ or broad width (Fig. S5†). As an alternative, the overtone envelopes of the $\text{Cr}-\text{Cr}$ quadruple bonds' vibration are obviously displayed around 700 cm^{-1} ($2 \times \sim 350\text{ cm}^{-1}$)

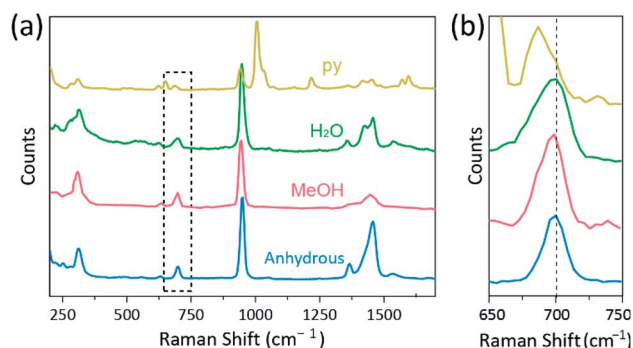


Fig. 4 (a) Raman spectra of $\text{Cr}_2(\text{OAc})_4$ (blue) and $\text{Cr}_2(\text{OAc})_4\text{L}_2$ ($\text{L} = \text{MeOH}$ (red), H_2O (green), and py (yellow)). (b) Detailed Raman spectra inside the dashed box in (a). The dashed line represents the center of the overtone mode of $\text{Cr}_2(\text{OAc})_4$. The spectra were obtained by confocal Raman spectroscopy with 532 nm excitation wavelength.

(Fig. 4b).²⁹ Indeed, as the basicity of the axial ligand increases, the overtone band is red-shifted accordingly.³⁰ This clue reflects that the bond strength of the quadruple bonds being weaker, as

Table 1 Unit cell parameters of $\text{Cr}_2(\text{OAc})_4\text{L}_2$ determined by single-crystal X-ray diffraction

L	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Volume (Å ³)	Space group	Note
H_2O	13.105	8.568	13.838	90.00	116.71	90.00	1388	$C2/c$	31
MeOH	8.065	7.406	13.296	90.00	92.84	90.00	793.2	$P2_1/n$	32
py	12.875	8.589	19.524	90.00	90.00	90.00	2159	$Pbca$	33



increasing the Lewis basicity of the axial ligands.²⁹ Also, the degree of red-shifts of the Cr(II) acetates in Raman spectra is correlated to its Cr–Cr distances. Thus, the overtone band of Cr₂(OAc)₄ shows the highest wavenumber, but Cr₂(OAc)₄(py)₂ have the lowest wavenumber among the Cr–Cr quadruply bonded complexes.

Conclusion

We developed a feasible and rapid way to synthesize sub-millimeter-scale single crystals of Cr₂(OAc)₄L₂, where L = H₂O, MeOH, and py. The key to success is the removal of oxidizing agents dissolved in the ligand solvents before dissolving crystalline powder of Cr₂(OAc)₄. Also, dissolution of Cr₂(OAc)₄ in certain ligand solvents occurs only when the coordination bonds are formed between anhydrous Cr(II) acetate (Lewis acid) and the ligand molecules (Lewis base). Our result demonstrates that various molecules can coordinate as axial ligands to multiply bonded organometallic complexes by a facile process. Such versatility and simplicity can further be expanded to replace the paddle-wheel ligands and metal atoms, achieving an even more diverse combination to develop the large extent of M–M based network system such as M–M chained coordination polymers and metal–organic frameworks. Design and preparation of such novel complexes would contribute to the fundamental understanding of delta orbitals and multiple bonds and their applications to various fields of physics, chemistry, and related engineering.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

