

Supporting Information for

**A Metal–Organic Framework Supported Single Site Chromium (III)
Catalyst for Ethylene Oligomerization at Low Pressure and
Temperature**

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Contents of the Supporting Information

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Materials

1,3,6,8-tetrabromopyrene, (4-(ethoxycarbonyl)phenyl)boronic acid, tetrakis(triphenylphosphine) palladium(0), tripotassium phosphate, zirconyl chloride octahydrate, benzoic acid, anhydrous heptane, chromium(II) chloride, and diethylaluminum chloride (1.0 M in heptane) were purchased and used as is from Sigma Aldrich (St. Louis, MO). Hydrochloric acid, nitric acid, acetone, N,N-dimethylformamide, 1,4-dioxane were purchased and used as is from Fisher Scientific (Hampton, NH). Chromium (III) oxide (Surface Area ~ 325 m²/g) was purchased and used as is from Alfa Aesar (Haverhill, MA). Ultrapure deionized water (18.2 M Ω .cm resistivity) was obtained from a Millipore Milli-Q-Biocl A10 instrument (Millipore Inc., Billerica, MA). Argon gas used during the reactor charging, nitrogen gas used for the adsorption/desorption measurements, and hydrogen gas for catalysis were ordered from Airgas (Radnor, PA) with Ultra High Purity Grade 5. Ethylene gas (99.9%) used for catalysis was ordered from Airgas (Radnor, PA).

Experimental Procedure

NU-1000. 1,3,5,8-(p-benzoate)pyrene, was synthesized according to the reported procedure.¹ NU-1000 was synthesized according to the procedure by Wang et al.¹

Cr-SIM-NU-1000. Cr-SIM-NU-1000 was prepared by mixing 200 mg NU-1000 into 25 mL of a 0.1 M CrCl₂ solution in N,N-dimethylformamide (DMF) and heated overnight at 100°C. CrCl₂ was used since it oxidizes readily in air or moisture, and is more soluble in DMF than CrCl₃. The sample was washed with fresh DMF until the green supernatant turned colorless. Then the sample was washed with acetone to exchange the solvent and remove DMF. The sample was dried at 80°C in a vacuum oven for 2 hours, and then thermally activated at 120°C under dynamic vacuum for 12 hours.

Single Crystal Cr-SIM-NU-1000. Single crystal NU-1000 was prepared by mixing 70 mg ZrCl₄ and 2 g benzoic acid into 6 mL of N,N-diethylformamide (DEF) in one vial and 40 mg of 1,3,5,8-(p-benzoate)pyrene in 4 mL DEF in a separate vial after which both vials were heated at 100°C for 1 h. The vials were then cooled to room temperature and the solutions mixed along with 150 μ L of trifluoroacetic acid, and subsequently placed in an oven at 120°C for 1 day. The solution was then cooled to room temperature again, and the solvent was exchanged to DMF. An acid wash was performed as per the reported NU-1000 procedure.¹ After washing the crystals with DMF 3 times, the Cr-SIM procedure was performed as described above.

Ethylene Oligomerization

In an argon glovebox, 10 mg Cr-SIM-NU-1000, 5 mL anhydrous heptane, and 0.1 mL of diethylaluminum chloride (1.0 M in heptane) were charged into a 50 mL 4590 micro bench top autoclave Parr reactor. The reactor was then sealed, transferred out of the glovebox and connected to the gas inlet, pressure gauge, and thermocouple at the reactor station. The reactor was then set to stir at 300 rpm and pressurized with 4 bar H₂ and 1 bar C₂H₄. After 1 hour, gas samples were taken by airtight gas syringe and analyzed by gas chromatography. The reactor was then cooled to -20°C with a mixture of dry ice and acetone before being vented and opened, after which the solvent was collected to be analyzed on by gas chromatography mass spectrometry.

Measurements

N₂ adsorption isotherms were measured on a Micromeritics Tristar II 3020 (Micromeritics, Norcross, GA) at 77K with 30-50 mg pre-activated sample at 120 °C for 12 h under high vacuum using a SmartVac Prep (Micromeritics, Norcross, GA). BET surface area was calculated in the region $P/P_o = 0.005-0.05$ and pore-size distributions were obtained via DFT calculations using a carbon slit-pore model with a N₂ kernel.

Inductively coupled plasma optical-emission spectroscopy (ICP-OES) was performed at the QBIC facility on a Thermo iCAP 7600 Spectrometer (ThermoFisher, Waltham, MA). In each preparation, ~3 mg samples were digested in 2 mL concentrated nitric acid in a 2-5 mL Biotage (Uppsala, Sweden) microwave vial. Biotage SPX microwave reactor (software version 2.3, build 6250) was used to heat the mixture to 150 °C for 5 min. 300 µL of the digested sample was removed and diluted to 10 mL with ultrapure deionized water.

Powder X-ray Diffraction (PXRD) data were collected at the IMSERC X-ray Facility at Northwestern University on a Stoe-STADI-P powder diffractometer equipped with an asymmetric curved Germanium monochromator (CuK α 1 radiation, $\lambda = 1.54056$ Å) and one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). The line focused Cu X-ray tube was operated at 40 kV and 40 mA. Powder was packed in a 3 mm metallic mask and sandwiched between two layers of polyimide tape. Intensity data from 1 to 25 degrees 2θ were collected over a period of 10 mins. The instrument was calibrated against a NIST Silicon standard (640d) prior the measurement.

Single-crystal X-ray diffraction (SC-XRD) data was collected at 210 K using a Bruker KAPPA APEX II (Bruker, Billerica, MA) equipped with an APEX2 CCD detector, Cryostream 80-400K (Oxford Cryosystems, Oxford, United Kingdom), and CuK α I μ S microfocus source with MX Optics and a Kappa geometry goniometer. Refinement results are summarized in Table S1 and S2. Crystallographic data in CIF format have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC1874677. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.)

Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) line scans were collected at Northwestern University's EPIC/NUANCE facility using a Hitachi SU8030 FE-SEM (Dallas, TX) microscope. All samples were coated with 8 nm OsO₄ before imaging.

