Supporting Information

Probing Coordination Complexes by Carbon Nanotube-Assisted Low Voltage Paper Spray Ionization Mass Spectrometry

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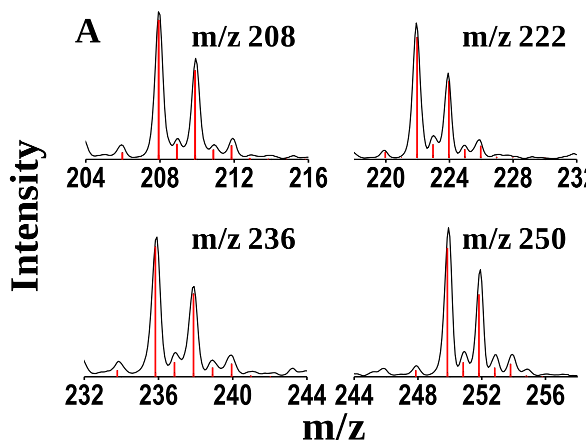

B

No	m/z	Complex ions
1	208	$[Cr(CH_3OH)(H_2O)_3Cl_2]^+$
2	222	$[Cr(CH_3OH)_2(H_2O)_2Cl_2]^+$
3	236	$[Cr(CH_3OH)_3(H_2O)_1Cl_2]^+$
4	250	$[Cr(CH_3OH)_4Cl_2]^+$

Figure S1. A) Experimental and simulated (sticks) mass spectra of different methanol substituted chromium complexes and B) a list of different methanol substituted chromium complexes observed.

Supporting Information 2:

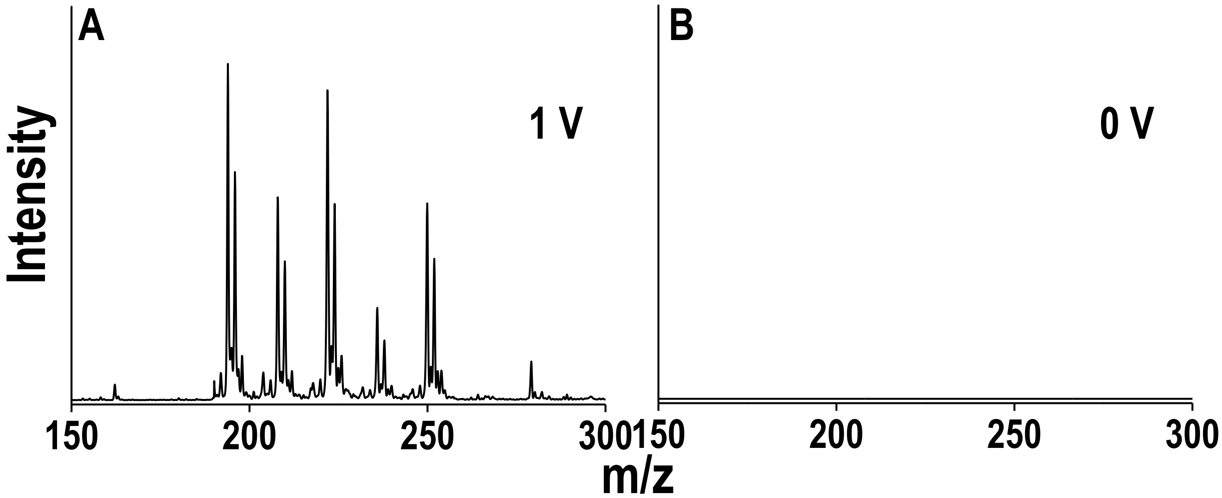

Figure S2. Analysis of $CrCl_3.6H_2O$ at A) 1 V and B) 0 V.

Supporting Information 3:

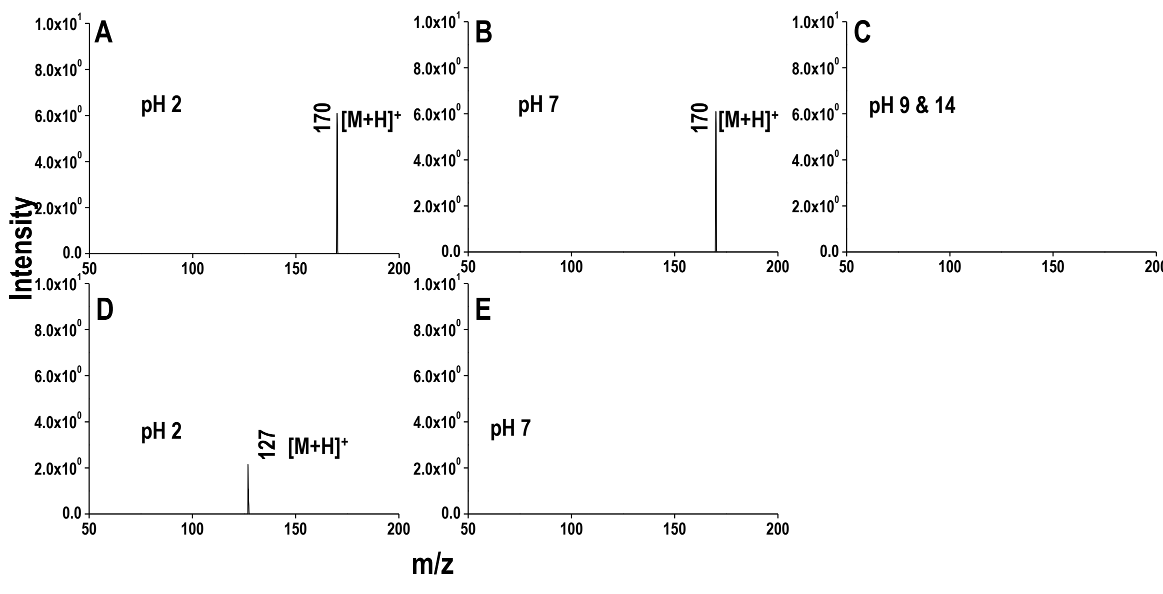

Figure S3. 0 V mass spectra of DPA at A) pH 2, B) pH 7 , C) pH 9 &14, and thymine at C) pH 2 and, E) pH 7.