- 1 F. A. Cotton, C. A. Murillo and R. A. Walton, *Multiple Bonds Between Metal Atoms*, Springer-Verlag, New York, 2005.
- 2 F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pipal and D. A. Ucko, *J. Am. Chem. Soc.*, 1970, **92**, 2926–2927.
- 3 T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fetting, G. J. Long and P. P. Power, *Science*, 2005, **310**, 844–847.
- 4 F. R. Wagner, A. Noor and R. Kempe, *Nat. Chem.*, 2009, **1**, 529–536.
- 5 K. A. Kreisel, G. P. A. Yap, O. Dmitrenko, C. R. Landis and K. H. Theopold, *J. Am. Chem. Soc.*, 2007, **129**, 14162–14163.
- 6 A. Falceto, K. H. Theopold and S. Alvarez, *Inorg. Chem.*, 2015, **54**, 10966–10977.
- 7 F. A. Cotton, H. Chen, L. M. Daniels and X. Feng, *J. Am. Chem. Soc.*, 1992, **114**, 8980–8983.
- 8 E. D. Bloch, W. L. Queen, M. R. Hudson, J. A. Mason, D. J. Xiao, L. J. Murray, R. Flacau, C. M. Brown and J. R. Long, *Angew. Chem., Int. Ed.*, 2016, **55**, 8605–8609.
- 9 L. J. Murray, M. Dinca, J. Yano, S. Chavan, S. Bordiga, C. M. Brown and J. R. Long, *J. Am. Chem. Soc.*, 2010, **132**, 7856–7857.
- 10 F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1965, **4**, 330–333.
- 11 W. Clegg, C. D. Garner, L. Akhter and M. H. Al-Samman, *Inorg. Chem.*, 1983, **22**, 2466–2468.
- 12 F. A. Cotton, C. E. Rice and G. W. Rice, *J. Am. Chem. Soc.*, 1977, **99**, 4704–4707.
- 13 S. N. Ketkar and M. Fink, *J. Am. Chem. Soc.*, 1985, **107**, 338–340.
- 14 M. Pourbaix, *Atlas of electrochemical equilibria in aqueous solutions*, National Association of Corrosion Engineers, 1974.
- 15 F. A. Cotton, E. A. Hillard, C. A. Murillo and H. C. Zhou, *J. Am. Chem. Soc.*, 2000, **122**, 416–417.
- 16 F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, 1980, **19**, 328–331.
- 17 J. C. Reeve, *J. Chem. Educ.*, 1985, **62**, 444.
- 18 F. A. Cotton, M. W. Extine and G. W. Rice, *Inorg. Chem.*, 1978, **17**, 176–186.
- 19 H.-C. Chang, J.-T. Li, C.-C. Wang, T.-W. Lin, H.-C. Lee, G.-H. Lee and S.-M. Peng, *Eur. J. Inorg. Chem.*, 1999, **1999**, 1243–1251.
- 20 M. Yang, T.-W. Lin, C.-C. Chou, H.-C. Lee, H.-C. Chang, G.-H. Lee, M. Leung and S.-M. Peng, *Chem. Commun.*, 1997, 2279–2280.
- 21 L. J. Murray, M. Dinca, J. Yano, S. Chavan, S. Bordiga, C. M. Brown and J. R. Long, *J. Am. Chem. Soc.*, 2010, **132**, 7856–7857.
- 22 O. Levy, B. Bogoslavsky and A. Bino, *Inorg. Chim. Acta*, 2012, **391**, 179–181.
- 23 F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pipal and D. A. Ucko, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1971, **27**, 1664–1671.
- 24 R. D. Cannon and J. S. Stillman, *Inorg. Chem.*, 1975, **14**, 2207–2214.
- 25 Y. M. Huang, H. R. Tsai, S. H. Lai, S. J. Lee, I. C. Chen, C. L. Huang, S. M. Peng and W. Z. Wang, *J. Phys. Chem. C*, 2011, **115**, 13919–13926.
- 26 R. E. Da Re, J. L. Eglin, C. N. Carlson, K. D. John, D. E. Morris, W. H. Woodruff, J. A. Bailey, E. Batista, R. L. Martin, F. A. Cotton, E. A. Hillard, C. A. Murillo, A. P. Sattelberger and R. J. Donohoe, *J. Am. Chem. Soc.*, 2010, **132**, 1839–1847.
- 27 W. C. Trogler and H. B. Gray, *Acc. Chem. Res.*, 1978, **11**, 232–239.
- 28 F. A. Cotton, P. E. Fanwick, R. H. Niswander and J. C. Sekutowski, *J. Am. Chem. Soc.*, 1978, **100**, 4725–4732.
- 29 R. E. Da Re, J. L. Eglin, C. N. Carlson, K. D. John, D. E. Morris, W. H. Woodruff, J. A. Bailey, E. Batista, R. L. Martin, F. A. Cotton, E. A. Hillard, C. A. Murillo, A. P. Sattelberger and R. J. Donohoe, *J. Am. Chem. Soc.*, 2010, **132**, 1839–1847.
- 30 Note that in case of Cr₂(OAc)₄(py)₂ a weak peak near 680 cm^{−1} was assigned as the overtone mode instead of the strong peak near 650 cm^{−1}, because it too much deviates from 700 cm^{−1}. This assignment is nonetheless