X-ray photoelectron spectra were collected at Keck-II/NUANCE facility at NU using a Thermo Scientific ESCALAB 250Xi (Al K α radiation, 1486.6 eV). All measurements were performed with an electron flood gun and were calibrated to C1s peak at 284.8 eV.

Gas chromatography mass spectrometry was conducted at the IMSERC facility at NU on an Agilent 6890 GCMS (Agilent Technologies, Santa Clara, CA) equipped with an Agilent J&W DB-5 capillary column and 5973 MS.

Gas chromatography for conversion analysis was conducted at the CleanCat facility at NU on an Agilent 7890A GC (Agilent Technologies, Santa Clara, CA) with an Agilent GS-GasPro capillary column and FID detector using helium carrier gas (99.999%, Airgas, Radnor, PA).

Catalysis was conducted at the CleanCat facility at NU using a 50 mL 4590 micro bench top autoclave Parr reactor (Parr Instruments, Moline, IL) connected to a gas manifold and a 4838 Reactor Controller (Parr Instruments, Moline, IL).

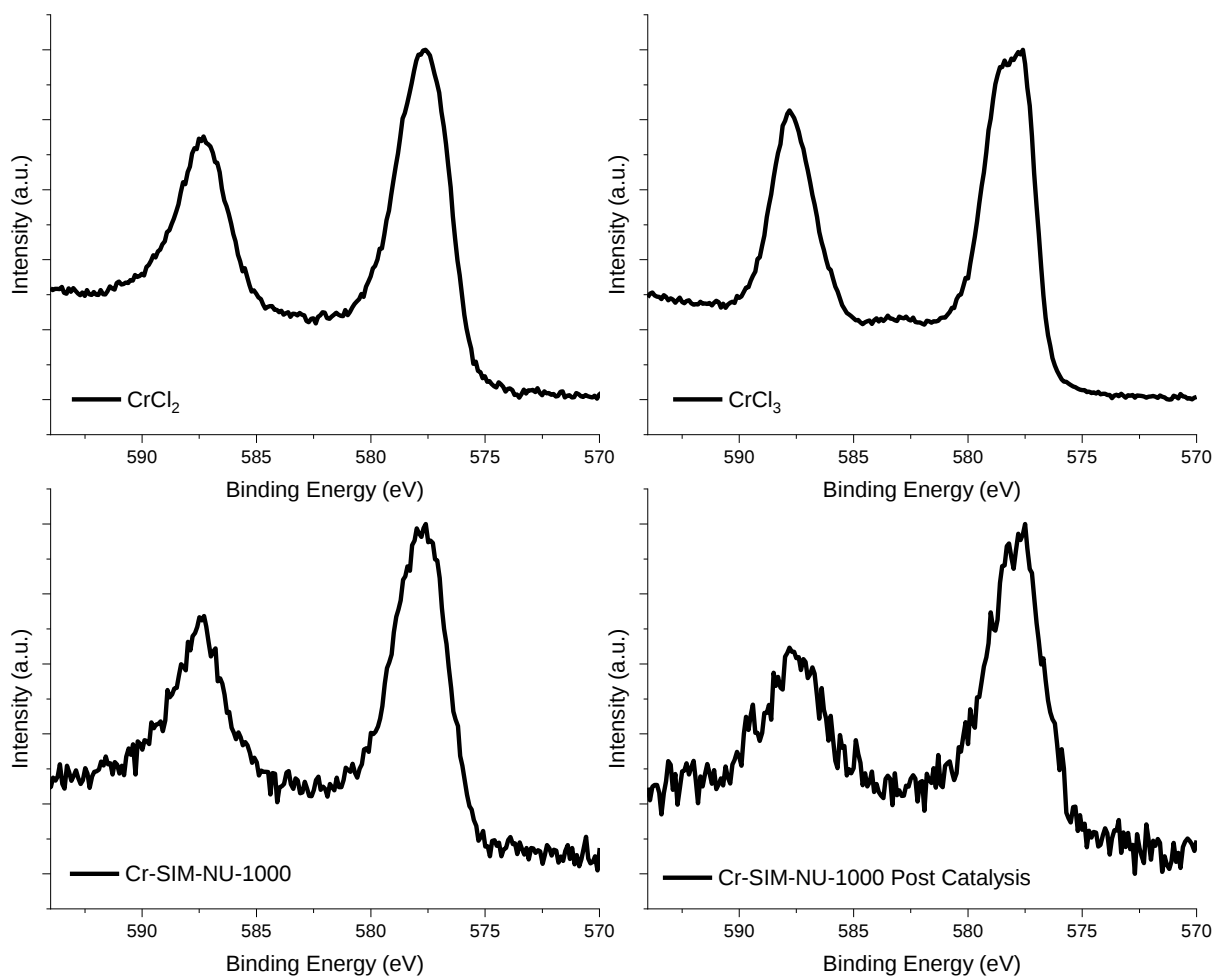


Figure S1. Cr 2p XPS spectra of CrCl_2 (top-left) and CrCl_3 (top-right) precursors as well as Cr-SIM-NU-1000 (bottom-left) and Cr-SIM-NU-1000 post catalysis (bottom-right). In each spectrum, left-hand peak refers to Cr 2p_{1/2} and right-hand peak refers to Cr 2p_{3/2}. For Cr^{3+} compounds in the NIST database, a general binding energy for the Cr 2p_{3/2} in chloride compounds is shown to be ~ 577.6 eV. In all the above spectra, the Cr 2p_{3/2} peaks line up with 577.6 eV very well, implying that the Cr^{2+} chloride precursor used for synthesis has been oxidized to Cr^{3+} (presumably by air) before or during installation in NU-1000, and that the Cr ion retains (or returns to) the oxidation state of 3+, post-catalysis – again presumably due to exposure to air.