Supporting Information 4:

A

No	Voltage (V)	Signal Intensity				
		$[Cr(H_2O)_4Cl_2]^+$	$[Cr(CH_3OH)(H_2O)_2Cl_2]^+$	$[Cr(CH_3OH)_2(H_2O)_2Cl_2]^+$	$[Cr(CH_3OH)_3(H_2O)Cl_2]^+$	$[Cr(CH_3OH)_4Cl_2]^+$
1	1	5.3×10^2	2.8×10^2	3.9×10^2	1.7×10^2	3.2×10^2
2	10	1.5×10^2	1.7×10^2	3.9×10^2	1.6×10^2	2.9×10^2
3	50	9.7×10^0	1.7×10^2	5.6×10^2	2.2×10^2	4.3×10^2
4	100	8.6×10^0	1.7×10^2	5.5×10^2	2.2×10^2	3.6×10^2
5	200	4.4×10^0	1.1×10^2	2.7×10^2	1.1×10^2	1.1×10^2
6	300	2.6×10^0	8.6×10^0	2.1×10^2	1.0×10^2	9.5×10^0
7	400	3.7×10^0	1.1×10^2	3.4×10^2	1.8×10^2	1.5×10^0
8	500	4.2×10^0	1.7×10^2	3.9×10^2	3.1×10^2	1.8×10^2
9	600	2.4×10^0	1.0×10^2	1.9×10^2	1.7×10^2	6.6×10^0

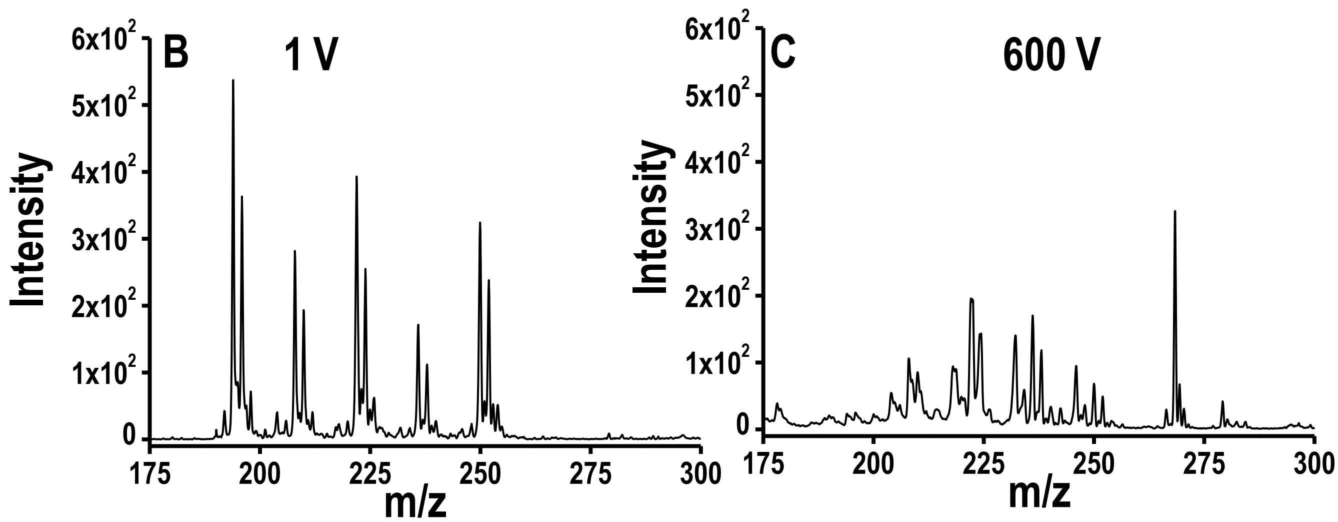

Figure S4. A) Absolute intensity values of various complexes detected at various voltages, B) 1 V mass spectrum of $CrCl_3.6H_2O$ in methanol and C) mass spectrum of $CrCl_3.6H_2O$ at 600 V.

Supporting Information 5:

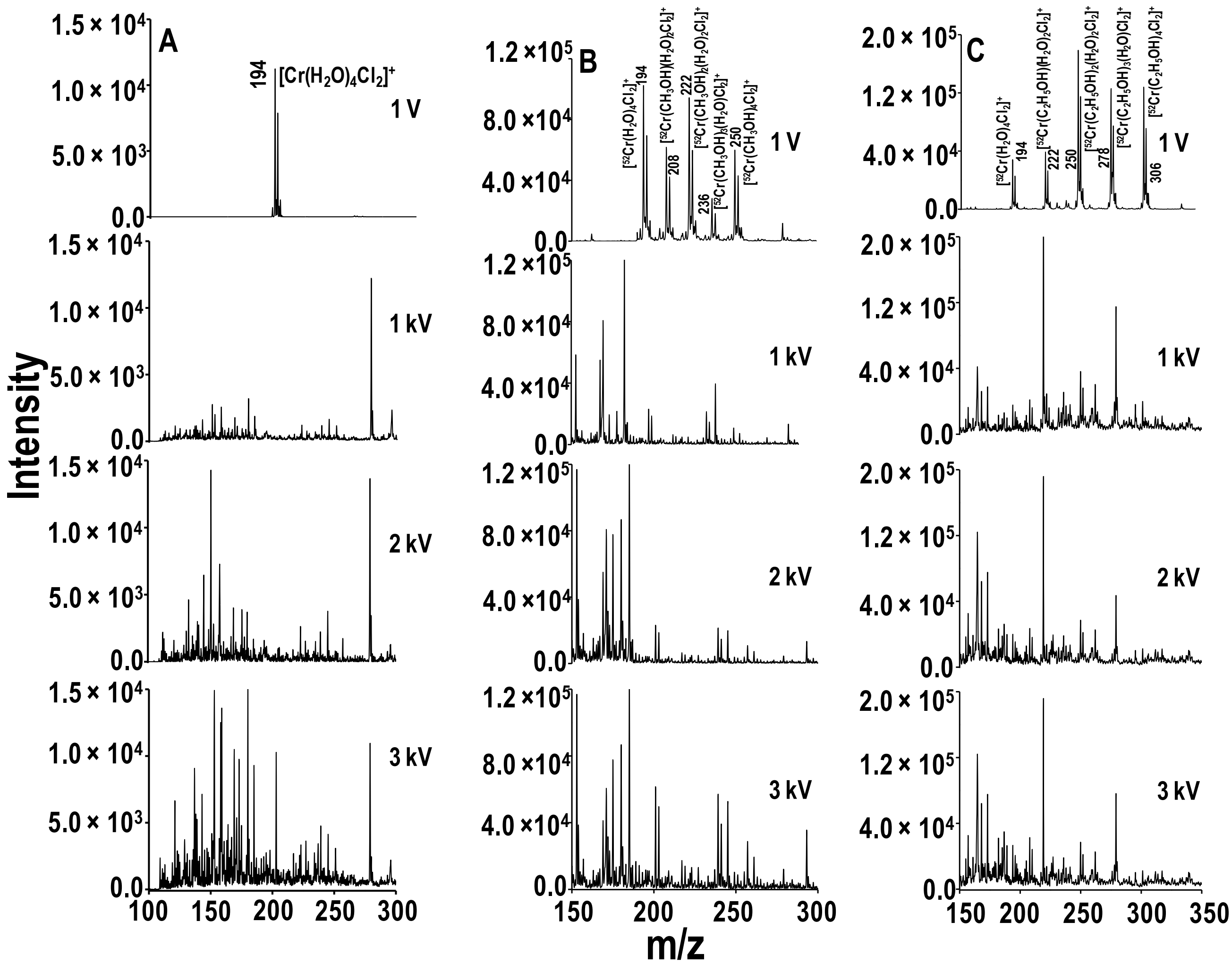

Figure S5. Comparison between low voltage and normal paper spray analysis. Mass spectra represent paper spray analysis of various complex ions of $CrCl_3.6H_2O$ at different voltages in A) water, B) methanol, and C) ethanol. The 1 V spectra are collected from a CNT coated paper (low voltage PS). All other high voltage spectra are collected from a normal Whatman 42 filter paper (normal PS). All the complexes are indicated with their m/z ratio.

Supporting Information 6:

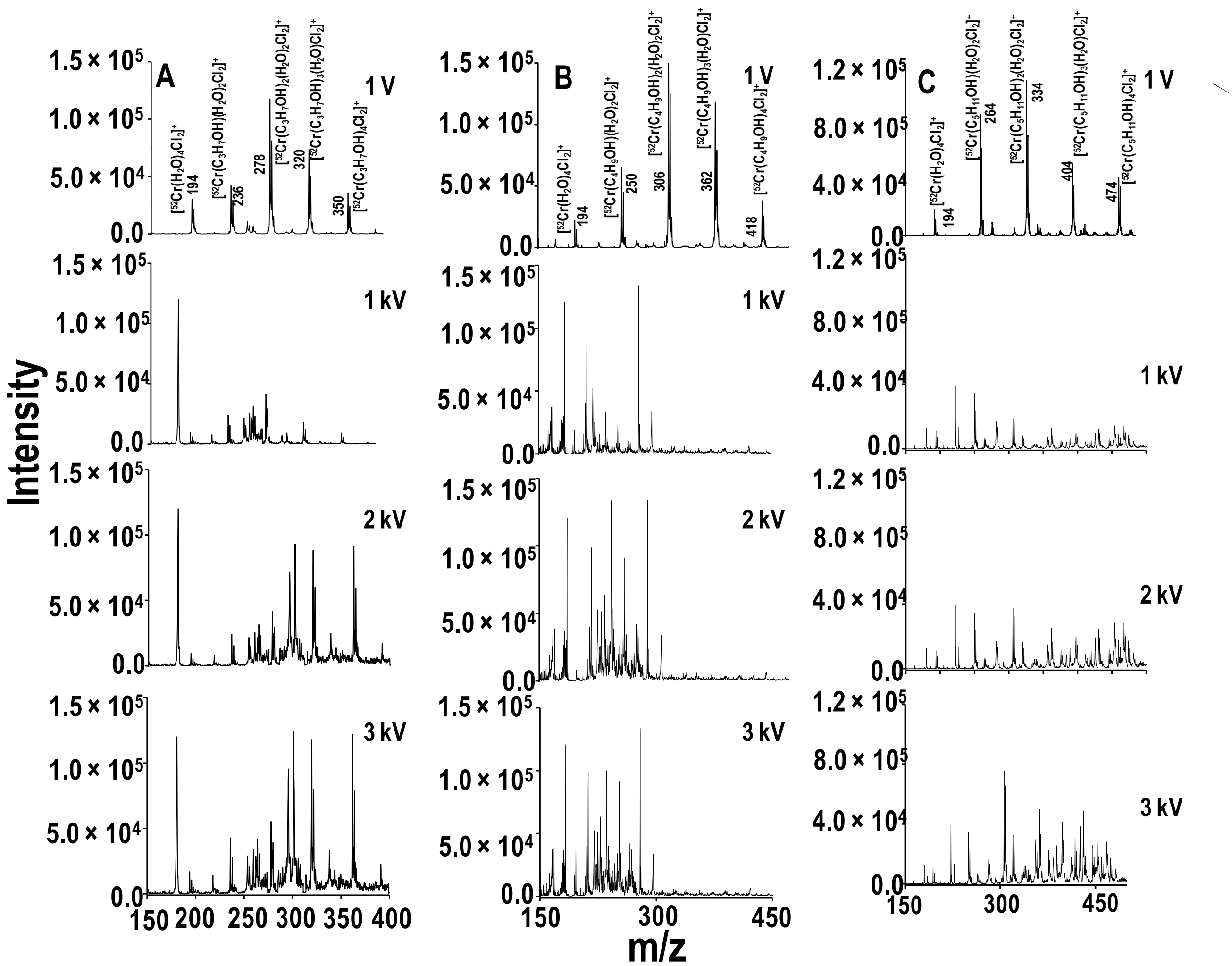

Figure S6. Comparison between low voltage and normal paper spray analysis. Mass spectra represent paper spray analysis of various complex ions of $CrCl_3.6H_2O$ at different voltages in A) propanol, B) butanol, and C) pentanol. The 1 V spectra are collected from a CNT coated paper (low voltage PS). All other high voltage spectra are collected from a normal Whatman 42 filter paper (normal PS). All the complexes are indicated with their m/z ratio.

