

Supplementary Information

A cobalt(II) complex with unique paraSHIFT responses to anions

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Contents

1. General experimental details	3
2. Synthetic methods.....	4
Scheme S1 – Synthesis of [CoMe ₆ TrenCl]Cl.....	4
Scheme S2 – Synthesis of [Co(d ₃ -Me) ₆ TrenCl]Cl.....	4
3. Supplementary figures	5
Figure S1 – The paramagnetic region of ¹ H NMR (D ₂ O, 7T) for [CoMe ₆ TrenCl]Cl (top) and [Co(d ₃ -Me) ₆ TrenCl]Cl (bottom) prepared by the same procedure.	5
Figure S2 – Changes in the ratio of ¹ H peak integrals at 140 and 165 ppm upon the addition of fluoride	6
Figure S3 – Absorption spectra of CoMe ₆ TrenCl (5 mM, 90:10 H ₂ O:D ₂ O, pH 6.5) with the addition of NaF	7
Figure S4 – ¹⁹ F NMR spectra (9.4 T) of varying concentrations of NaF in the presence of CoMe ₆ TrenCl	8
Figure S5 – Signal:noise ratios as a function of acquisition time for the paramagnetic region of ¹ H NMR spectra of [CoMe ₆ TrenCl]Cl.....	9
Figure S6 – Effects of addition of (a, b) acetate, (c, d) lactate and (e, f) citrate to [CoMe ₆ TrenCl]Cl.....	10
Figure S7 - Paramagnetic region of ¹ H NMR spectrum of [CoMe ₆ TrenCl]Cl.....	11
4. References.....	12

1. General experimental details

All reactions were carried out at atmospheric pressure under nitrogen, unless otherwise stated. All manipulations were performed by using conventional Schlenk techniques.

Instrumentation

^1H NMR spectra were recorded at 300 K at a frequency of 300.17 MHz or 400.19 MHz, and ^{19}F NMR spectra were recorded at 300K at a frequency of 376.46 MHz by means of a Bruker DPX 400 instrument. For paramagnetic ^1H NMR, an acquisition time of 25.5 ms and delay time of 5 ms were employed, with between 176 and 80000 scans collected, corresponding to between 10 sec and 75 min total acquisition time. For paramagnetic ^{19}F NMR, an acquisition time of 0.734 sec and delay time of 1 sec was employed, with 240 scans, corresponding to 7 min 11 sec total acquisition time. The ^1H NMR and ^{19}F NMR signals are reported as chemical shifts (δ) in ppm. The H_2O peak was used as the internal reference in ^1H NMR spectra.

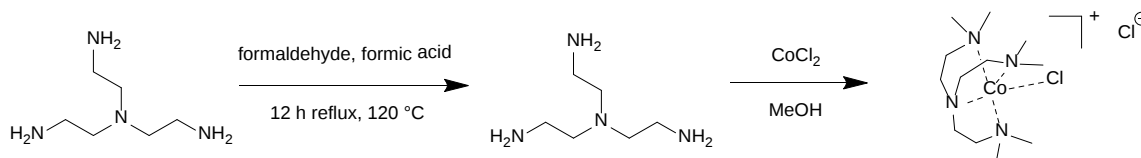
High resolution mass spectra (HRMS) were obtained using a Bruker 7T Apex Qe Fourier Transform Ion Cyclotron Resonance mass spectrometer (FTICR-MS) equipped with an Apollo II ESI/APCI/MALDI dual source. Absorbance measurements were collected using a bench top Perkin Elmer Enspire Multimode Plate Reader.

Calculation of association constants

Association binding constants were calculated using open source python based BindFit.¹ Errors represent the asymptotic error at the 95% confidence interval level.