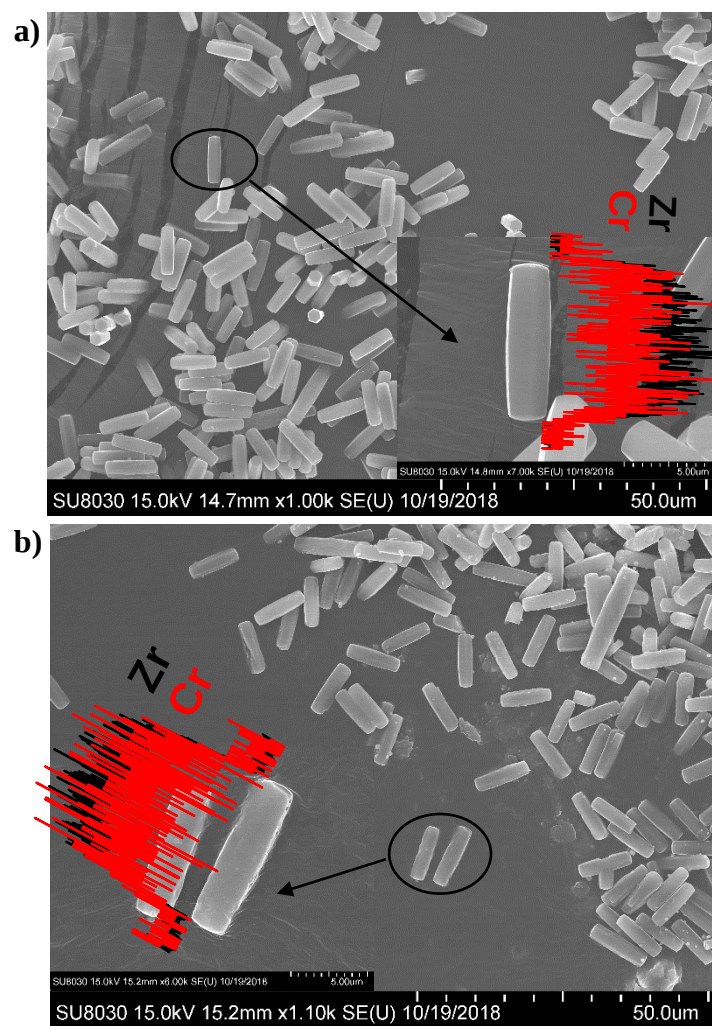


Figure S2. SEM images and EDS line scans of a) Cr-SIM-NU-1000 and b) Cr-SIM-NU-1000 post catalysis.

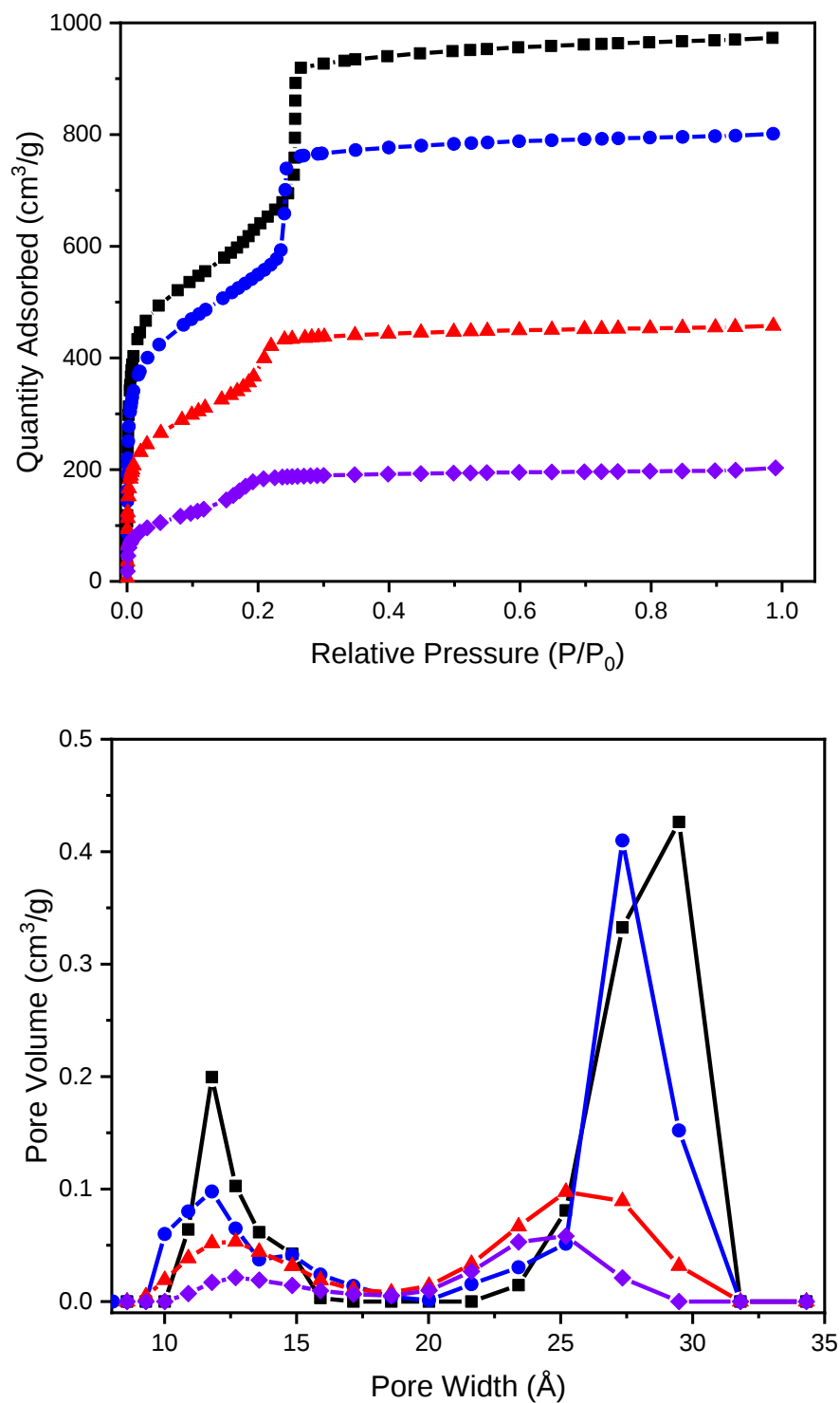


Figure S3. a) N₂ adsorption isotherms and b) Pore-size distributions of NU-1000 (black), Cr-SIM-NU-1000 (blue), Cr-SIM-NU-1000 post catalysis (red), and Cr-SIM-NU-1000 post 24 hours of catalysis (purple).