Supporting Information 7:

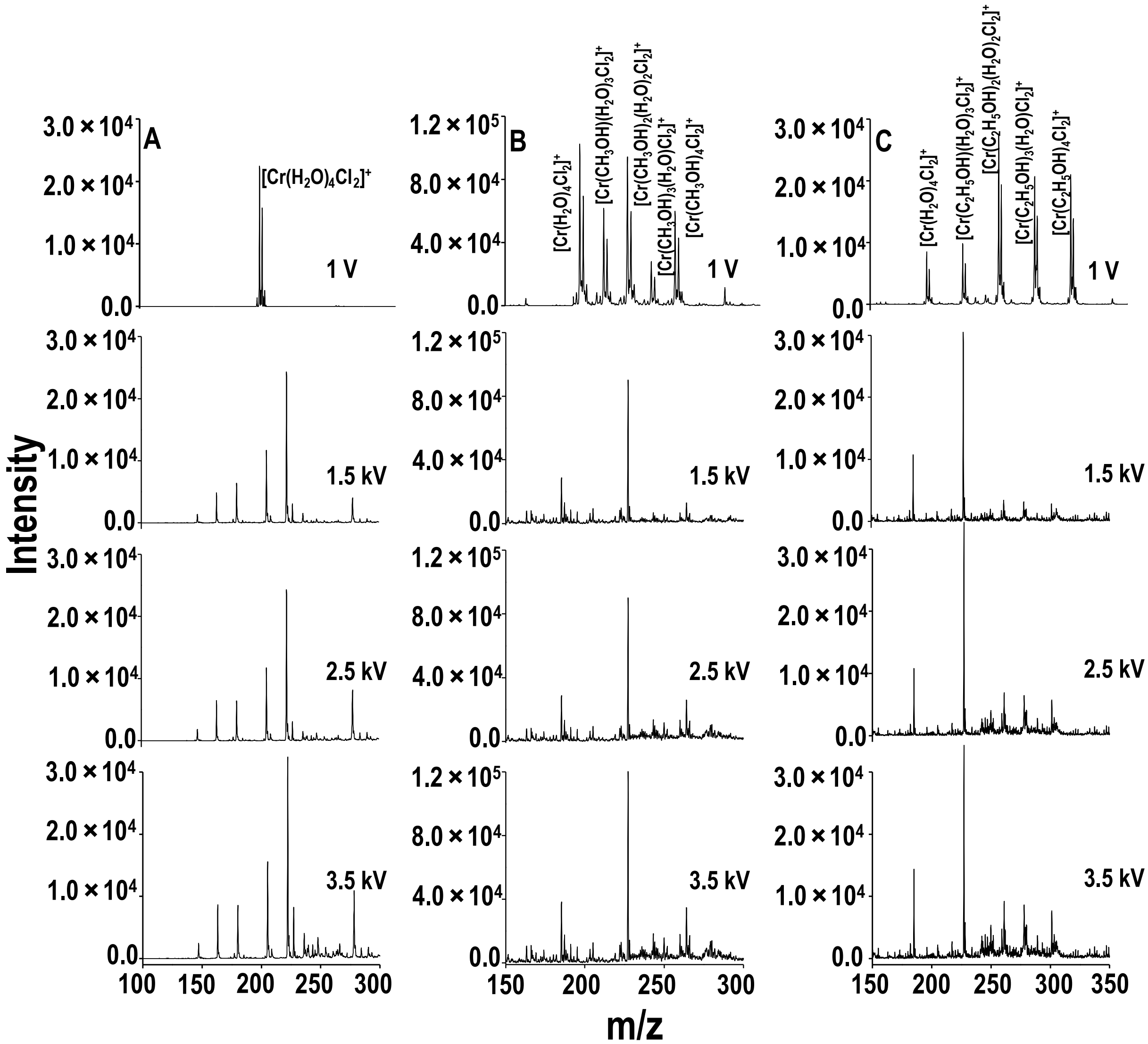

Figure S7. Comparison between low voltage and ESI MS analysis. The figure represents mass spectra of various complex ions of $CrCl_3.6H_2O$ at different voltages in A) water, B) methanol, and C) ethanol. The 1 V spectra are collected from a CNT coated paper (low voltage PS). All other high voltage spectra are collected from ESI measurements. All the compelxes are indicated with their m/z ratio.

Supporting Information 8:

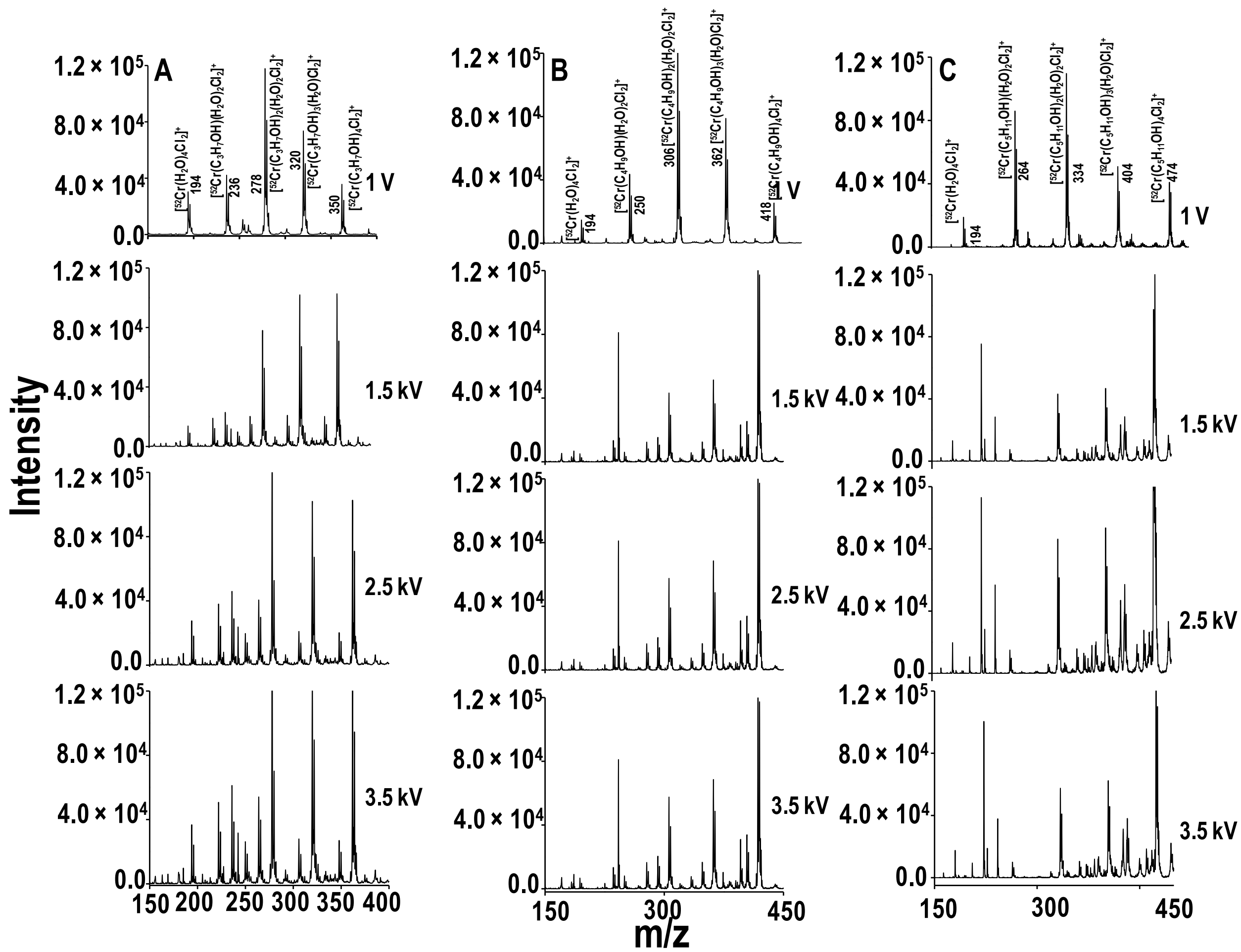

Figure S8. Comparison between low voltage and ESI MS analysis. The figure represents mass spectra of various complex ions of $CrCl_3.6H_2O$ at different voltages in A) propanol, B) butanol, and C) pentanol. The 1 V spectra are collected from a CNT coated paper (low voltage PS). All other high voltage spectra are collected from ESI measurements. All the compelxes are indicated with their m/z ratio.

Supporting Information 9:

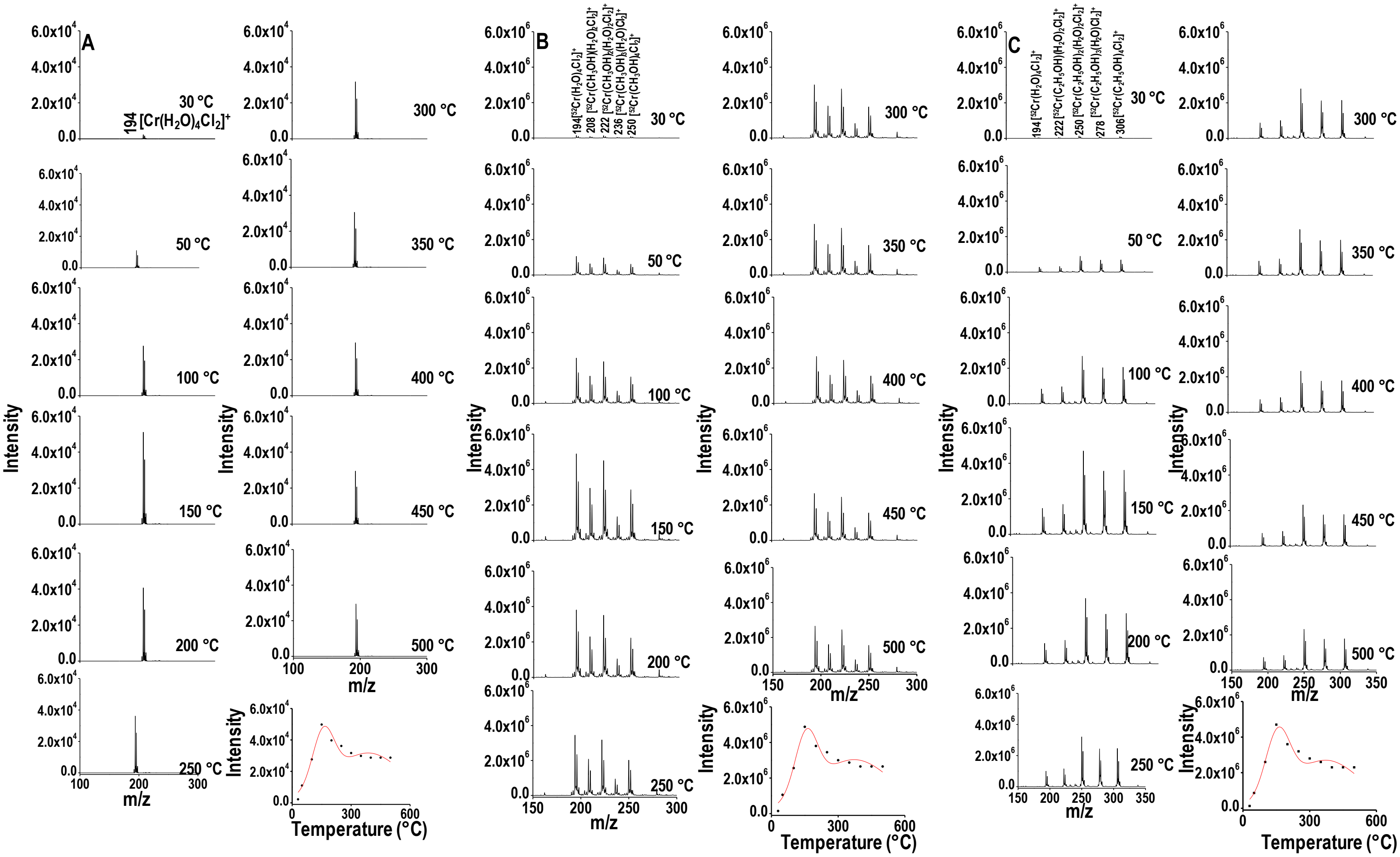

Figure S9. Mass spectra of $CrCl_3.6H_2O$ at different MS inlet temperatures in A) water, B) methanol and C) ethanol. The variation of signal intensity of various complexes with respect to the MS inlet temperature is also shown.

