Supporting Information

A new access route to dimetal sandwich complexes, including a radical anion

Nicholas S. Labrum, Yaroslav Losovyj, and Kenneth G. Caulton*

E-mail address: caulton@indiana.edu

Department of Chemistry, Indiana University, Bloomington, Indiana 47405-7102, United States

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General Methods. All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques or in a glovebox under ultra-high purity nitrogen. Solvents were purchased from commercial sources, purified using Innovative Technology SPS-400 PureSolv solvent system or by distilling from conventional drying agents and degassed by the freeze-pump-thaw method thrice prior to use. Glassware was oven-dried at 150 °C overnight and flame dried prior to use. THF was stored over activated 4 Å molecular sieves and sodium metal pieces. Deuterated THFd$_8$ solvent (dried over NaK), was subjected to three freeze-pump-thaw cycles, vacuum transferred and stored over 4 Å molecular sieves in the glovebox prior to use. All starting reagents were commercially available; naphthalene was sublimed prior to use and Cr[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ was prepared according to a previously reported procedure.[1] All ^{1}H NMR spectra were collected at 25 °C on a Varian Inova-400 spectrometer operating at 400.11 MHz. ^{1}H NMR spectra of paramagnetic compounds were collected with 0.1 s relaxation delay and at least 1024 transients per spectra. Spectra were referenced to the residual respective protio impurities in solvent employed.

[K(18-crown-6)][Cr$_2$(C$_{10}$H$_8$)$_2$]. A 20 ml vial was charged with a portion of Cr[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (151.2 mg, 0.294 mmol), 2 mL of THF, and a blackened Teflon stir bar. In a separate 20 mL vial, 1 molar equivalent of K[(18-crown-6)][C$_{10}$H$_8$]^2 (168.5 mg, 0.294 mmol) was dissolved in 2 mL of THF resulting in a dark green solution. This was then added to the rapidly stirring violet Cr[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ solution. In time of mixing, the color changed to dark red and was allowed to stir for 30 min without any additional color change. Yield: 68.5 mg, 71.5% based on C$_{10}$H$_8$. Single crystals suitable for an XRD study were grown by pentane vapor diffusion into a concentrated THF solution at room temperature over 24 hrs. The synthesis has been replicated ten times in the course of this study.

A sample for an X-band EPR experiment was prepared by precipitating [K(18-crown-6)][Cr$_2$(C$_{10}$H$_8$)$_2$] by the addition of pentane to a concentrated THF solution stored at −35 °C for 12 hrs. The product was isolated, and crystals were grown by pentane vapor diffusion into a concentrated THF solution at room temperature over 24 hrs.

We have attempted to determine exact mass, using HRMS (ESI/Orbitrap XL, 30,000 resolving power, anion detection). While anions containing Cr$_2$ were detected by observed exact mass and isotope envelope intensities, no molecular ion Cr$_2$(C$_{10}$H$_8$)$_2$$^-$ was detected, even under varied ionization conditions. Since no ions of reaction byproducts, Cr[N(SiMe$_3$)$_2$]$_3$$^-$ or Cr[N(SiMe$_3$)$_2$]$_2$$^-$, are detected, this further supports product purity.

Multiple samples of this compound prove themselves to be extraordinarily air sensitive, because of their negative oxidation state, and thus combustion analysis is not offered. A number of examples of zero valent chromium and molybdenum complexes with naphthalene have been characterized similarly (our reference 5 has elemental analysis on only one out of three molecules