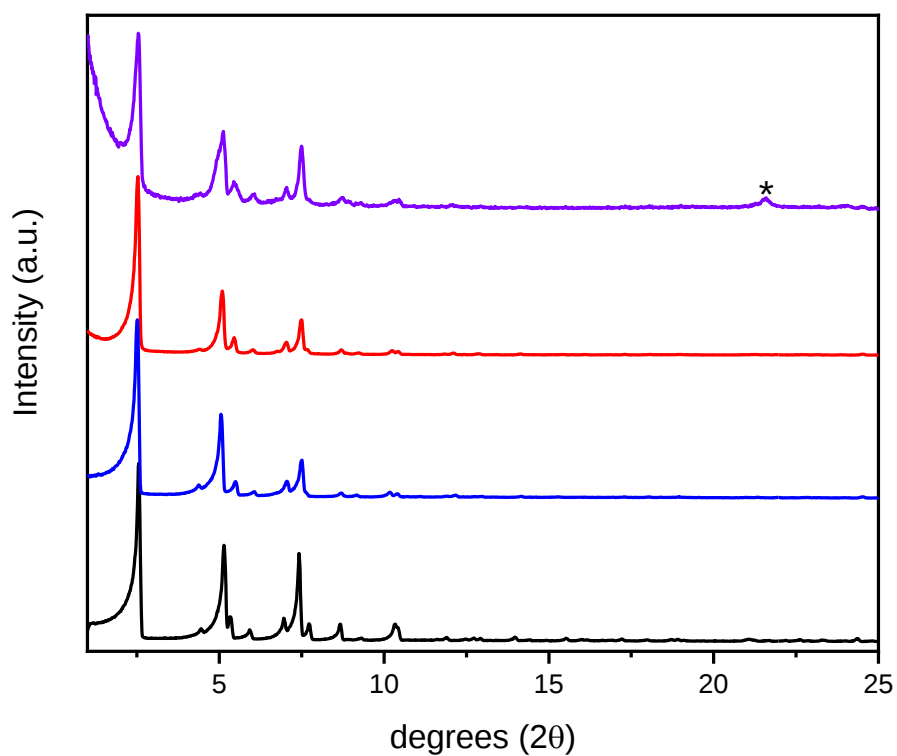


Figure S4. Powder X-ray diffraction patterns for NU-1000 (black), Cr-SIM-NU-1000 (blue), Cr-SIM-NU-1000 post catalysis (red), and Cr-SIM-NU-1000 post 24 hours of catalysis (purple). The post 24 hours of catalysis sample shows amorphous character at the beginning of the pattern in addition to a new peak at 21.5 degrees (*) corresponding to amorphous and crystalline polyethylene respectively.

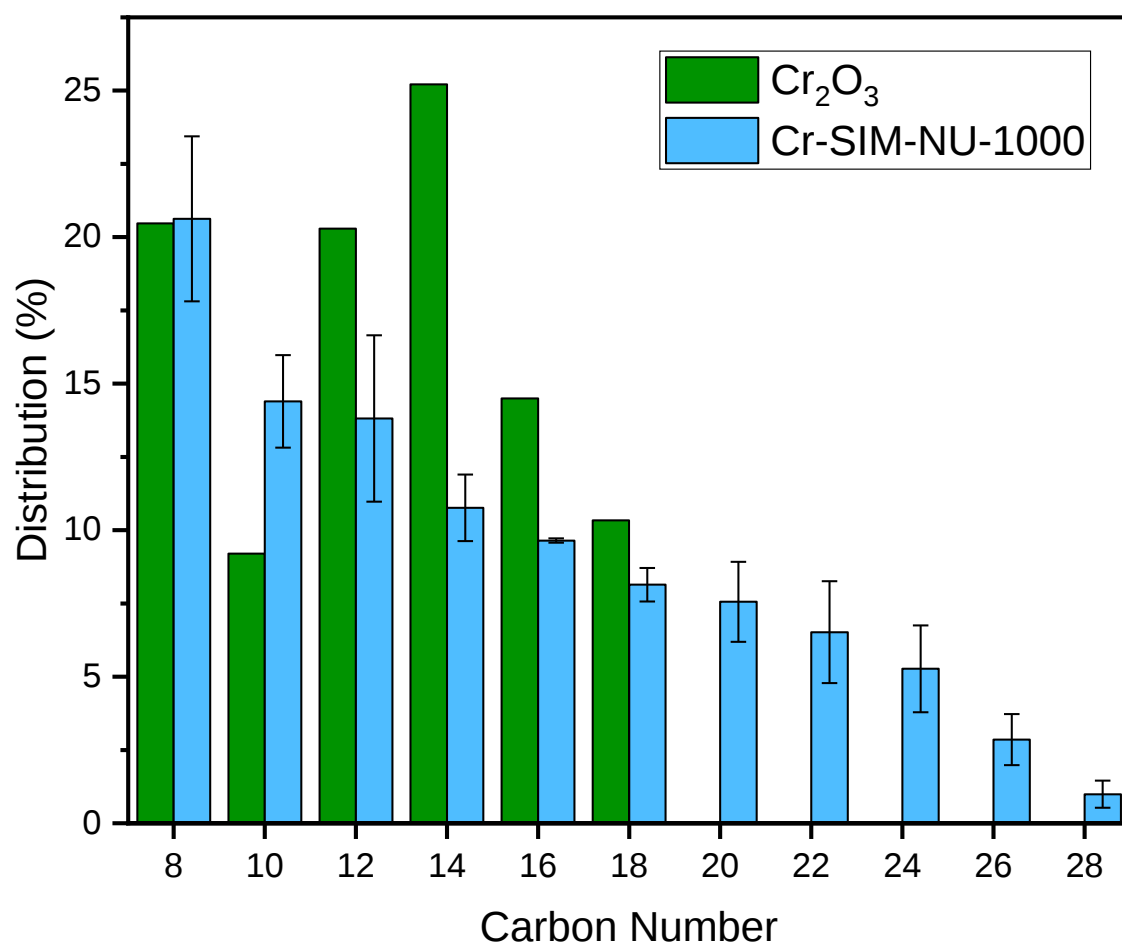


Figure S5. Percent distribution of hydrocarbon products by chain length for Cr-SIM-NU-1000 (blue) and Cr_2O_3 (green) with error bars for Cr-SIM-NU-1000 based on standard deviation.

