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

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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

$^1$H 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 $^1$H 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 $^1$H NMR and $^{19}$F NMR signals are reported as chemical shifts (δ) in ppm. The H$_2$O peak was used as the internal reference in $^1$H 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. 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](image)

**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 µL, 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](image)
3. Supplementary figures

Figure S1 – The paramagnetic region of $^1$H NMR ($D_2O, 7T$) for $[CoMe_6TrenCl]Cl$ (top) and $[Co(d_3-Me)_6TrenCl]Cl$ (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 $^1$H peak integrals at 140 and 165 ppm upon the addition of fluoride (1 mM complex, 90:10 H$_2$O:D$_2$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 CoMe$_6$TrenCl (1 mM, 90:10 H$_2$O:D$_2$O, pH 6.5). The induced downfield paramagnetic shift was calculated relative to NaF (640 mM) with no CoMe$_6$TrenCl present (-120.05 ppm).
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 (1 mM, 90:10 H$_2$O:D$_2$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 $^1$H 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 $^1$H NMR spectrum of [CoMe$_6$TrenCl]Cl (1 mM, 90:10 H$_2$O:D$_2$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