Supporting Information 10:

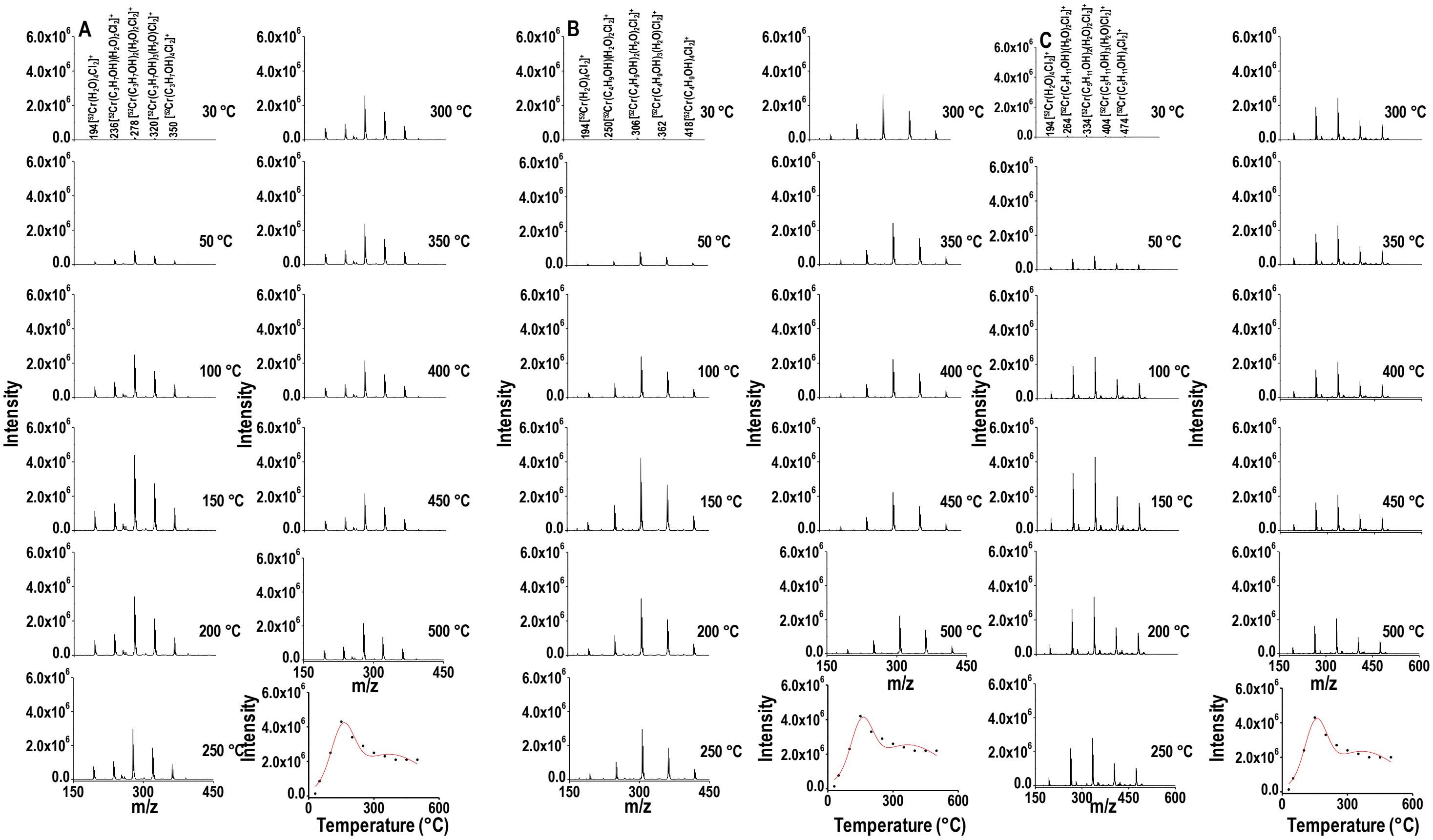

Figure S10. Mass spectra of $CrCl_3.6H_2O$ at different mass inlet temperatures in A) propanol, B) butanol and C) pentanol. The variation of signal intensity of various complexes with respect to the mass inlet temperature is also shown.

Supporting Information 11:

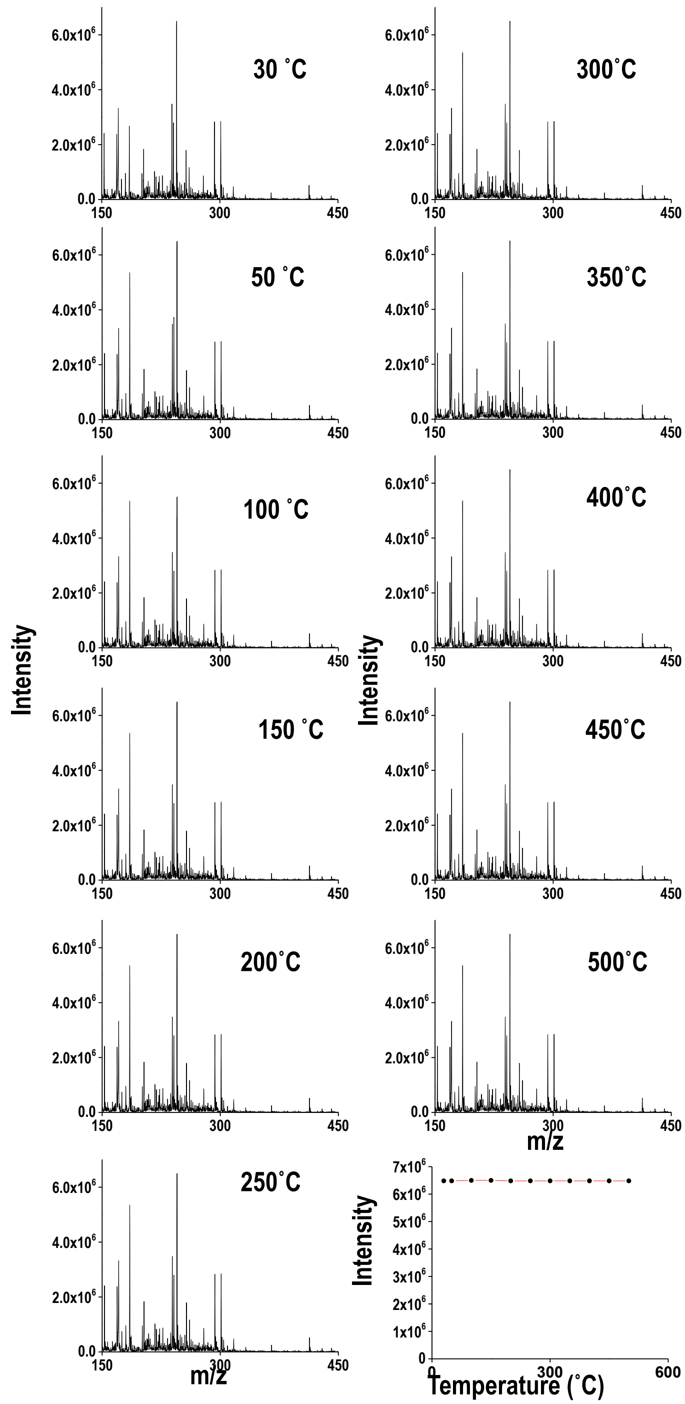

Figure S11. Conventional paper spray mass spectra of $CrCl_3.6H_2O$ at different MS inlet temperatures. The variation of signal intensity of the base peak with respect to the MS inlet temperature is also shown.

