Supporting Information

A Homoleptic Chromium(III) Carboxylate

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Experimental

General Information

Unless otherwise stated, all operations were carried out under N_2 in a glovebox. Solvents were purchased in anhydrous form, purged with N_2 prior to use and stored over activated 13X molecular sieves in a glovebox. Chromium(III) chloride tris(tetrahydrofuran) was purchased from a commercial source and further dried with trimethylsilylchloride per literature method.[1] Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA). Electronic absorption spectra were recorded on an Agilent 8453 diode array spectrophotometer (300-900 nm range). Vibrational spectra were collected on neat samples using a Perkin Elmer Frontier FT-IR spectrometer with a Pike Technologies GladiATR sample cell under N_2 flow. Mass spectra were collected at the Phillips 66 Research Center in Bartlesville, OK. Analysis was performed by field desorption time-of-flight mass spectrometry as follows: The sample was deposited to the field desorption (FD) emitter via syringe needle. Following solvent evaporation (< 1 minute), the emitter-probe assembly was inserted in the mass spectrometer ion source region for analysis. Mass analysis was performed with a time-of-flight mass spectrometer (AccuTOF-GCx, Jeol Inc. Peabody MA, USA) with data acquired by use of the MsAxel software. Mass spectral drift compensation was performed using octamethylcyclotetrasiloxane as the internal calibrant.

Sodium 2-ethylhexanoate (NaEH): A round bottom flask (250mL) was charged with sodium hydroxide (13.87g, 0.347 mol) and anhydrous methanol (200mL). Anhydrous 2-ethylhexanoic acid (50g, 0.347 mol) was added dropwise to the stirred solution and allowed to mix for 15 min. The solvent was removed by a rotary vapory and the viscous liquid dried at 185°C under vacuum for 18h. The product was isolated as an off-white solid in high yield (55.96g, 97%).

$Cr(EH)_3 \cdot (NaEH)_{0.1}$ (1): 3.1 equivalents sodium 2-ethylhexanoate (NaEH: 10.01g, 60.2 mmol) dissolved in anhydrous tetrahydrofuran (60 mL) was added to a THF slurry (100mL) containing $CrCl_3(THF)_3$ (7.27g, 19.4 mmol) and stirred for 24h producing a green solution and a white precipitate (NaCl). The solvent was removed under vacuum and the green solid was extracted with cyclohexane (400mL), filtered through Celite and dried under vacuum producing the product as a glassy green solid in good yield (7.10 g, 73%). UV/VIS (ethylbenzene): λ_{max} (ε) = 448 (54 $M^{-1}\,cm^{-1}$), 600 (47 $M^{-1}\,cm^{-1}$) nm. Anal. Calcd. for $C_{24.8}H_{46.5}O_{6.2}Na_{0.1}Cr$: C, 59.8; H, 9.4. Found: C, 59.5; H, 9.7. μ_{eff} = 3.4 μ_B (300K). FD-MS: *m/z* 481.28 $[M]^+$.

UV/VIS Spectra

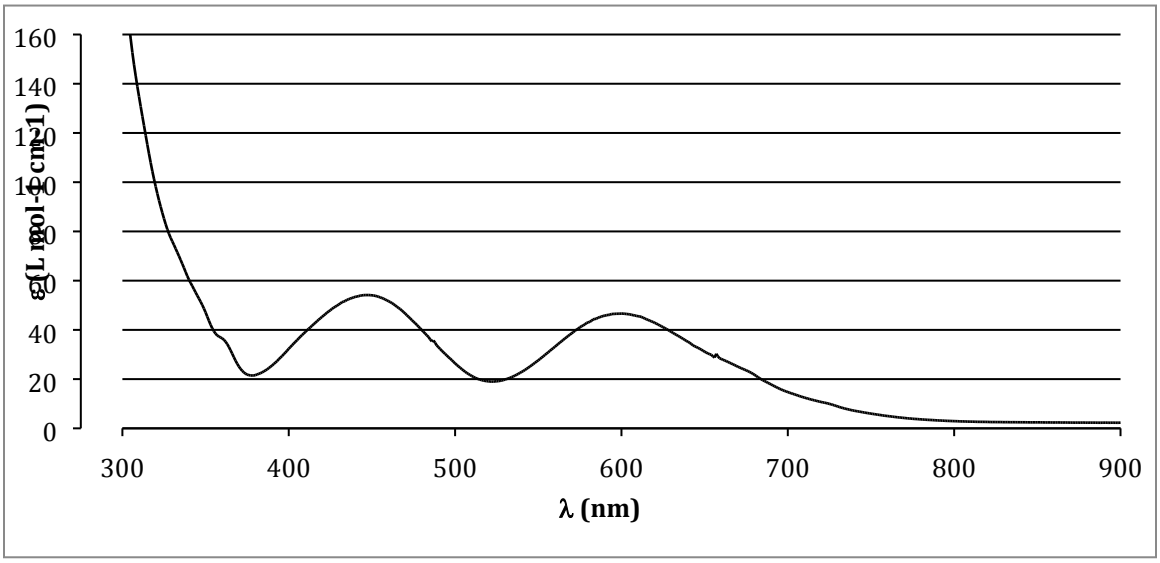

Figure S1. Electronic spectrum of **1** in ethylbenzene.