2. Synthetic methods

CoMe₆TrenCl was synthesised according to a literature procedure, according to Scheme S1.²

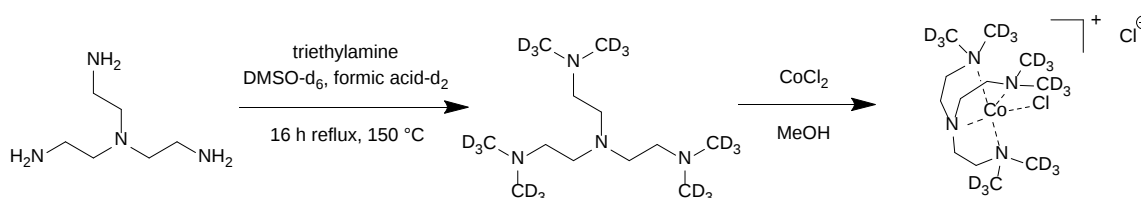


Scheme S1 – Synthesis of [CoMe₆TrenCl]Cl

Synthesis of [Co(d₃-Me)₆TrenCl]Cl

[Co(d₃-Me)₆TrenCl]Cl was prepared by adaptation of a literature procedure.³ Tris(2-aminoethyl)amine (300 μ L, 2 mmol), d₆-DMSO (6 mL, 84 mmol), and triethylamine (5.58 mL, 40 mmol) were combined and stirred in an ice bath. To this mixture, d₂-formic acid (1.51 mL, 40 mmol) was added dropwise, producing an orange colour and was heated to reflux at 150 °C for 16 h to give a yellow solution. Excess d₆-DMSO, triethylamine and formic acid, were removed by distillation, leaving approximately 2 mL of yellow solution. A portion of this solution (0.5 mL) was diluted with dry methanol (5 mL), degassed with nitrogen gas, and anhydrous CoCl₂ (100 mg) (previously dried by heating *in vacuo*) was added in one addition, with the resulting mixture stirred under nitrogen for 1 h. The greenish solution was added dropwise to diethyl ether (30 mL), generating a precipitate that was centrifuged and washed with diethyl ether to give a pinkish precipitate (32 mg) containing [Co(d₃-Me)₆TrenCl]Cl with formate adducts. HRMS (ESI+) *m/z*: [M]⁺ Calculated for C₁₂H₁₂D₁₈ClCoN₄ 342.26153; found 342.26150.

[Co(Me)₆TrenCl]Cl was also synthesised according to the same procedure above for direct comparison, using non-deuterated DMSO and formic acid. HRMS (ESI+) *m/z*: [M]⁺ Calculated for C₁₂H₃₀ClCoN₄ 324.14855; Found 324.14850.