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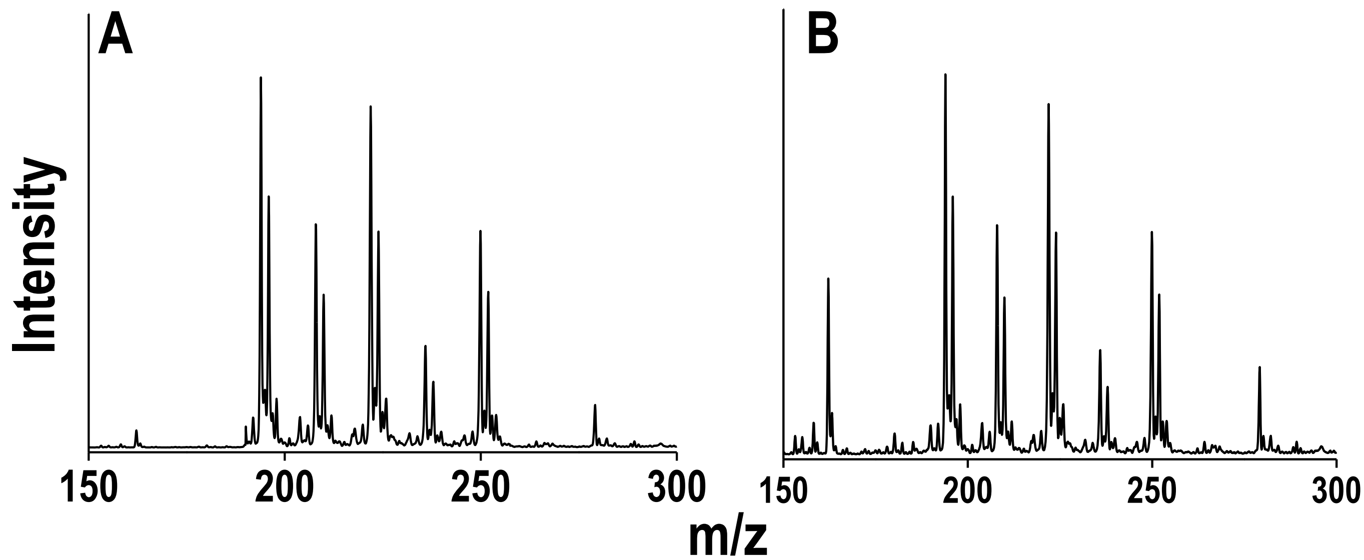

Figure S12. Mass spectra of $CrCl_3.6H_2O$ in methanol, A) at 1 V and B) that collected by introducing 3 µL of solution in front of the MS inlet.

Supporting Information 13:

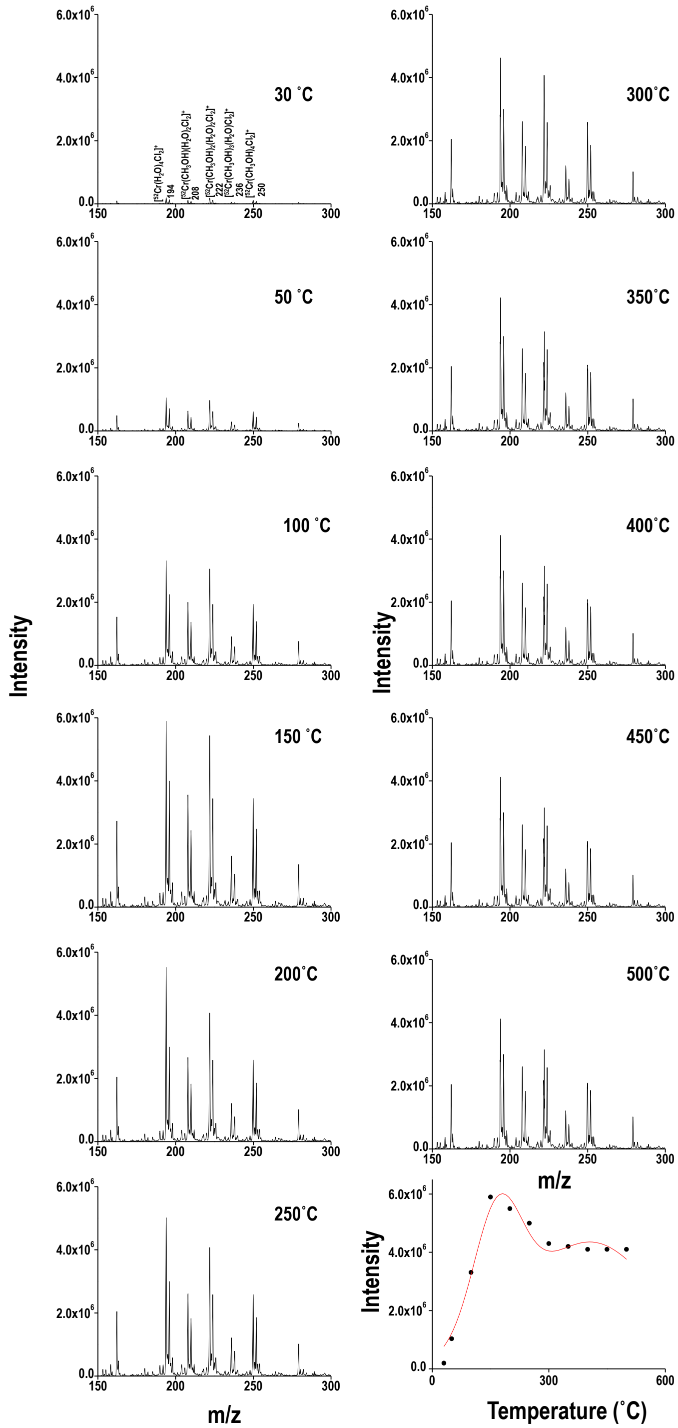

Figure S13. Mass spectra of $CrCl_3.6H_2O$ collected by directly introducing the analyte in front of MS inlet at different MS inlet temperatures. Variation of signal intensity of the base peak with respect to the MS inlet temperature is also shown.