Field Desorption Mass Spectra

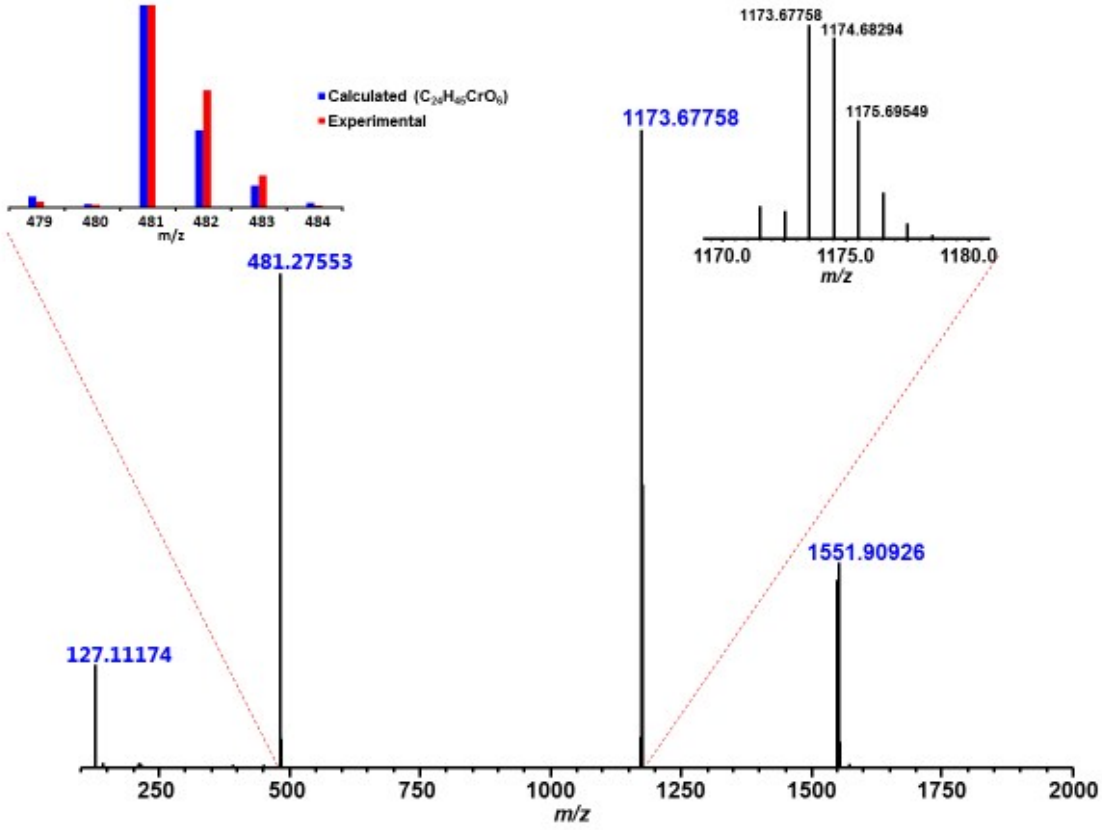

Figure S2. Positive-ion Field Desorption Mass Spectrum of **1**.
Comments on the FD-MS spectrum: The simulated isotopic distribution for $Cr(EH)_3$ deviates somewhat from the experimental distribution. This deviation is believed to be caused by a self-protonation mechanism which leads to overlay of the ionized molecule and the protonated molecular ion. *m/z* values measured on this FD-MS instrument demonstrate an accuracy of ±0.01 Dalton, as reported in the manuscript.