Scheme S2 – Synthesis of [Co(d₃-Me)₆TrenCl]Cl

3. Supplementary figures

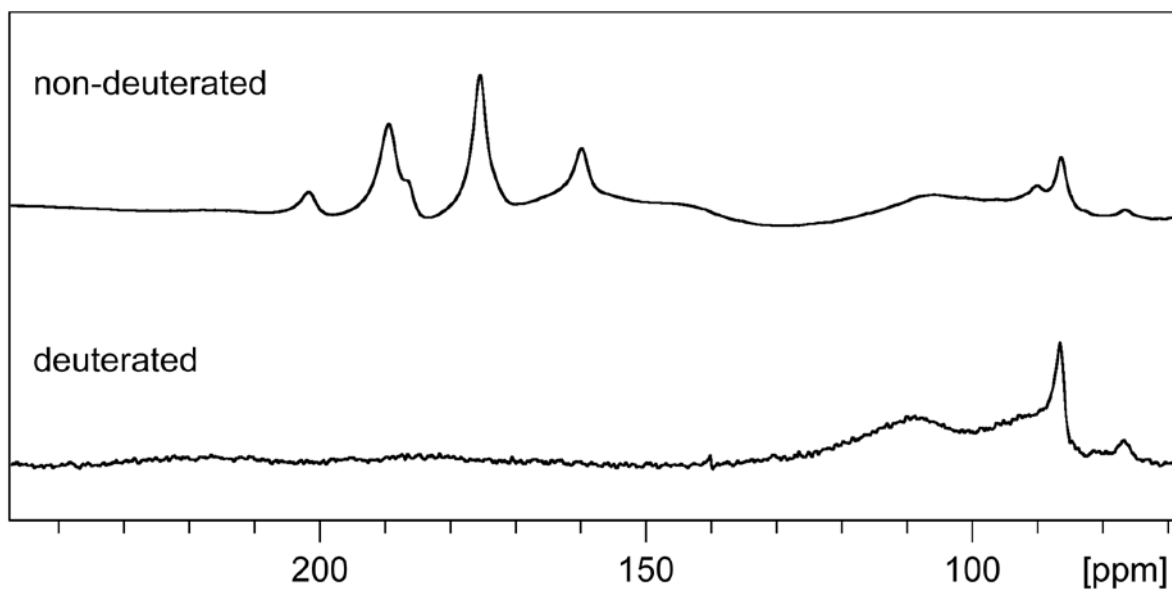


Figure S1 – The paramagnetic region of ^1H NMR (D_2O , 7T) for $[\text{CoMe}_6\text{TrenCl}]\text{Cl}$ (top) and $[\text{Co}(\text{d}_3\text{-Me})_6\text{TrenCl}]\text{Cl}$ (bottom) prepared by the same procedure. Residual formate and triethylamine adducts in both complexes give rise to the additional splitting for the non-deuterated complex, as well as the sharp signal at 87 ppm.

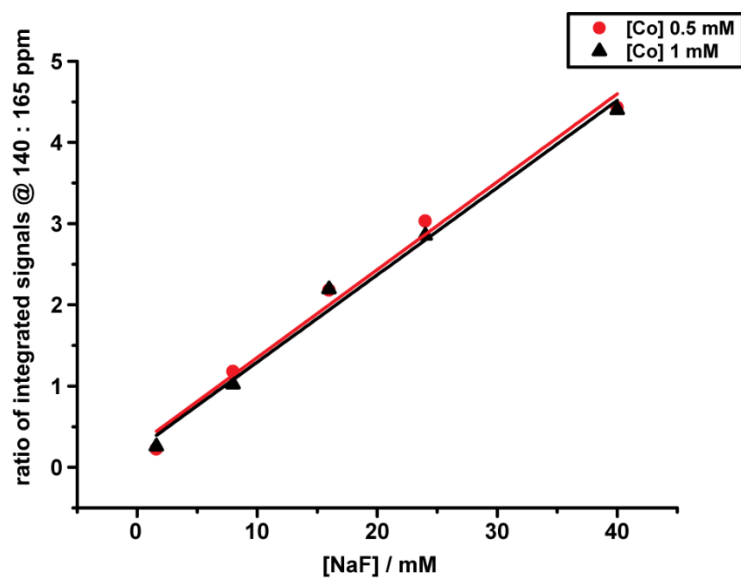


Figure S2 – Changes in the ratio of ^1H peak integrals at 140 and 165 ppm upon the addition of fluoride (1 mM complex, 90:10 $\text{H}_2\text{O}:\text{D}_2\text{O}$ pH 6.5).

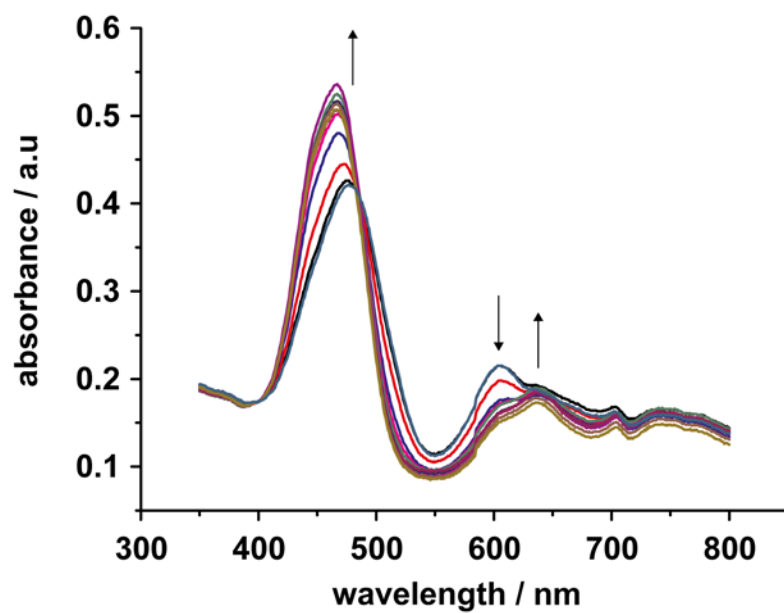


Figure S3 – Absorption spectra of CoMe₆TrenCl (5 mM, 90:10 H₂O:D₂O, pH 6.5) with the addition of NaF (up to 640 mM). NaF addition resulted in an increased absorption at 455 and 635 nm and a concomitant decrease at 605 nm.