Table S1 Crystal data and structure refinement for Cr-SIM-NU-1000.	
Identification code	Cr-SIM-NU-1000
Empirical formula	C _{21.46} H ₁₀ Cl _{0.25} Cr _{0.25} O ₈ Zr _{1.5}
Formula weight	554.48
Temperature/K	210.0
Crystal system	hexagonal
Space group	P6/mmm
a/Å	39.100(2)
b/Å	39.100(2)
c/Å	16.7147(9)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	120
Volume/Å ³	22131(3)
Z	12
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	0.499
μ/mm^{-1}	2.261
F(000)	3276.0
Crystal size/mm ³	0.18 × 0.066 × 0.063
Radiation	CuK α (λ = 1.54178)
2 Θ range for data collection/ $^\circ$	2.608 to 121.834
Index ranges	-43 ≤ h ≤ 43, -44 ≤ k ≤ 41, -18 ≤ l ≤ 18
Reflections collected	88732
Independent reflections	6316 [R_{int} = 0.2081, R_{sigma} = 0.0681]
Data/restraints/parameters	6316/106/100
Goodness-of-fit on F ²	1.401
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.1403, wR_2 = 0.3816
Final R indexes [all data]	R_1 = 0.1642, wR_2 = 0.4006
Largest diff. peak/hole / e Å ⁻³	1.48/-2.13

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Cr-SIM-NU-1000. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.				
Atom	x	y	z	$U(eq)$
Zr2	5358.9(2)	717.8(4)	0	120.2(11)
Zr1	4547.3(5)	0	1052.3(6)	109.2(7)
O2	5192.3(16)	385(3)	1071(5)	120(4)
O1	4736(4)	374(4)	0	131(5)
O3	4574(4)	0	2361(6)	122(4)
O4	4078(3)	-591(3)	1499(5)	206(7)
O5	4003(4)	0	919(9)	184(7)
O6	4159(4)	-1064(3)	800(5)	274(11)
C9	2823(3)	-2199(3)	4153(7)	413(12)
C8	2809(4)	-2213(4)	3282(7)	413(12)
C12	2511(3)	-2511(3)	2910(10)	413(12)
C10	3124(5)	-1902(5)	4588(5)	413(12)
C1	3924(9)	-925(7)	1337(10)	365(8)
C3	3520(4)	-1179(3)	2449(6)	365(8)
C4	3228(4)	-1473(3)	2920(6)	365(8)
C5	3124(4)	-1865(3)	2805(6)	365(8)
C6	3313(4)	-1964(3)	2220(7)	365(8)
C7	3605(4)	-1670(3)	1749(6)	365(8)
C2	3709(4)	-1277(3)	1864(6)	365(8)
C11	2508(5)	-2508(5)	4558(5)	413(12)
Cr1	3788(5)	-361(7)	0	197(9)
Cl1A	3283(17)	-520(30)	0	750(80)

Table S3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Cr-SIM-NU-1000. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+ \dots]$.						
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr2	233(2)	38.7(7)	24.3(7)	0	0	19.4(4)
Zr1	185.7(14)	74.9(8)	29.9(6)	0	6.7(6)	37.5(4)
O2	189(9)	107(7)	37(5)	8(5)	4(2)	53(4)
O1	258(14)	163(10)	11(3)	0	0	136(10)
O3	206(10)	61(5)	52(5)	0	46(6)	30(2)
O4	205(10)	149(8)	54(4)	8(5)	23(5)	-69(8)
O5	190(9)	310(20)	94(9)	0	-1(8)	154(12)

O6	390(20)	105(6)	63(5)	-6(4)	21(7)	-77(8)
C9	320(12)	313(11)	39(3)	6(5)	-2(6)	-268(9)
C8	320(12)	313(11)	39(3)	6(5)	-2(6)	-268(9)
C12	320(12)	313(11)	39(3)	6(5)	-2(6)	-268(9)
C10	320(12)	313(11)	39(3)	6(5)	-2(6)	-268(9)
C1	373(11)	212(7)	75(3)	3(5)	38(5)	-180(7)
C3	373(11)	212(7)	75(3)	3(5)	38(5)	-180(7)
C4	373(11)	212(7)	75(3)	3(5)	38(5)	-180(7)
C5	373(11)	212(7)	75(3)	3(5)	38(5)	-180(7)
C6	373(11)	212(7)	75(3)	3(5)	38(5)	-180(7)
C7	373(11)	212(7)	75(3)	3(5)	38(5)	-180(7)
C2	373(11)	212(7)	75(3)	3(5)	38(5)	-180(7)
C11	320(12)	313(11)	39(3)	6(5)	-2(6)	-268(9)
Cr1	216(17)	330(30)	43(5)	0	0	135(17)
Cl1A	170(40)	940(150)	700(140)	0	0	-50(70)