acceptable, because the Raman peaks of $\text{Cr}_2(\text{OAc})(\text{py})_2$ that are common to other complexes are substantially weaker than the uncommon peaks.

- 31 $\text{Cr}_2(\text{OAc})_4(\text{H}_2\text{O})_2$: $\text{C}_8\text{H}_{12}\text{O}_{10}\text{Cr}_2$, $M_r = 372.18$, crystal dimensions $0.10 \times 0.09 \times 0.02 \text{ mm}^3$, monoclinic, $C2/c$, $a = 13.105(3) \text{ \AA}$, $b = 8.5680(17) \text{ \AA}$, $c = 13.838(3) \text{ \AA}$, $\beta = 116.71(3)^\circ$, $V = 1388.0(6) \text{ \AA}^3$, $T = -173^\circ\text{C}$, $Z = 4$, $r_{\text{cal}} = 1.781 \text{ g cm}^{-3}$, $m = 0.15 \text{ cm}^{-1}$, 1968 unique reflections out of 2076 with $I > 2s(I)$, 94 parameters, $2.925^\circ < q < 29.848^\circ$, $R_1 = 0.0425$, $wR_2 = 0.1183$, $\text{GOF} = 0.927$. CCDC deposit number 1131602.
- 32 $\text{Cr}_2(\text{OAc})_4(\text{MeOH})_2$: $\text{C}_{10}\text{H}_{18}\text{O}_{10}\text{Cr}_2$, $M_r = 402.24$, crystal dimensions $0.05 \times 0.04 \times 0.05 \text{ mm}^3$, monoclinic, $P2_1/n$,

$a = 8.0650(16) \text{ \AA}$, $b = 7.4060(15) \text{ \AA}$, $c = 13.296(3) \text{ \AA}$, $\beta = 92.84(3)^\circ$, $V = 793.2(3) \text{ \AA}^3$, $T = -173^\circ\text{C}$, $Z = 2$, $r_{\text{cal}} = 1.684 \text{ g cm}^{-3}$, $m = 0.135 \text{ cm}^{-1}$, 2197 unique reflections out of 2277 with $I > 2s(I)$, 105 parameters, $3.102^\circ < q < 29.841^\circ$, $R_1 = 0.0439$, $wR_2 = 0.1198$, $\text{GOF} = 0.862$. Refer to ref. 7.

- 33 $\text{Cr}_2(\text{OAc})_4(\text{py})_2$: $\text{C}_{18}\text{H}_{22}\text{O}_8\text{N}_2\text{Cr}_2$, $M_r = 496.36$, crystal dimensions $0.09 \times 0.08 \times 0.09 \text{ mm}^3$, orthorhombic, $Pbca$, $a = 12.875(3) \text{ \AA}$, $b = 8.5890(17) \text{ \AA}$, $c = 19.524(4) \text{ \AA}$, $V = 2159.0(7) \text{ \AA}^3$, $T = -173^\circ\text{C}$, $Z = 4$, $r_{\text{cal}} = 1.533 \text{ g cm}^{-3}$, $m = 0.10 \text{ cm}^{-1}$, 2797 unique reflections out of 3243 with $I > 2s(I)$, 138 parameters, $2.579^\circ < q < 29.860^\circ$, $R_1 = 0.0452$, $wR_2 = 0.1206$, $\text{GOF} = 1.043$. CCDC deposit number 1100915.