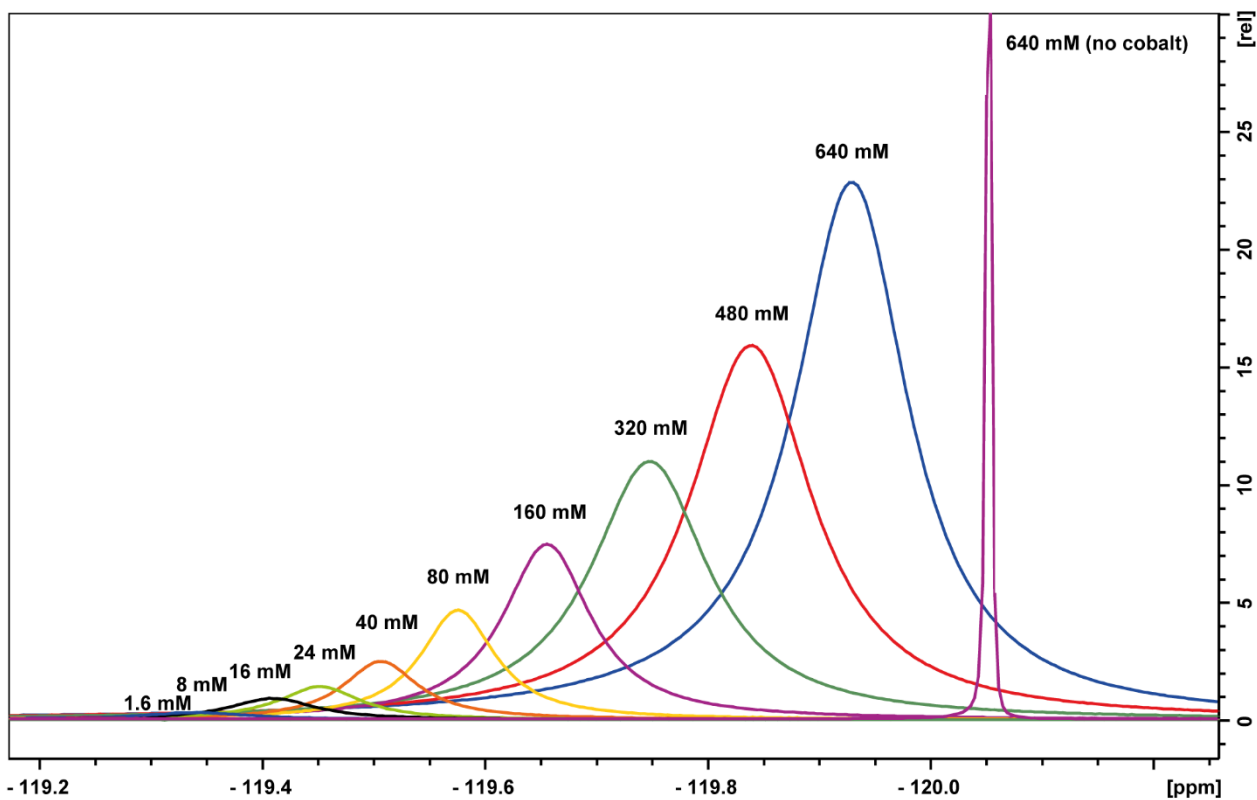


Figure S4 – ^{19}F NMR spectra (9.4 T) of varying concentrations of NaF in the presence of CoMe₆TrenCl (1 mM, 90:10 H₂O:D₂O, pH 6.5). The induced downfield paramagnetic shift was calculated relative to NaF (640 mM) with no CoMe₆TrenCl present (-120.05 ppm).