Table S4 Bond Lengths for Cr-SIM-NU-1000.					
Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zr2	Zr1	3.4836(14)	O1	Cr1 ⁶	2.271(16)
Zr2	Zr1 ¹	3.4837(14)	O4	C1	1.16(3)
Zr2	Zr1 ²	3.4837(14)	O5	Cr1	1.967(18)
Zr2	Zr1 ³	3.4837(14)	O5	Cr1 ⁶	1.967(17)
Zr2	O2 ¹	2.117(9)	O6	C1	1.56(4)
Zr2	O2	2.117(9)	C9	C8	1.456(16)
Zr2	O1 ⁴	2.114(14)	C9	C10	1.377(16)
Zr2	O1	2.114(14)	C9	C11	1.396(10)
Zr2	O6 ³	2.150(11)	C8	C12	1.320(14)
Zr2	O6 ²	2.150(11)	C8	C5	1.527(12)
Zr2	O6 ⁵	2.150(11)	C10	C10 ⁷	1.377(17)
Zr2	O6 ⁶	2.150(11)	C1	C2	1.49(2)
Zr1	O2 ³	2.198(7)	C3	C4	1.3900
Zr1	O2	2.198(7)	C3	C2	1.3900
Zr1	O1	2.168(7)	C4	C5	1.3900
Zr1	O1 ⁶	2.168(7)	C5	C6	1.3900
Zr1	O3	2.191(10)	C6	C7	1.3900
Zr1	O4 ⁵	2.241(8)	C7	C2	1.3900
Zr1	O4	2.241(8)	C11	C11 ⁸	1.478(17)
Zr1	O5	2.140(16)	Cr1	Cr1 ⁶	2.44(5)
Zr1	Cr1 ⁶	3.117(15)	Cr1	Cl1A	1.75(7)

Zr1	Cr1	3.117(15)				
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¹+X₁+Y₁-Z₁; ²1-X₁-Y₁-Z₁; ³1-X₁-Y₁+Z₁; ⁴1+Y₁-X₁+Y₁+Z₁; ⁵-Y₁+X₁-Y₁+Z₁; ⁶-Y₁+X₁-Y₁-Z₁; ⁷+X₁+Y₁1-Z₁; ⁸-Y₁-X₁1-Z₁

Table S5 Bond Angles for Cr-SIM-NU-1000.							
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Zr1 ¹	Zr2	Zr1 ²	91.51(5)	O1 ⁴	Zr1	O4	75.5(3)
Zr1	Zr2	Zr1 ³	91.50(5)	O1 ⁴	Zr1	Cr1	46.8(4)
Zr1 ¹	Zr2	Zr1 ³	61.08(6)	O1	Zr1	Cr1	76.9(5)
Zr1 ³	Zr2	Zr1 ²	60.65(4)	O1	Zr1	Cr1 ⁴	46.8(4)
Zr1	Zr2	Zr1 ²	61.08(6)	O1 ⁴	Zr1	Cr1 ⁴	76.9(5)
Zr1	Zr2	Zr1 ¹	60.65(4)	O3	Zr1	Zr2 ³	118.7(2)
O2	Zr2	Zr1	36.95(16)	O3	Zr1	Zr2	118.7(2)
O2	Zr2	Zr1 ³	93.2(3)	O3	Zr1	O2 ²	86.9(4)
O2 ¹	Zr2	Zr1 ¹	36.95(15)	O3	Zr1	O2	86.9(4)
O2 ¹	Zr2	Zr1 ²	93.2(3)	O3	Zr1	O4	71.4(2)
O2	Zr2	Zr1 ¹	93.2(3)	O3	Zr1	O4 ⁵	71.5(2)
O2 ¹	Zr2	Zr1 ³	36.95(16)	O3	Zr1	Cr1 ⁴	126.8(4)
O2	Zr2	Zr1 ²	36.95(16)	O3	Zr1	Cr1	126.8(4)
O2 ¹	Zr2	Zr1	93.2(3)	O4	Zr1	Zr2	161.0(4)
O2 ¹	Zr2	O2	115.6(6)	O4 ⁵	Zr1	Zr2	72.5(3)
O2	Zr2	O6 ⁴	144.8(5)	O4 ⁵	Zr1	Zr2 ³	161.0(4)
O2 ¹	Zr2	O6 ²	144.8(5)	O4	Zr1	Zr2 ³	72.5(3)
O2 ¹	Zr2	O6 ⁴	76.4(3)	O4	Zr1	O4 ⁵	126.4(7)
O2	Zr2	O6 ³	144.8(5)	O4	Zr1	Cr1 ⁴	108.5(5)
O2	Zr2	O6 ⁵	76.4(3)	O4	Zr1	Cr1	67.5(5)
O2 ¹	Zr2	O6 ⁵	144.7(5)	O4 ⁵	Zr1	Cr1 ⁴	67.5(5)
O2	Zr2	O6 ²	76.4(3)	O4 ⁵	Zr1	Cr1	108.5(5)
O2 ¹	Zr2	O6 ³	76.4(3)	O5	Zr1	Zr2	116.9(2)
O1	Zr2	Zr1 ³	92.3(3)	O5	Zr1	Zr2 ³	116.9(2)
O1 ⁶	Zr2	Zr1 ³	36.06(16)	O5	Zr1	O2 ²	143.4(2)
O1 ⁶	Zr2	Zr1 ¹	92.3(3)	O5	Zr1	O2	143.4(2)
O1	Zr2	Zr1	36.06(16)	O5	Zr1	O1 ⁴	85.3(5)
O1 ⁶	Zr2	Zr1	92.3(3)	O5	Zr1	O1	85.3(5)
O1	Zr2	Zr1 ²	92.3(3)	O5	Zr1	O3	98.7(5)
O1	Zr2	Zr1 ¹	36.06(16)	O5	Zr1	O4	74.5(4)