reported), and a vanadium analog has been shown to consistently give erroneous combustion analysis; see *Bis*(pyrene)metal complexes of vanadium, niobium and titanium: isolable homoleptic pyrene complexes of transition metals, Kucera, Benjamin E.; Jilek, Robert E.; Brennessel, William W.; Ellis, John E. Acta Crystallographica, Section C: Structural Chemistry (2014), 70(8), 749-753.
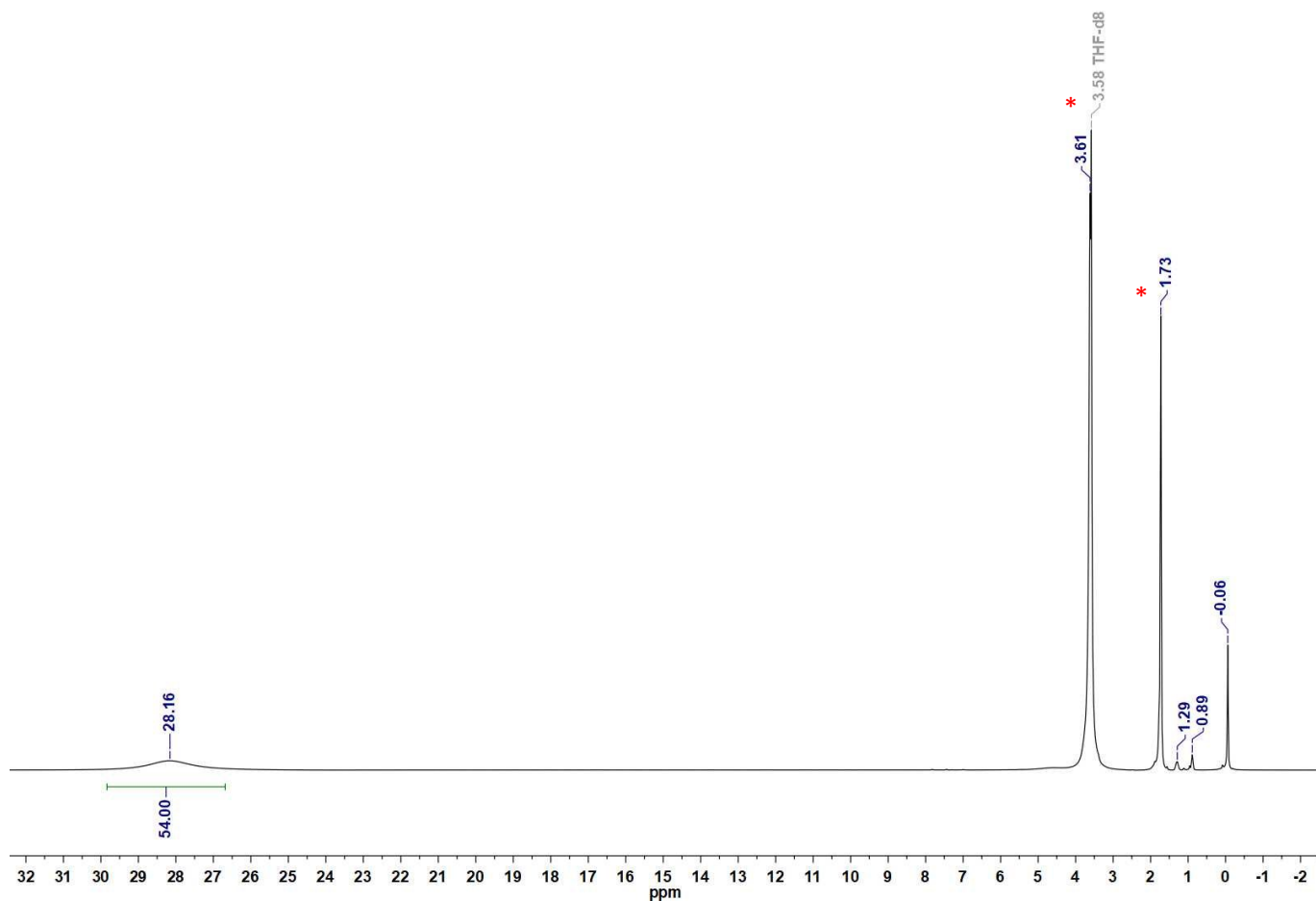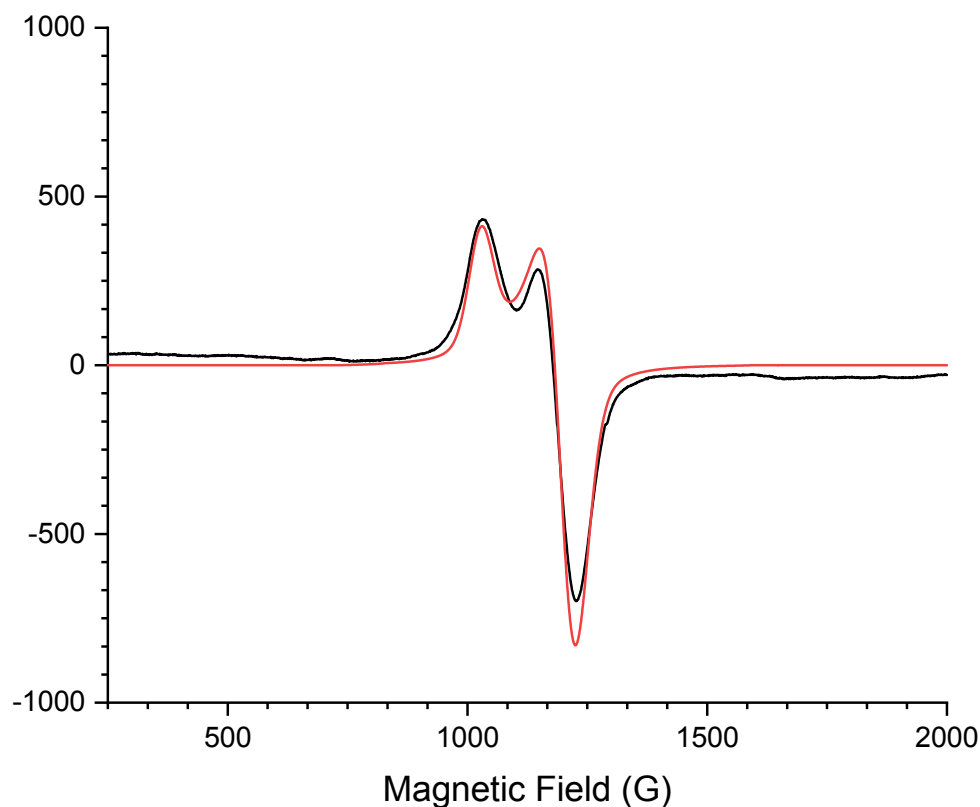
Figure S2. EPR spectrum of a 2.5 mM of [K(18-crown-6)][(Cr$_2$(C$_{10}$H$_8$)$_2$] in 2-methyltetrahydrofuran at 77 K (black) and simulated EPR spectrum using one Cr atom (red); g$_x$ = 1.9743, g$_y$ = 1.9990, g$_z$ = 2.0000. Modulation amplitude = 2 G.

