

ELECTRONIC SUPPLEMENTARY INFORMATION

S1. EXAFS TABLES

Table S1: Overview of the fitting data of the EXAFS experiment discussed in Figure 4 in the main paper. The error is shown within parentheses and the underlined values were fixed during the optimization procedure.

Molality LiCl (mol/kg)	S_0^2	N(O)	N(Cl)	R(O) (Å)	R(Cl) (Å)	σ^2 (O) (Å ²)	σ^2 (Cl) (Å ²)	E_0 (eV)	F (%)
16	0.42 (0.08)	3.48 (0.86)	2.52	1.99 (0.01)	2.31 (0.01)	<u>0.0021</u>	0.0020 (0.001)	-0.88 (1.16)	56.38
14	0.45 (0.03)	3.70 (0.32)	2.30	1.99 (0.01)	2.31 (0.01)	<u>0.0021</u>	<u>0.0020</u>	-0.92 (0.95)	51.02
12	0.42 (0.04)	4.18 (0.42)	1.82	1.99 (0.01)	2.31 (0.01)	<u>0.0021</u>	<u>0.0020</u>	-0.42 (1.05)	55.28
10	0.43 (0.06)	4.79 (0.67)	1.21	1.99 (0.01)	2.30 (0.01)	<u>0.0021</u>	<u>0.0020</u>	-0.10 (1.17)	57.45
8	<u>0.69</u>	3.67 (0.21)		1.97 (0.01)		<u>0.0021</u>		-3.53 (1.53)	61.12
6	<u>0.69</u>	3.61 (0.19)		1.96 (0.01)		<u>0.0021</u>		-3.85 (1.44)	57.89
4	<u>0.69</u>	5.25 (0.17)		1.96 (0.01)		<u>0.0021</u>		-2.63 (0.84)	39.16
2	<u>0.69</u>	5.30 (0.19)		1.97 (0.01)		<u>0.0021</u>		-1.75 (0.91)	42.62
0	0.69 (0.04)	<u>5.96</u>		1.97 (0.01)		0.0021 (0.001)		-1.27 (0.90)	40.57

Table S2: Overview of the fitting data of the EXAFS experiment discussed in Figure 7 in the main paper. The error is shown within parentheses and the underlined values were fixed during the optimization procedure.

mol % H ₂ O	mol % EG	mol % ChCl	S_0^2	N(O)	N(Cl)	R(O) (Å)	R(Cl) (Å)	σ^2 (O) (Å ²)	σ^2 (Cl) (Å ²)	E_0 (eV)	F (%)
0	67	33	0.61 (0.20)	3.03 (2.33)	2.97	2.00 (0.02)	2.29 (0.01)	0.0016 (0.0025)	0.0020 (0.0018)	1.20 (1.45)	40.0 9
0	73	27	0.65 (0.02)	3.38 (0.18)	2.62	2.00 (0.01)	2.29 (0.01)	<u>0.0016</u>	<u>0.0020</u>	1.82 (0.59)	33.3 0
0	80	20	0.62 (0.04)	3.52 (0.62)	2.48	2.00 (0.01)	2.29 (0.01)	0.0019 (0.001)	<u>0.0020</u>	1.93 (0.78)	38.7 3
0	87	13	0.67 (0.03)	3.86 (0.22)	2.14	2.00 (0.01)	2.28 (0.01)	<u>0.0025</u>	<u>0.0020</u>	2.16 (0.63)	34.0 2
0	93	7	0.68 (0.03)	4.19 (0.25)	1.81	1.99 (0.01)	2.28 (0.01)	<u>0.0025</u>	<u>0.0020</u>	2.12 (0.66)	35.8 8
0	100	0	0.66 (0.04)	4.86 (0.35)	1.14	1.98 (0.01)	2.27 (0.01)	<u>0.0025</u>	<u>0.0020</u>	1.28 (0.62)	32.9 4
12	88	0	<u>0.71</u>	5.18 (0.16)		1.97 (0.01)		<u>0.0025</u>		0.40 (0.75)	37.8 7

31	69	0	<u>0.71</u>	5.74 (0.14)	1.97 (0.01)	<u>0.0025</u>	1.46 (0.61)	31.7 5
59	41	0	<u>0.71</u>	5.89 (0.13)	1.96 (0.01)	<u>0.0025</u>	1.53 (0.54)	28.6 6
100	0	0	0.71 (0.03)	<u>6</u>	1.96 (0.01)	0.0025 (0.0003)	1.74 (0.63)	32.1 2

S2. UV/VIS SPECTRA OF Cr(III) DISSOLVED IN ALCOHOLS

To study the influence of alcohols on the coordination chemistry of chromium(III) salts in solution, solutions of 0.02 mol/L $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ were prepared in water, methanol, ethanol, iso-propanol, ethylene glycol (EG), and glycerol as solvents, and were analyzed by UV/Vis spectroscopy. The corresponding UV/Vis spectra can be found in Figure S1. In Figure S2, the wavelength positions and absorbance values are shown as a function of the solvent, for each of the three chromium(III) salts. For all salts it is observed that when dissolved in water, the same UV/Vis spectra are obtained with low wavelength and absorbance values. However, when dissolved in one of the alcohols, the UV/Vis spectra show a much stronger absorbance. Moreover, the bulkier the alcohol, the larger the absorbance. This is a strong indication that the increase in intensity of the bands is caused by a more asymmetric environment of the central chromium(III) ion and thus a partial elimination of the Laporte selection rule. Additionally, redshift of the absorbance bands is observed when a chromium(III) salt is dissolved in an alcohol instead of in water. The magnitude of this redshift is dependent on the counter ion of the chromium salt (Cl^- , NO_3^- , or SO_4^{2-}). Hence this indicates that the alcohols coordinating the central metal ion, stabilize the presence of anions in the first coordination sphere. However, this shift also depends on the type of alcohol, which is an indication that the redshift is due to a combined effect of the alcohol and anion ligands, as already indicated in the main paper.