O1 ⁶	Zr2	Zr1 ²	36.06(16)		O5	Zr1	O4 ⁵	74.5(4)
O1	Zr2	O2	72.93(19)		O5	Zr1	Cr1	38.6(4)
O1	Zr2	O2 ¹	72.92(19)		O5	Zr1	Cr1 ⁴	38.6(4)
O1 ⁶	Zr2	O2 ¹	72.93(19)		Cr1	Zr1	Zr2	111.0(3)
O1 ⁶	Zr2	O2	72.93(19)		Cr1	Zr1	Zr2 ³	79.1(3)
O1	Zr2	O1 ⁶	113.2(6)		Cr1 ⁴	Zr1	Zr2 ³	111.0(3)
O1	Zr2	O6 ⁴	80.3(5)		Cr1 ⁴	Zr1	Zr2	79.1(3)
O1 ⁶	Zr2	O6 ³	80.3(5)		Cr1 ⁴	Zr1	Cr1	46.1(8)
O1 ⁶	Zr2	O6 ⁴	140.3(4)		Zr2	O2	Zr1 ²	107.7(3)
O1	Zr2	O6 ²	140.3(4)		Zr2	O2	Zr1	107.7(3)
O1 ⁶	Zr2	O6 ⁵	140.3(4)		Zr1	O2	Zr1 ²	107.3(5)
O1	Zr2	O6 ³	140.3(4)		Zr2	O1	Zr1 ¹	108.9(4)
O1 ⁶	Zr2	O6 ²	80.3(5)		Zr2	O1	Zr1	108.9(4)
O1	Zr2	O6 ⁵	80.3(5)		Zr2	O1	Cr1 ⁴	147.7(9)
O6 ⁵	Zr2	Zr1	77.3(3)		Zr1	O1	Zr1 ¹	108.5(5)
O6 ⁵	Zr2	Zr1 ³	168.5(3)		Zr1 ¹	O1	Cr1 ⁴	89.2(6)
O6 ²	Zr2	Zr1 ³	114.1(5)		Zr1	O1	Cr1 ⁴	89.2(6)
O6 ²	Zr2	Zr1	110.6(3)		C1	O4	Zr1	141.0(14)
O6 ³	Zr2	Zr1	168.5(3)		Cr1	O5	Zr1	98.7(8)
O6 ²	Zr2	Zr1 ¹	168.5(3)		Cr1 ⁴	O5	Zr1	98.7(8)
O6 ²	Zr2	Zr1 ²	77.3(3)		Cr1	O5	Cr1 ⁴	76.8(13)
O6 ³	Zr2	Zr1 ³	77.3(3)		C1	O6	Zr2 ³	128.4(10)
O6 ³	Zr2	Zr1 ¹	110.6(3)		C10	C9	C8	124.1(9)
O6 ⁴	Zr2	Zr1	114.1(5)		C10	C9	C11	119.0(10)
O6 ⁴	Zr2	Zr1 ³	110.6(3)		C11	C9	C8	116.8(8)
O6 ⁵	Zr2	Zr1 ²	110.6(3)		C9	C8	C5	119.3(9)
O6 ⁴	Zr2	Zr1 ²	168.5(3)		C12	C8	C9	120.3(10)
O6 ³	Zr2	Zr1 ²	114.1(5)		C12	C8	C5	120.2(11)
O6 ⁴	Zr2	Zr1 ¹	77.3(3)		C8	C12	C8 ⁷	123.8(16)
O6 ⁵	Zr2	Zr1 ¹	114.1(5)		C9	C10	C10 ⁸	121.9(6)
O6 ⁵	Zr2	O6 ⁴	76.9(6)		O4	C1	O6	117.3(19)
O6 ²	Zr2	O6 ³	76.9(6)		O4	C1	C2	129.5(17)
O6 ⁴	Zr2	O6 ²	113.9(7)		C2	C1	O6	100(2)
O6 ⁴	Zr2	O6 ³	68.4(9)		C4	C3	C2	120.0
O6 ⁵	Zr2	O6 ²	68.4(9)		C5	C4	C3	120.0
O6 ⁵	Zr2	O6 ³	113.9(7)		C4	C5	C8	124.8(10)
Zr2	Zr1	Zr2 ³	88.50(5)		C4	C5	C6	120.0
O2 ²	Zr1	Zr2 ³	35.4(2)		C6	C5	C8	115.2(10)
O2	Zr1	Zr2 ³	90.7(2)		C5	C6	C7	120.0
O2	Zr1	Zr2	35.4(2)		C2	C7	C6	120.0
O2 ²	Zr1	Zr2	90.7(2)		C3	C2	C1	107.0(17)

O2	Zr1	O2 ²	72.7(5)		C7	C2	C1	131.1(14)
O2	Zr1	O4 ⁵	73.2(5)		C7	C2	C3	120.0
O2	Zr1	O4	140.2(5)		C9 ⁷	C11	C9	121.9(11)
O2 ²	Zr1	O4 ⁵	140.2(5)		C9 ⁷	C11	C11 ⁹	119.0(6)
O2 ²	Zr1	O4	73.2(5)		C9	C11	C11 ⁹	119.0(6)
O2 ²	Zr1	Cr1	111.2(4)		Zr1 ¹	Cr1	Zr1	68.7(4)
O2 ²	Zr1	Cr1 ⁴	145.7(3)		O1 ⁴	Cr1	Zr1	44.0(3)
O2	Zr1	Cr1	145.7(3)		O1 ⁴	Cr1	Zr1 ¹	44.0(3)
O2	Zr1	Cr1 ⁴	111.2(4)		O1 ⁴	Cr1	Cr1 ⁴	91.1(7)
O1 ⁴	Zr1	Zr2 ³	35.0(4)		O5 ¹	Cr1	Zr1	98.4(9)
O1	Zr1	Zr2 ³	89.8(3)		O5	Cr1	Zr1	42.7(6)
O1 ⁴	Zr1	Zr2	89.8(3)		O5	Cr1	Zr1 ¹	98.4(9)
O1	Zr1	Zr2	35.0(4)		O5 ¹	Cr1	Zr1 ¹	42.7(6)
O1	Zr1	O2	70.3(4)		O5	Cr1	O1 ⁴	86.7(8)
O1 ⁴	Zr1	O2	110.9(4)		O5 ¹	Cr1	O1 ⁴	86.7(8)
O1	Zr1	O2 ²	110.9(4)		O5	Cr1	O5 ¹	102.7(13)
O1 ⁴	Zr1	O2 ²	70.3(4)		O5	Cr1	Cr1 ⁴	51.6(6)
O1 ⁴	Zr1	O1	71.5(5)		O5 ¹	Cr1	Cr1 ⁴	51.6(6)
O1 ⁴	Zr1	O3	144.1(3)		Cr1 ⁴	Cr1	Zr1	66.9(4)
O1	Zr1	O3	144.1(3)		Cr1 ⁴	Cr1	Zr1 ¹	66.9(4)
O1	Zr1	O4 ⁵	75.5(3)		Cl1A	Cr1	Zr1	144.2(12)
O1	Zr1	O4	142.4(4)		Cl1A	Cr1	O5	105(3)
O1 ⁴	Zr1	O4 ⁵	142.4(4)		Cl1A	Cr1	Cr1 ⁴	107(4)