Crystallographic Data

MSC#18033 Labrum

A brown crystal (approximate dimensions 0.400 x 0.200 x 0.200 mm^3) was placed onto the tip of MiTeGen and mounted on an Apex Kappa Duo diffractometer and measured at 173 K.

Data Collection

A preliminary set of cell constants was calculated from reflections harvested from three sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 1198 reflections. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 20 seconds and a detector distance of 4.0 cm. A randomly oriented region of reciprocal space was surveyed to achieve complete data with a

redundancy of 4. Sections of frames were collected with 0.50° steps in ω and φ scans. Data to a resolution of 0.74 Å were considered in the reduction. Final cell constants were calculated from

Table S1. Comparison of two [K(18-crown-6)][$Cr_2(C_{10}H_8)_2$] structure determinations

the xyz centroids of 9958 strong reflections from the actual data collection after integration (SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version). The intensity data were corrected for absorption (SADABS, An empirical correction for absorption anisotropy, R. Blessing, Acta Cryst. A51, 33 - 38 (1995)).

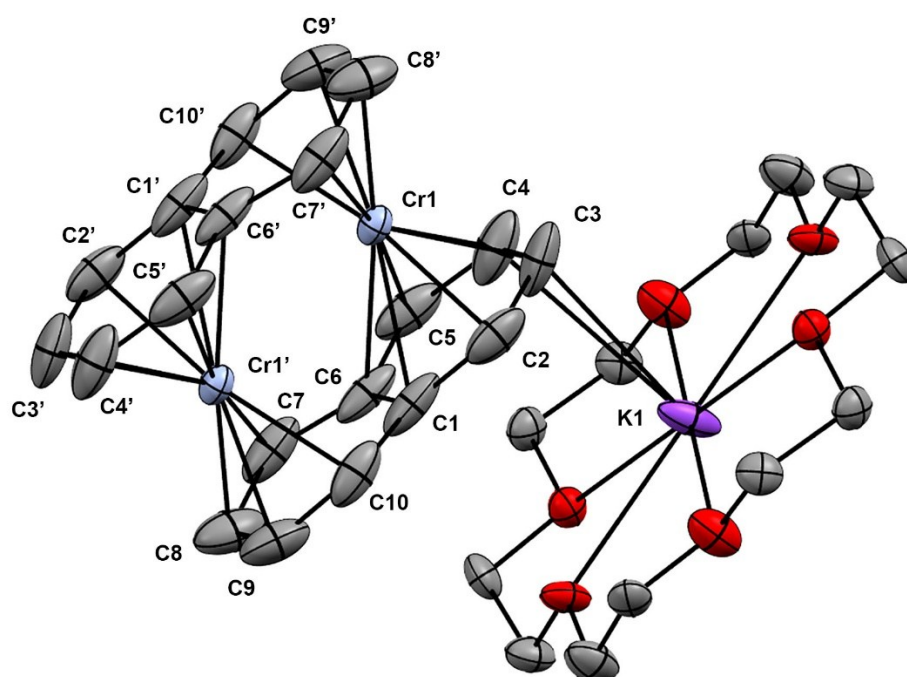**Structure Solution and Refinement**

The space group P-1 was determined based on intensity statistics and systematic absences. The structure was solved using Superflip (Palatinus L., Chapuis G. (2007): Superflip - a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. J. Appl. Cryst. 40, 786-790) and refined (full-matrix-least squares) using the Oxford University Crystals for Windows system (Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. J. Appl. Cryst. 2003, 36, 1487). The result of the solution provided all non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with individual relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0375 and wR2 = 0.1004 (F^2, all data). The remaining electron density is located within the $C_{10}H_8$ ring and 18-crown-6 framework.