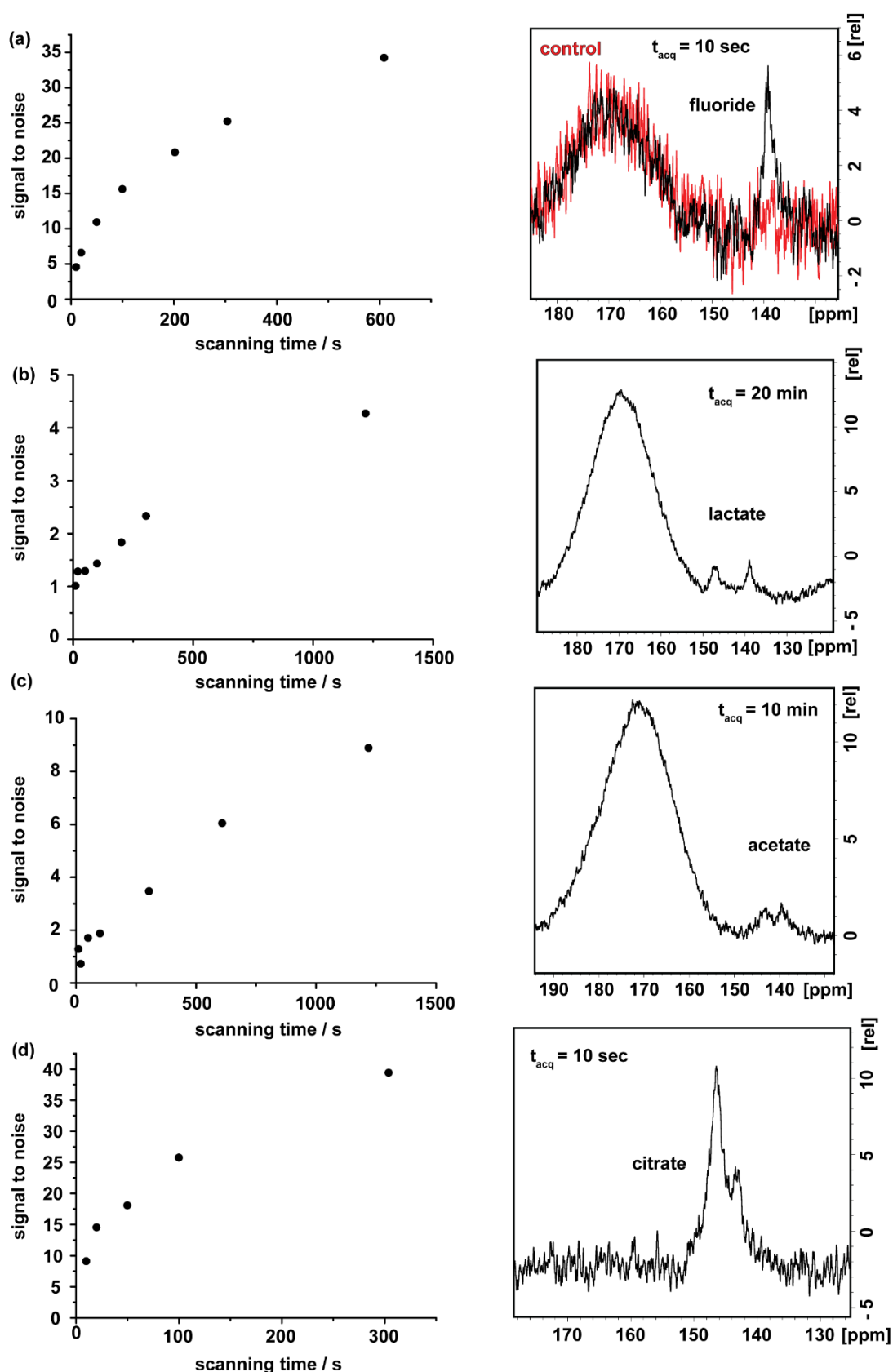


Figure S5 – Signal:noise ratios as a function of acquisition time for the paramagnetic region of ^1H NMR spectra of $[\text{CoMe}_6\text{TrenCl}]\text{Cl}$ (1 mM, 90:10 $\text{H}_2\text{O}:\text{D}_2\text{O}$, pH 6.5) in the presence of 1 mM (a) fluoride, (b) lactate, (c) acetate and (d) citrate. Representative spectra for the lowest total acquisition time required for detection (with signal:noise > 4) are shown, with overlay of control scan with no anions present in (a). Spectra were acquired at 9.4 T with a pre-saturation time of 66 s (1024 scans), acquisition time of 25.5 ms and delay time of 5 ms (945 scans per 60 s).