¹+X₁+Y₁-Z₁; ²1-X₁-Y₁+Z₁; ³1-X₁-Y₁-Z₁; ⁴-Y₁+X₁-Y₁-Z₁; ⁵-Y₁+X₁-Y₁+Z₁; ⁶1+Y₁-X₁+Y₁+Z₁; ⁷-Y₁-X₁+Z₁; ⁸+X₁+Y₁1-Z₁; ⁹-Y₁-X₁1-Z₁

Table S6 Hydrogen Atom Coordinates (Å×10 ⁴) and Isotropic Displacement Parameters (Å ² ×10 ³) for Cr-SIM-NU-1000.				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H12	2511.35	-2511.35	2347.9	496
H10	3334.98	-1692.71	4315.07	496
H3	3589.97	-913.85	2526.67	438
H4	3100.11	-1406.77	3315.22	438
H6	3243.23	-2228.82	2142.34	438
H7	3733.09	-1735.91	1353.79	438

Table S7 Atomic Occupancy for Cr-SIM-NU-1000.					
Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
C10	0.73(3)	H10	0.5	Cr1	0.25
Cl1A	0.25				

Table S8 Solvent masks information for Cr-SIM-NU-1000.						
Number	X	Y	Z	Volume	Electron count	Content
1	-0.443	-0.996	-0.108	17323.4	3864.3	?

Single-crystal X-ray Diffraction Analyses

Single crystals of Cr-SIM-NU-1000 were mounted on MicroMesh (MiTeGen) with paratone oil. The data was collected on a 'Bruker APEX-II CCD' diffractometer with a Cu K α microfocus X-ray source. The crystals were kept at 210 K under a nitrogen stream during data collection. Using Olex2 [2] software, the structure was solved with the ShelXS [3] structure solution program using Direct Methods and refined with the ShelXL [4] refinement package using Least Squares minimisation. The disordered non-coordinated solvents were removed using the PLATON SQUEEZE program. The refinement results are summarized in Table S1. Crystallographic data for the Cr-SIM-NU-1000 crystal structure in CIF format has been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC-1874677. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.)

Crystal structure determination of [Cr-SIM-NU-1000]

Crystal Data for $C_{21.4575}H_{10}Cl_{0.25}Cr_{0.25}O_8Zr_{1.5}$ ($M = 554.48$ g/mol): hexagonal, space group P6/mmm (no. 191), $a = 39.100(2)$ Å, $c = 16.7147(9)$ Å, $V = 22131(3)$ Å³, $Z = 12$, $T = 210.0$ K, $\mu(\text{CuK}\alpha) = 2.261$ mm⁻¹, $D_{\text{calc}} = 0.499$ g/cm³, 88732 reflections measured ($2.608^\circ \leq 2\theta \leq 121.834^\circ$), 6316 unique ($R_{\text{int}} = 0.2081$, $R_{\text{sigma}} = 0.0681$) which were used in all calculations. The final R_1 was 0.1403 ($I > 2\sigma(I)$) and wR_2 was 0.4006 (all data).

Refinement model description

Number of restraints - 106, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups

2. Restrained distances

C10_\$1-C10_\$3

1.4 with sigma of 0.02

C11_\$1-C11

1.5 with sigma of 0.02

Cr1-O1_\$4

2.158 with sigma of 0.02

C9_\$2-C9_\$1

2.48 with sigma of 0.02

3. Restrained planarity

C12_\$1, C8_\$2, C9_\$2, C10_\$2, C10, C9, C8, C12, C8_\$3, C9_\$3, C10_\$3, C10_\$1,

C8_\$1, C9_\$1

with sigma of 0.1

C12_\$1, C8_\$1, C9_\$1, C10_\$1, C10_\$3, C9_\$3, C8_\$3, C12, C8, C9, C11, C10,

C10_\$2, C9_\$2, C11_\$1, C8_\$2

with sigma of 0.1

4. Uiso/Uanis restraints and constraints

Uanis(C11) $\approx$ Ueq, Uanis(C9) $\approx$ Ueq, Uanis(C10) $\approx$ Ueq, Uanis(C8)
 $\approx$ Ueq, Uanis(C12) $\approx$ Ueq, Uanis(C6) $\approx$ Ueq, Uanis(C5) $\approx$ Ueq,
 Uanis(C4) $\approx$ Ueq, Uanis(C3) $\approx$ Ueq, Uanis(C2) $\approx$ Ueq, Uanis(C7) $\approx$
 Ueq, Uanis(C1) $\approx$ Ueq: with sigma of 0.1 and sigma for terminal atoms of 0.2
 Uanis(Cl1A) $\approx$ Ueq: with sigma of 0.1 and sigma for terminal atoms of 0.2
 Uanis(C1) = Uanis(C2)
 Uanis(C2) = Uanis(C7) = Uanis(C6) = Uanis(C5) = Uanis(C4) = Uanis(C3)
 Uanis(C8) = Uanis(C12) = Uanis(C9) = Uanis(C11) = Uanis(C10)
 5. Others
 Fixed Sof: H10(0.5) Cr1(0.125) Cl1A(0.125)
 6.a Aromatic/amide H refined with riding coordinates:
 C12(H12), C10(H10), C3(H3), C4(H4), C6(H6), C7(H7)
 6.b Fitted hexagon refined as free rotating group:
 C3(C4,C5,C6,C7,C2)

References

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