Structure Description

The structure is a 1D polymer of the repeating [K(18-crown-6)][$Cr_2(C_{10}H_8)_2$] unit.

A second XRD experiment (MSC#18039, Figure S3) on single crystals grown from a concentrated THF solution layered with pentane and stored at −35 °C shows a polymorph of the same formula unit, [K(18-crown-6)][$Cr_2(C_{10}H_8)_2$], with dramatically different unit cell parameters and volume (see Table S1). Structure 18039 confirms the atom identities and connectivity of 18033; the Cr/Cr distance of 2.87 Å is within error of both structures but has only one formula unit in the asymmetric unit. However, due to twinning in 18039, all structural conclusions are based on the more accurate structure determination, 18033. Figure S3 shows the overlay of 18033 and 18039 based on chromium atoms, with RMS = 0.00274.

	18033		18039	
Crystal System, Space Group	Triclinic, P-1		Triclinic, P-1	
Unit Cell Dimensions	a = 10.5276(8) Å	α = 111.959(3)°	a = 8.961(2) Å	α = 106.454(16)°
	b = 13.9902(11) Å	β = 96.047(4)°	b = 9.162(2) Å	β = 120.049(16)°
	c = 16.3421(11) Å	γ = 92.045(4)°	c = 10.513(5) Å	γ = 101.141(12)°
Volume	2212.5(3) Å^3		736.1(4) Å^3	
Z	3		1	

Figure S3. Mercury diagram of 18039, [K(18-crown-6)][Cr$_2$(C$_{10}$H$_8$)$_2$], with thermal ellipsoids shown at 50% probability. Carbon and oxygen atoms (unlabeled) are shown in grey and red, respectively.
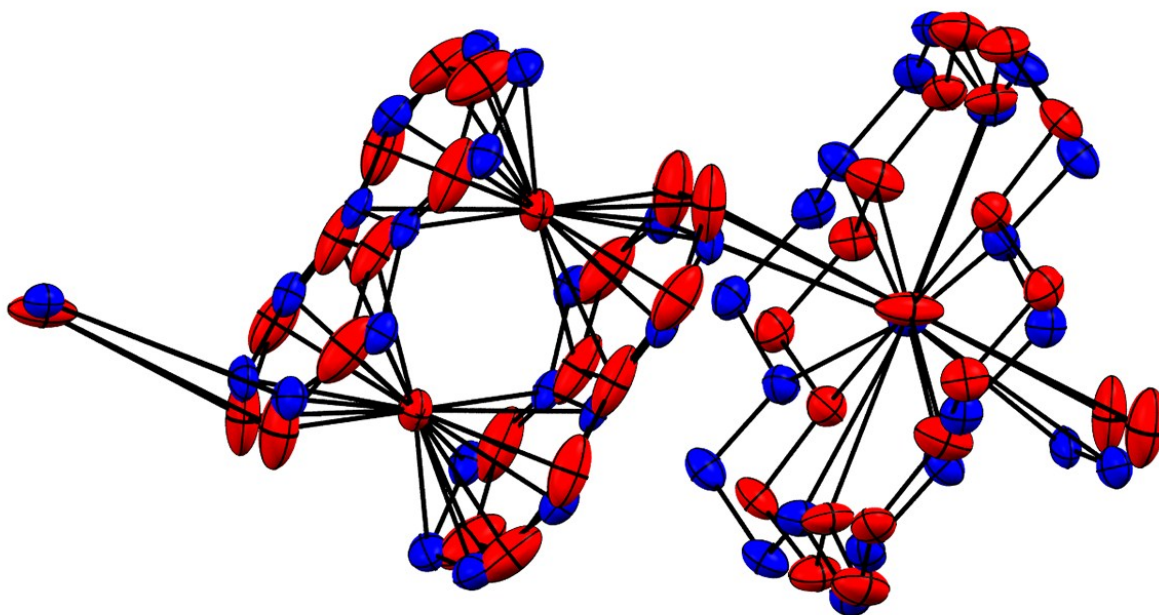
Figure S4. Overlay Mercury diagram of 18033 (blue) and 18039 (red), thermal ellipsoids shown at 50% probability. Chromium atoms RMS = 0.00274.
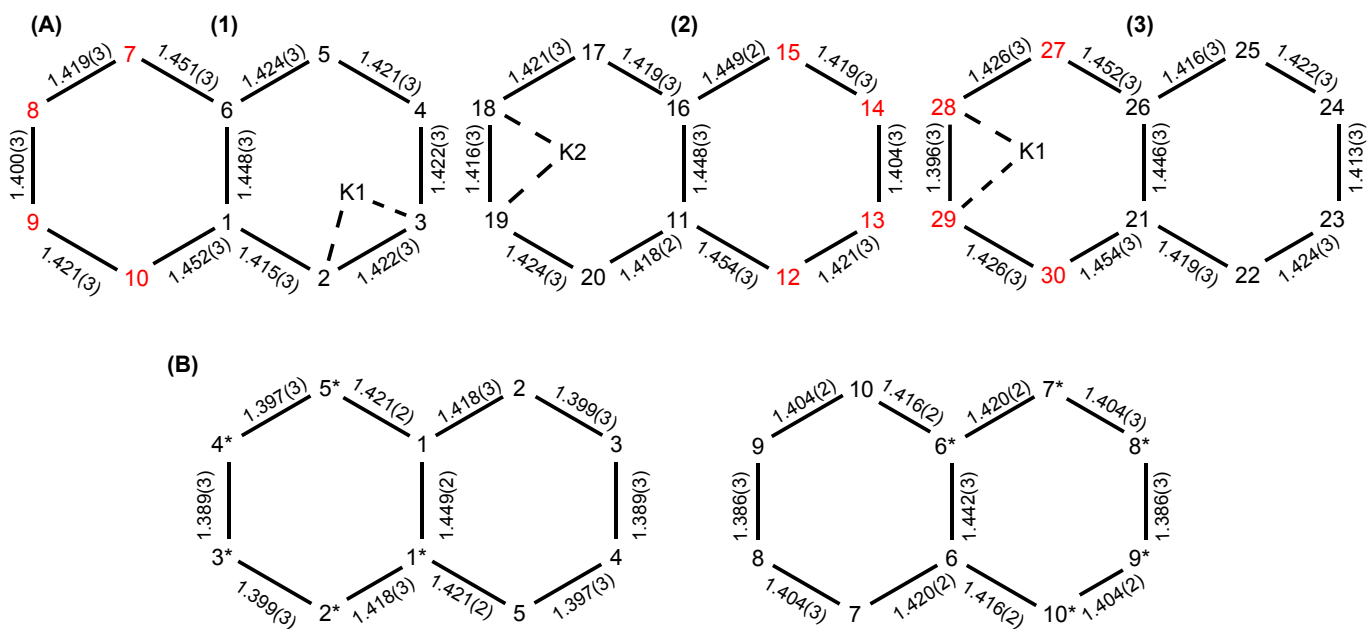
Figure S5. (A) Naphthalene ring C/C distances in [K(18-crown-6)][Cr$_2$(C$_{10}$H$_8$)$_2$]. Red numbers show η^4 Cr attachment and reveals the impact of that on C/C distances, and that K locations are uncorrelated with those. **(B)** Naphthalene ring C/C distances in two independent formula units of [K(18-crown-6)][C$_{10}$H$_8$] polymer.[2]