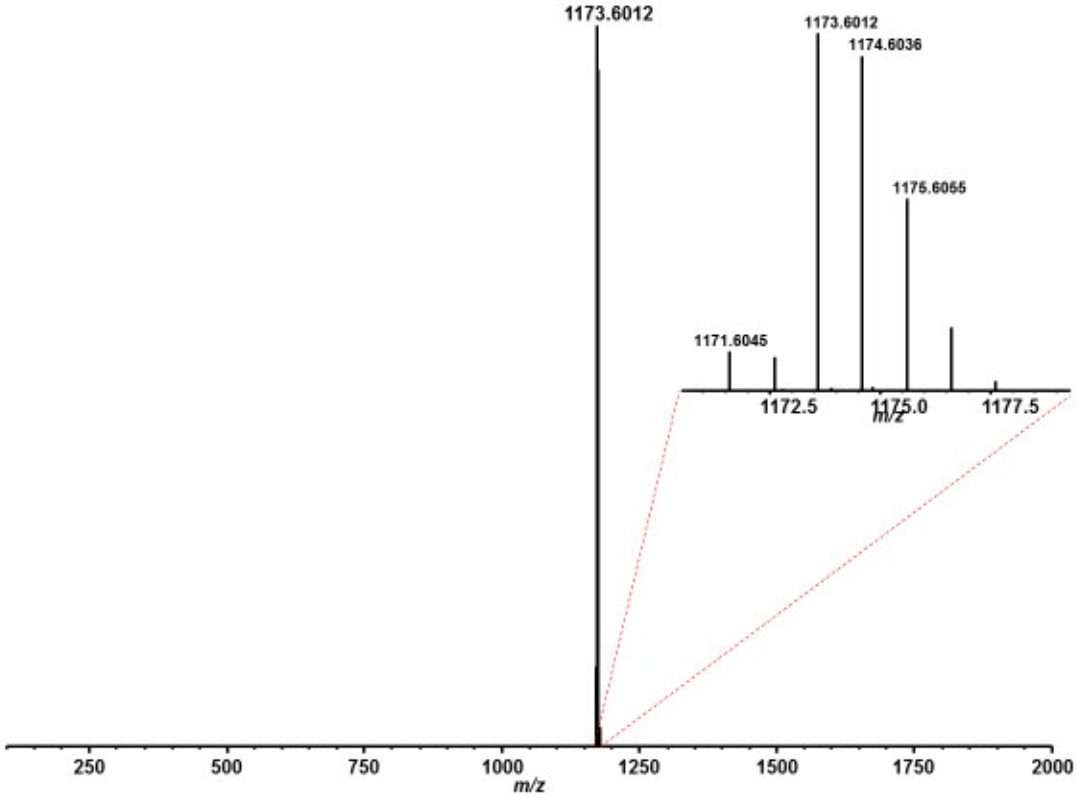

Figure S3. Positive-ion Field Desorption Mass Spectrum of **2**.

DFT Structures

Supplementary Table 1: UB3LYP/cc-pVDZ optimized structure of Chromium(III) 2-ethylhexanoate .

$E(B3LYP) + H_{corr} = \ -2437.16\ a.u$

Cr	0.41313	-0.33769	-0.22332
O	-1.21989	-0.63654	0.92646
O	-0.83330	-1.78216	-0.88523
O	1.11688	1.41622	0.49106
O	-0.34414	1.30419	-1.12024
O	2.06183	-0.67770	-1.33972
O	1.72027	-1.64998	0.57893
C	-1.59837	-1.55527	0.11658
C	0.38187	2.03425	-0.35628
C	2.47937	-1.48989	-0.44192
C	3.79637	-2.21591	-0.56526
H	4.20218	-1.94915	-1.55526
C	-2.89496	-2.30089	0.31494
H	-2.87343	-3.14152	-0.39875
C	0.38231	3.53878	-0.47226
H	1.00737	3.91008	0.35690
C	3.57673	-3.74223	-0.49534
H	4.57028	-4.22126	-0.52955
H	3.14115	-3.98936	0.48740
C	2.69421	-4.29996	-1.61462
H	2.60580	-5.39502	-1.53347
H	1.67410	-3.88331	-1.57686
H	3.11190	-4.07029	-2.60924
C	4.76986	-1.72761	0.53092
H	5.69317	-2.32744	0.44500
H	4.33484	-1.96157	1.51811
C	5.12045	-0.23754	0.45788
H	4.20233	0.37058	0.55247
H	5.53691	-0.00673	-0.54066
C	6.11876	0.19628	1.53703