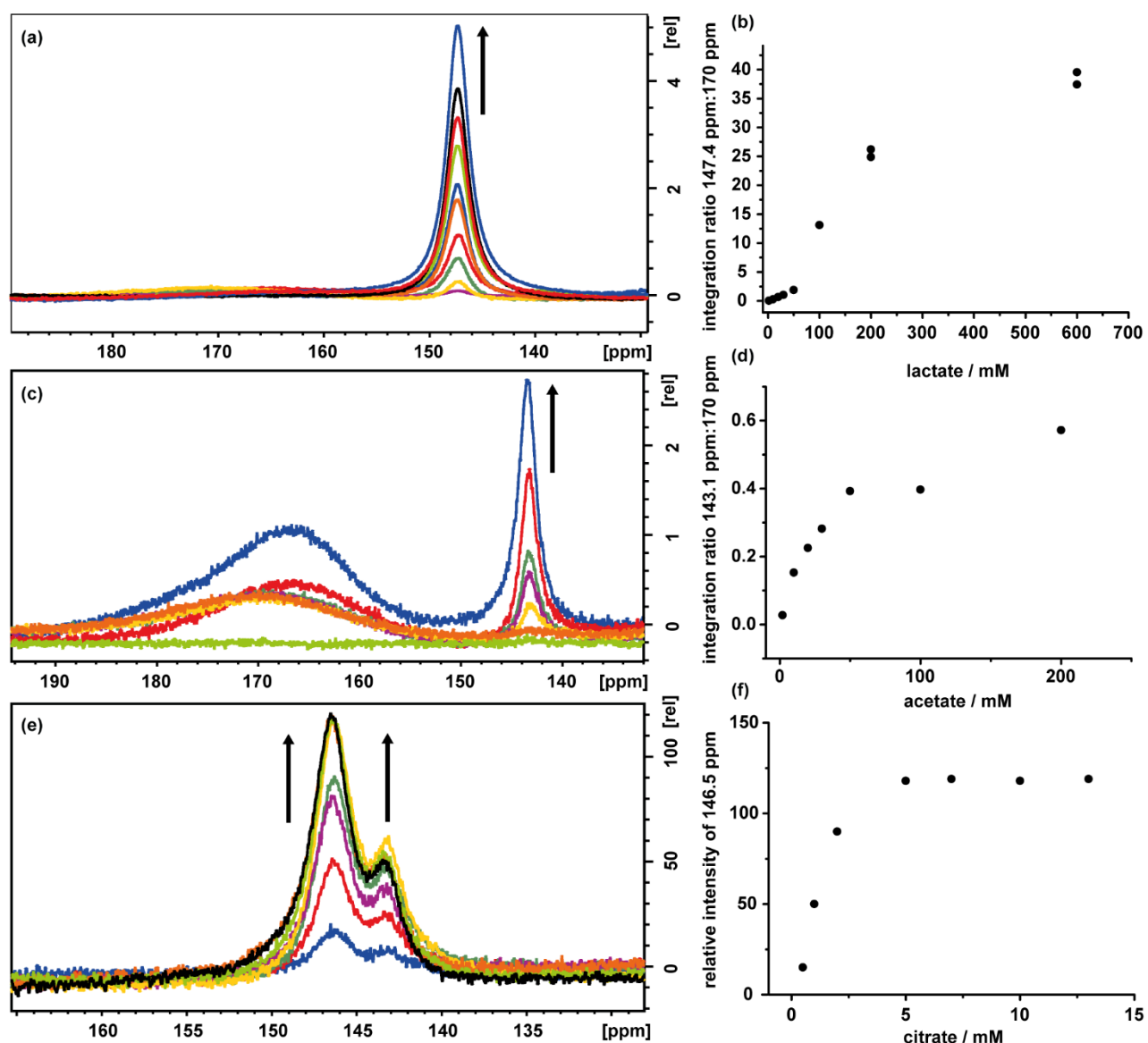


Figure S6 – Effects of addition of (a, b) acetate, (c, d) lactate and (e, f) citrate to [CoMe₆TrenCl]Cl. (a, c, e) paramagnetic region of ¹H NMR (1 mM complex, 90:10 H₂O:D₂O pH 6.5), (b, d) ratios of integrated peaks from paramagnetic NMR, (f) relative intensity of 146.5 ppm peak in paramagnetic NMR.