The average C/C distances in naphthalene rings (1): 1.426 Å; (2): 1.426 Å; and (3): 1.426 Å (Figure S4) are identical and are longer than the average in free naphthalene, 1.404 Å,[3] consistent with population of antibonding orbitals from the one electron reduction and coordination to a pi basic metal.

Support for the η^4/η^6 connectivity of naphthalene to chromium comes from the Cr/C distances (Table S2): every Cr has six short distances to one C_6 naphthalene subunit, then four to a different naphthalene unit in the dimer. The ring fusion carbons are then 0.4 Å farther from one chromium than from the second. This is evident by the pattern of distances within naphthalene rings: the η^4 connectivity leaves the central C/C distances of this butadiene fragment the shortest in the entire naphthalene. Each ring has shortest vs. longest C/C distances of 1.396 and 1.454 Å, with esd's uniformly 0.003 Å. Distances are not significantly altered by interaction with the K^+, so these generalizations are not perturbed by those. Two naphthalenes have 20 pi electrons to donate, so these cannot satisfy the 24 needed by two chromium, yet the Cr/Cr distances are too long for a Cr = Cr double bond. Apparently, electron deficient neutral $Cr_2(naphthalene)_2$ has a low-lying orbital which facilitates one electron reduction, even though full 18 electron configurations do not result.

It has been shown[4] that single electron reduction of naphthalene does change the short/long variation of C/C bond lengths, but does not change the average C/C distance, apparently because the impact of the single electron is distributed over 11 C/C bonds.   The fact that $[Cr_2(naphthalene)_2]^-$ does show overall lengthening, demonstrates the enhanced impact of two zerovalent metals on the two rings.