H	7.04059	-0.40800	1.44585
H	5.69977	-0.03778	2.53290
C	6.47234	1.68355	1.46779
H	7.18924	1.96550	2.25573
H	6.92572	1.94246	0.49562
H	5.57465	2.31275	1.59142
C	1.02871	3.95535	-1.81445
H	0.41510	3.55382	-2.63875
H	0.96461	5.05503	-1.88138
C	2.48423	3.51144	-1.97927
H	2.58317	2.41364	-1.97193
H	2.89486	3.87333	-2.93524
H	3.11922	3.90841	-1.16950
C	-1.04856	4.09674	-0.33008
H	-0.99590	5.18381	-0.50818
H	-1.67403	3.67391	-1.13545
C	-1.69889	3.81472	1.03022
H	-1.72084	2.72425	1.20319
H	-1.06758	4.23918	1.83367
C	-3.12987	4.35753	1.16996
H	-3.75756	3.93441	0.36380
H	-3.55502	3.97718	2.11520
C	-3.24000	5.88570	1.15606
H	-2.90865	6.31840	0.19774
H	-4.28113	6.20979	1.31654
H	-2.62493	6.33674	1.95413
C	-2.99983	-2.84226	1.75417
H	-3.99227	-3.30458	1.87871
H	-2.95619	-1.98934	2.45223
C	-1.91497	-3.86342	2.10714
H	-0.90529	-3.42572	2.03858
H	-2.04407	-4.23305	3.13676
H	-1.94882	-4.73522	1.43201
C	-4.05805	-1.35228	-0.07412
H	-3.80239	-0.85519	-1.02655
H	-4.13106	-0.55190	0.68275
C	-5.41272	-2.05091	-0.23619
H	-5.71144	-2.53080	0.71264
H	-5.31556	-2.86799	-0.97564
C	-6.52595	-1.09533	-0.68162
H	-6.61632	-0.27533	0.05439
H	-6.23403	-0.61628	-1.63416
C	-7.88143	-1.78553	-0.84900
H	-8.21780	-2.24334	0.09698
H	-8.65935	-1.07428	-1.16988
H	-7.83137	-2.58833	-1.60431

Supplementary Table 2: UB3LYP/cc-pVDZ optimized structure of μ_3-oxo-hexakis-(m_2-2-ethylhexanato-O,O')-triaquo-trichromium(III) cation (**2**)

$E(B3LYP) + H_{corr} = -4809.06\ a.u$

Cr	-1.83369400	-0.53714400	-0.00021800
O	-2.42363200	0.77302000	1.37906200
O	-0.77222700	2.29664800	1.48671000
O	-0.87932900	2.35139000	-1.36231000
O	-2.41862500	0.71326300	-1.43801100
C	-1.86728100	1.79763900	1.88894200
C	-1.91863400	1.80737700	-1.84853800
Cr	0.43655900	1.82317900	0.00409500
Cr	1.35368100	-1.33187000	-0.00163300
O	-0.01565200	-0.00824700	-0.02009000
O	-1.63141000	-1.91817800	-1.38991700
O	0.56737500	-2.39251000	-1.46662700
C	-0.62757200	-2.52328400	-1.87846300
O	0.53562800	-2.46809900	1.38467000
O	-1.62869800	-1.85817800	1.44825100
C	-0.64102500	-2.53936600	1.86141700
O	2.50903000	-0.43714000	-1.37211500
O	1.78325100	1.69127200	-1.46832800
C	2.50569600	0.72996000	-1.87634600
O	1.89984000	1.69160700	1.35357000
O	2.43566300	-0.49086000	1.46161200
C	2.53472700	0.71123400	1.85669900
O	2.90841800	-2.77401500	-0.01502700
H	3.41862000	-2.71824900	0.81085800
H	3.53283800	-2.55471100	-0.72782700
O	0.98506800	3.87492900	0.00349200
H	1.44801800	4.08687200	-0.82496300
H	1.63459900	4.02066400	0.71266900
O	-3.88515800	-1.08639700	0.01491800
H	-4.31293300	-0.65512400	0.77467900
H	-4.31438000	-0.71100200	-0.77314100
C	-0.86781000	-3.48234100	3.01319200
H	-0.21812200	-4.36218900	2.91911200
H	-0.59765600	-2.96086600	3.94679100
H	-1.92326200	-3.77506900	3.07134900
C	3.44932200	0.99850400	3.01919300
H	3.90965500	1.98958900	2.91262200

H	2.84188800	1.00866100	3.93977200
H	4.21523300	0.21977100	3.11918100
C	-2.54221800	2.44982900	3.06673900
H	-2.19700900	1.94586300	3.98520000
H	-2.26802100	3.51003500	3.13142500
H	-3.63133000	2.32784300	3.00499100
C	-2.58773300	2.50438500	-3.00389600
H	-3.62423800	2.16598400	-3.12161200
H	-2.54246800	3.59312900	-2.86745000
H	-2.03201500	2.25997900	-3.92458900
C	3.41005200	0.97880300	-3.05580000
H	2.89948300	0.61512700	-3.96326700
H	3.61441800	2.04946400	-3.17736300
H	4.34433000	0.41135800	-2.95087900
C	-0.86840900	-3.44524500	-3.04452700
H	-1.86506900	-3.89929000	-2.97218700
H	-0.83400200	-2.84793300	-3.97116800
H	-0.08668400	-4.21290600	-3.09864100

Reference

1) J. H. So and P. Boudjouk *Inorg. Chem.* 1990, **29**, 1592-3.