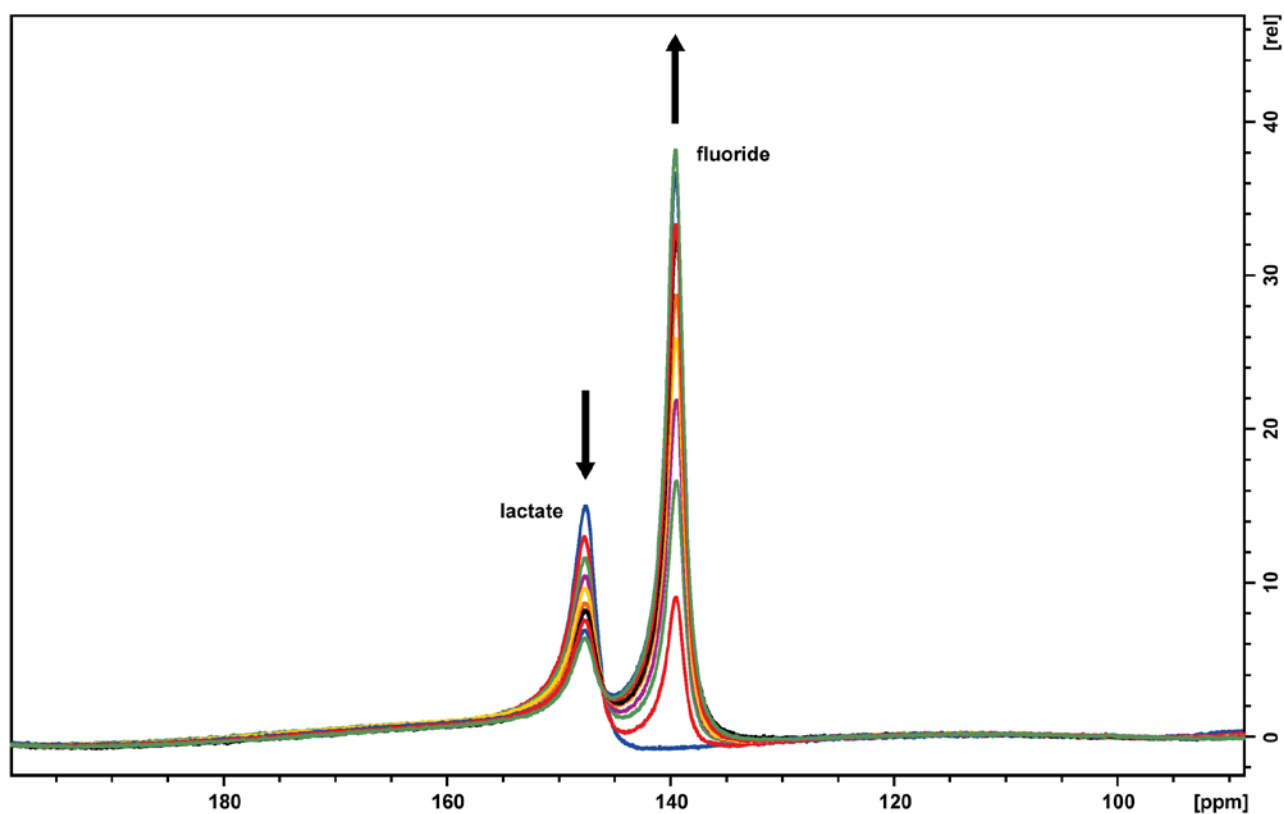


Figure S7 - Paramagnetic region of ^1H NMR spectrum of $[\text{CoMe}_6\text{TrenCl}]\text{Cl}$ (1 mM, 90:10 $\text{H}_2\text{O}:\text{D}_2\text{O}$, pH 6.5) in the presence of lactate (200 mM) and varying concentrations of NaF from 0 up to 200 mM, arrows indicate the decrease and increase of peaks upon increasing concentrations of NaF.

4. References

1. P. Thordarson, *Chemical Society Reviews*, 2011, **40**, 1305-1323.
2. S. Fu, Y. Liu, Y. Ding, X. Du, F. Song, R. Xiang and B. Ma, *Chemical Communications*, 2014, **50**, 2167-2169.
3. X. Jiang, C. Wang, Y. Wei, D. Xue, Z. Liu and J. Xiao, *Chemistry – A European Journal*, 2014, **20**, 58-63.