Table S2. Selected structural parameters for $[K(18\text{-crown-}6)][Cr_2(C_{10}H_8)_2]$

Bond lengths/Å

	C1	2.5673(18)		C1	2.2083(18)		C21	2.2080(17)
	C6	2.5687(17)		C2	2.1714(19)		C22	2.1772(19)
	C7	2.1790(18)		C3	2.0997(19)	Cr3	C23	2.1027(19)
	C8	2.1451(18)		C4	2.1002(18)		C24	2.1096(19)
	C9	2.1471(19)		C5	2.1754(18)		C25	2.177(2)
Cr1	C10	2.1779(19)	Cr2	C6	2.2084(17)		C26	2.2053(18)
	C11	2.2147(18)		C11	2.5654(17)		C21	2.5666(18)
	C16	2.2099(18)		C12	2.1802(18)		C26	2.5673(18)
	C17	2.1727(19)		C13	2.1470(18)	Cr3'	C27	2.1692(19)
	C18	2.1030(19)		C14	2.1464(19)		C28	2.1407(19)
	C19	2.1032(18)		C15	2.1795(19)		C29	2.1464(18)
	C20	2.1741(18)		C16	2.5683		C30	2.1700(18)

Angles/°

| Centroid-Cr1-Centroid	168.09	Centroid-Cr2-Centroid	168.44	Centroid-Cr3-Centroid	168.07

X-ray Photoelectron Spectroscopy. The Cr 2p3/2 binding energy was measured as 576.13 eV which is consistent with oxidation state below 2^+ from literature.[5] The oxygen 1s emission resolved unexpectedly into two signals, 530.4 and 532.6 eV, which we attribute to partial surface oxidation during sample handling, which then also displaces the Cr 2p signal to slightly higher BE. On the other hand, two C 1s peaks are resolved, with the lower intensity one at binding energy for OCH2 and the higher at the BE of aromatic carbon, in agreement with the 12:20 ratio of the crystallographic compound. The O:K atom ratio was measured as 5.2:1 in satisfactory agreement with the 1:1 K:Crown ether stoichiometry in the X-ray study.
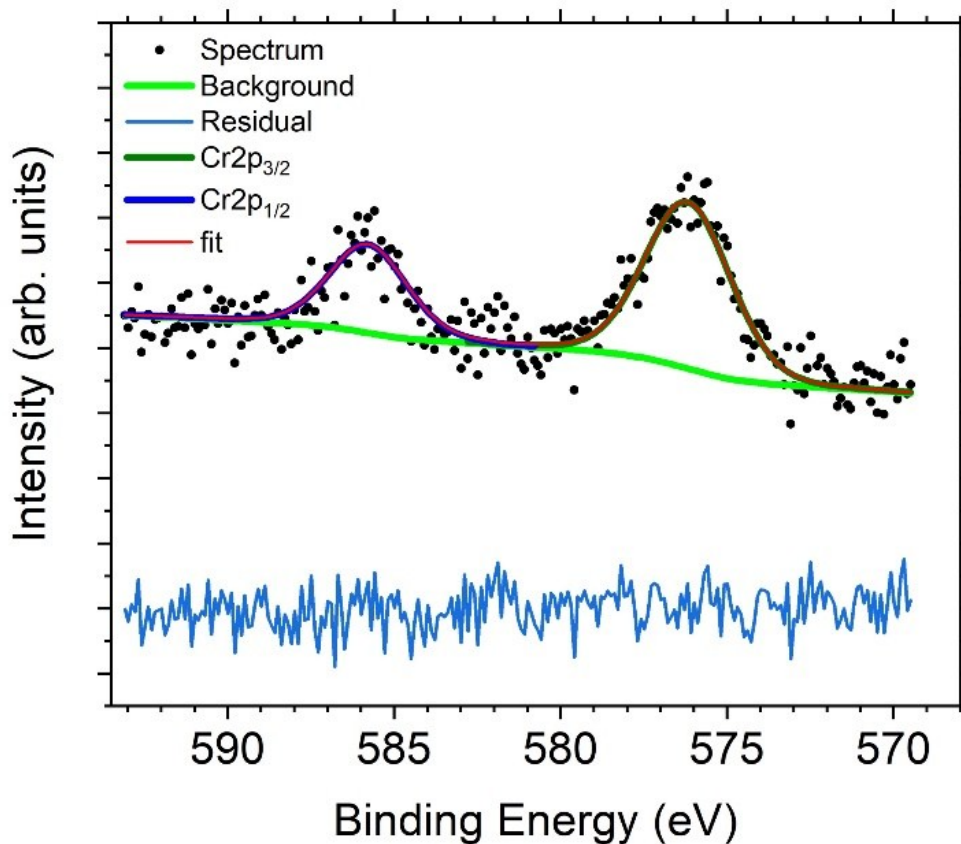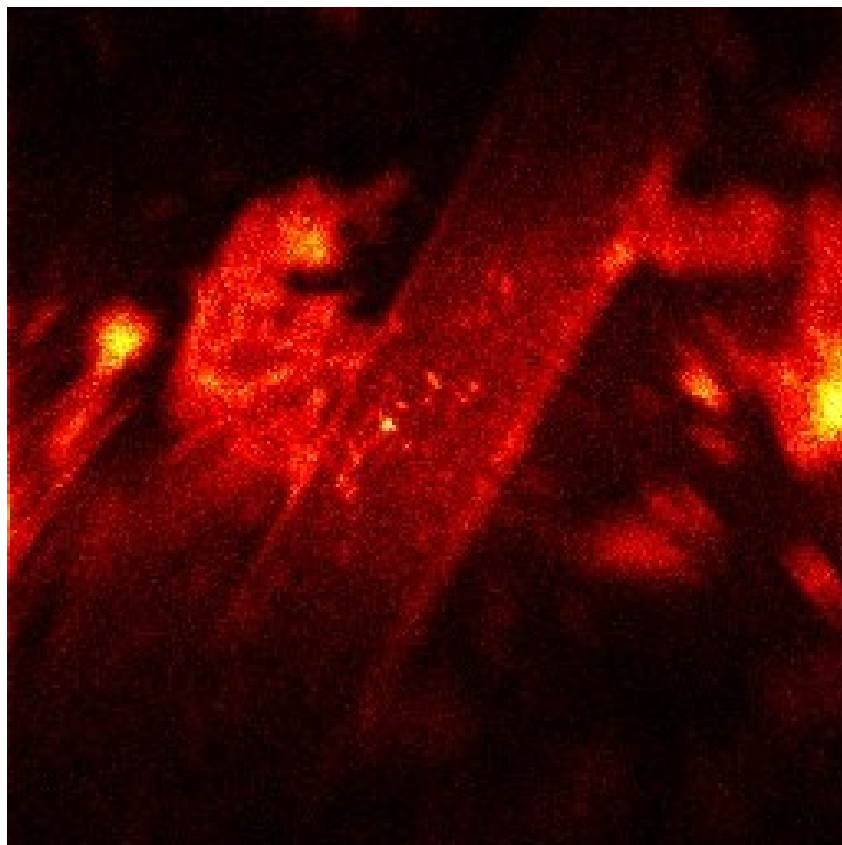