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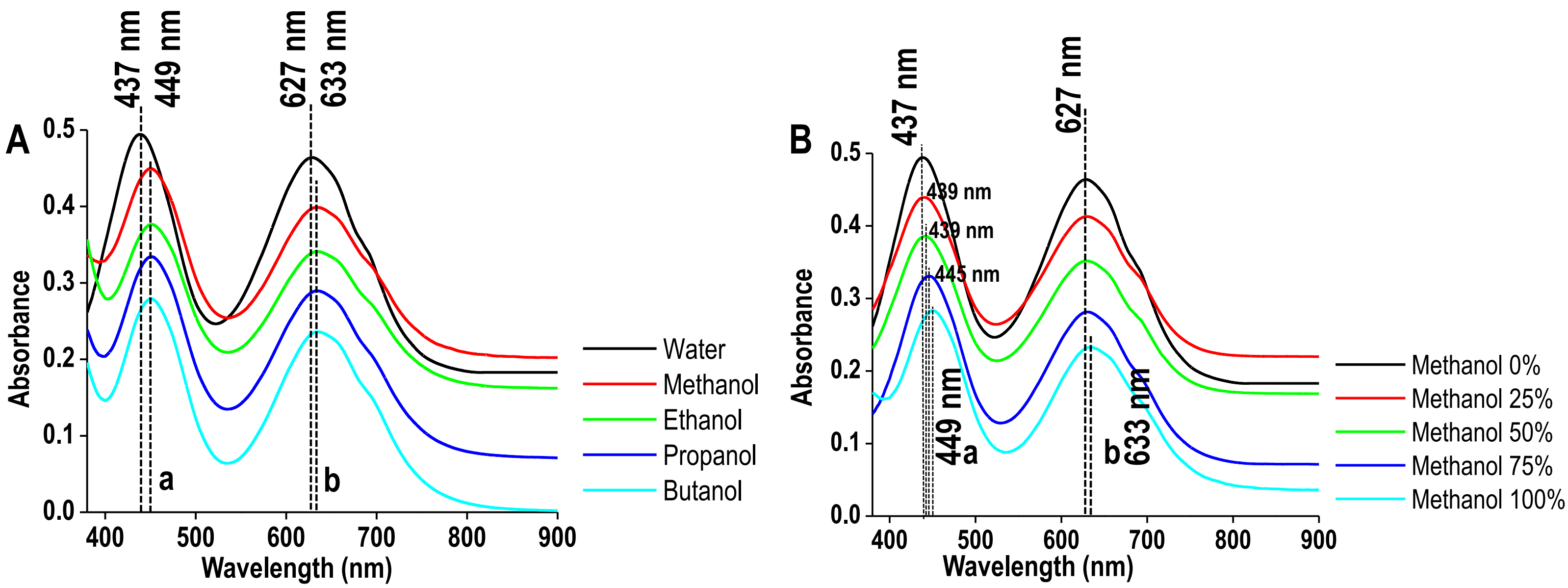

Figure S14. UV-visible spectra of $CrCl_3.6H_2O$ in A) different solvents and B) different percentage composition of methanol (in water). Shift in the peak positions is due to the formation of different complexes in solution. The spectra are shifted vertically for clarity. The peaks marked a and b are due to $^4A_2g \longrightarrow {}^4T_{1g}$ and $^4A_2g \longrightarrow {}^4T_{2g}$ transitions, respectively. Systematic red shift is seen in B upon changing the solvent composition.

Table S1. List of different mixed ligand complexes detected at 1 V with their m/z values

No	m/z	Mixed complex ions
1	264	$[Cr(CH_3OH)_3(C_2H_5OH)Cl_2]^+$
2	278	$[Cr(CH_3OH)_2(C_2H_5OH)_2Cl_2]^+$
3	292	$[Cr(CH_3OH)(C_2H_5OH)_3Cl_2]^+$
4	334	$[Cr(C_2H_5OH)_3(C_4H_9OH)Cl_2]^+$
5	362	$[Cr(C_2H_5OH)_2(C_4H_9OH)_2Cl_2]^+$
6	390	$[Cr(C_2H_5OH)(C_4H_9OH)_3Cl_2]^+$
7	376	$[Cr(C_3H_7OH)_3(C_4H_9OH)Cl_2]^+$
8	390	$[Cr(C_3H_7OH)_2(C_4H_9OH)_2Cl_2]^+$
9	404	$[Cr(C_3H_7OH)(C_4H_9OH)_3Cl_2]^+$

Table S2. List of different chromium bromide complexes detected at 1 V with their m/z values.

No	m/z	Complex ions
1	284	$[Cr(H_2O)_4Br_2]^+$
2	298	$[Cr(H_2O)_3(CH_3OH)Br_2]^+$
3	312	$[Cr(H_2O)_2(CH_3OH)_2Br_2]^+$
4	326	$[Cr(H_2O)(CH_3OH)_3Br_2]^+$
5	340	$[Cr(CH_3OH)_4Br_2]^+$
6	312	$[Cr(H_2O)_3(C_2H_5OH)Br_2]^+$
7	340	$[Cr(H_2O)_2(C_2H_5OH)_2Br_2]^+$
8	368	$[Cr(H_2O)(C_2H_5OH)_3Br_2]^+$
9	396	$[Cr(C_2H_5OH)_4Br_2]^+$
10	326	$[Cr(H_2O)_3(C_3H_7OH)Br_2]^+$
11	368	$[Cr(H_2O)_2(C_3H_7OH)_2Br_2]^+$
12	410	$[Cr(H_2O)(C_3H_7OH)_3Br_2]^+$
13	452	$[Cr(C_3H_7OH)_4Br_2]^+$
14	340	$[Cr(H_2O)_3(C_4H_{10}OH)Br_2]^+$
15	396	$[Cr(H_2O)_2(C_4H_{10}OH)_2Br_2]^+$
16	452	$[Cr(H_2O)(C_4H_{10}OH)_3Br_2]^+$
17	508	$[Cr(C_4H_{10}OH)_4Br_2]^+$