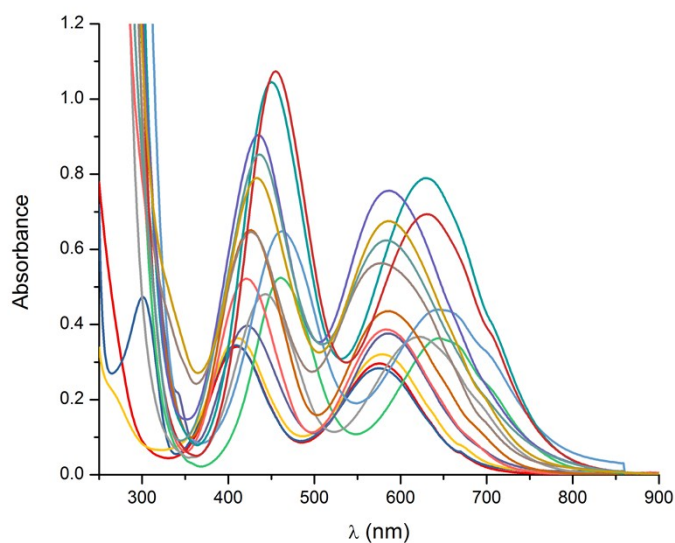


Figure S1: Overview of the UV/Vis spectra of all soluble combinations of each time one of the Cr(III) salts, dissolved in one of the possible alcohols (or water).

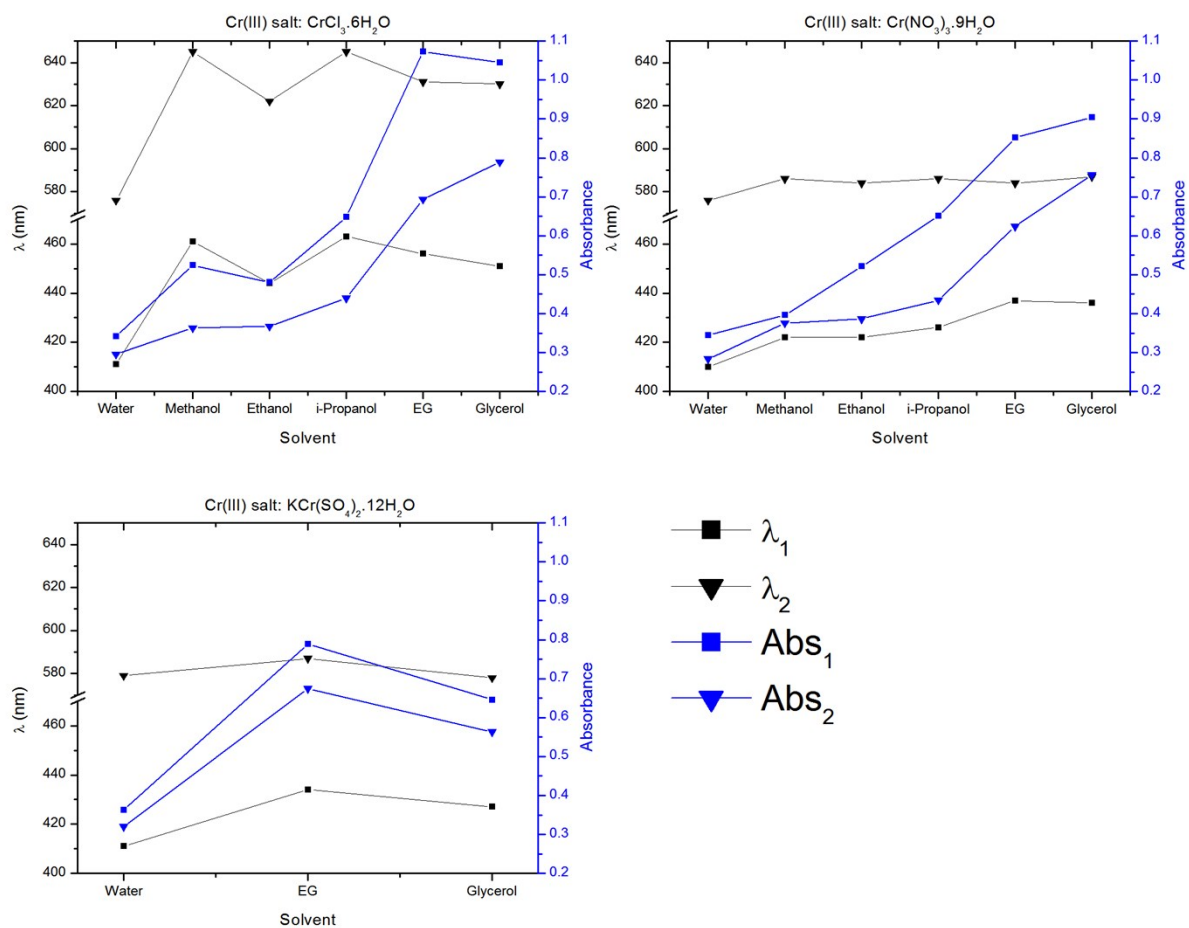


Figure S2: Illustration of the influence of different alcohols compared to water as solvent for three different chromium(III) salts. The $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ salt was only soluble in three of the solvents, no UV/Vis spectra are measured of the insoluble samples.