Figure S6. High resolution XPS spectrum of the $Cr2p_{1/2}$ and $Cr2p_{3/2}$ region.
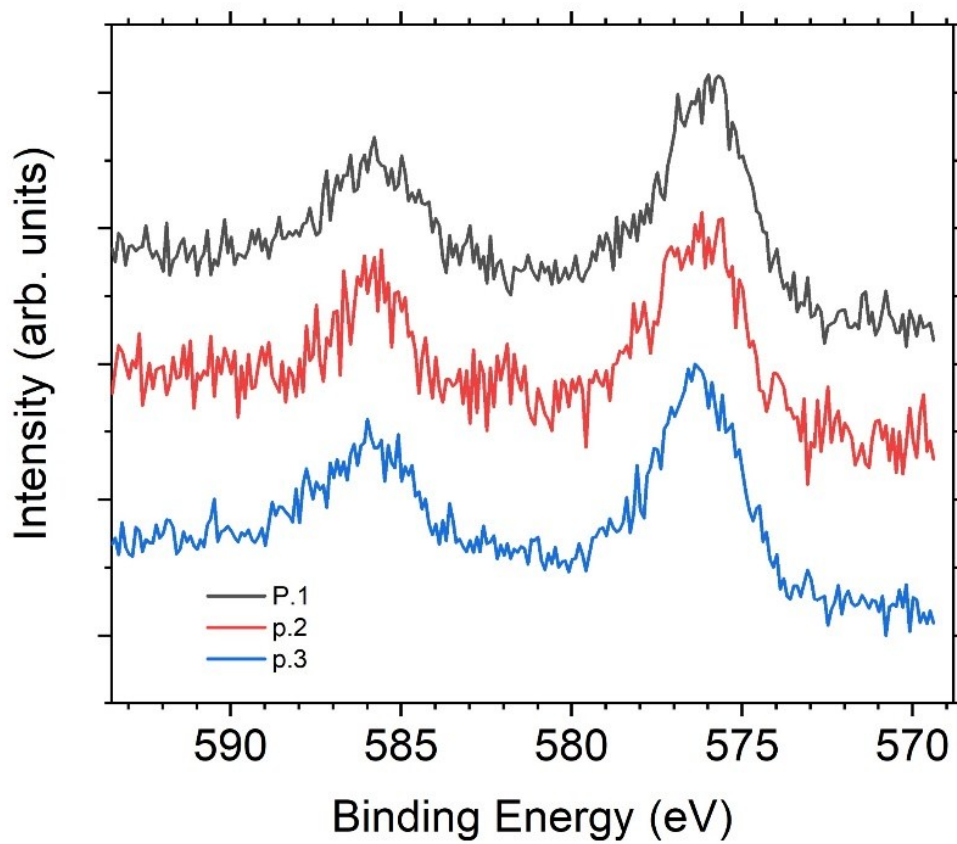
Figure S7. Stacked XPS spectra of the Cr2p$_{1/2}$ and Cr2p$_{3/2}$ region in three different locations on the crystal.
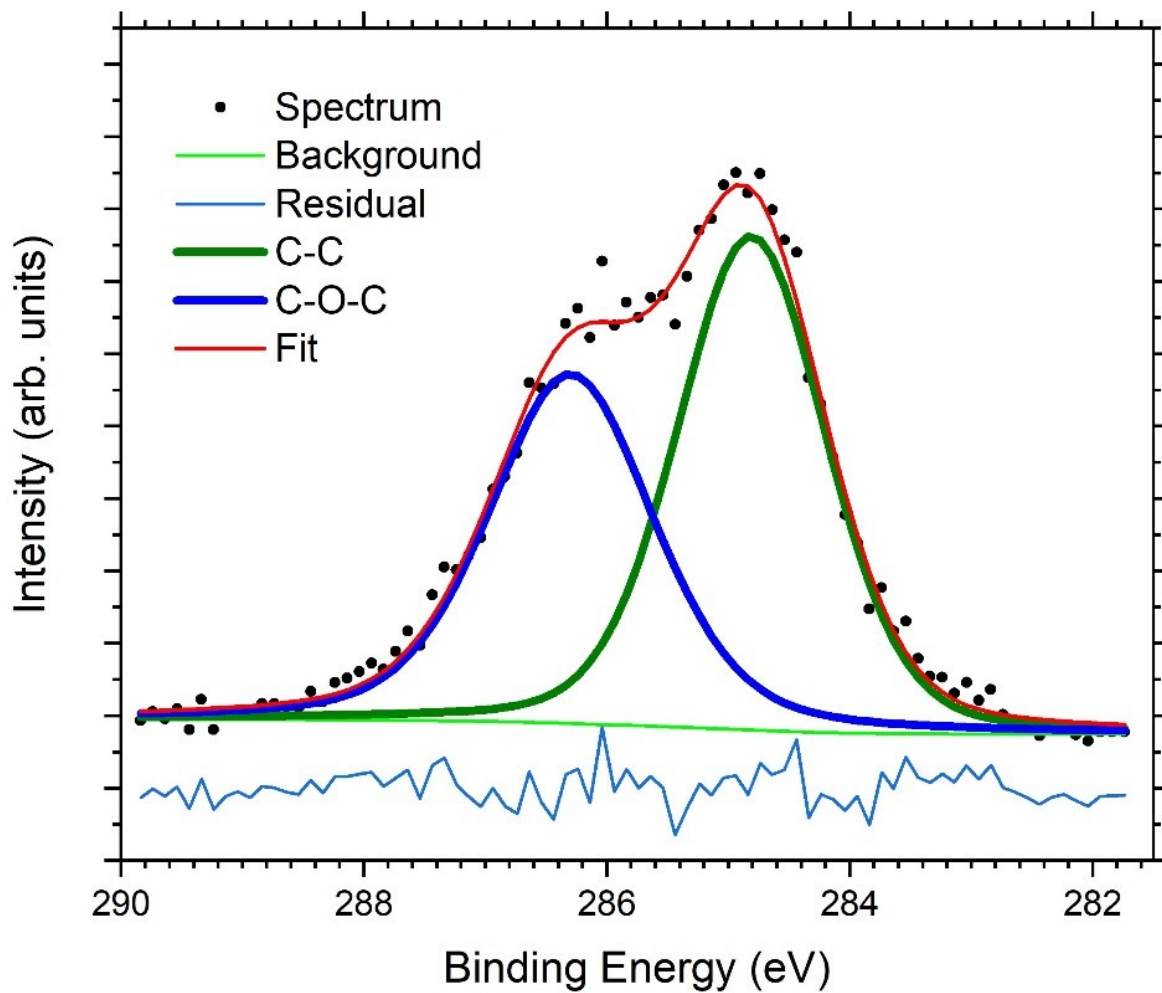
Figure S8. High resolution XPS spectrum of the C1s region.

Figure S9. Photo of crystalline sample for XPS study.

References

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