Supporting Information for

Reversible magnetogenic cobalt complexes

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 Table 1 Magnetic moments of Co(II) and Co(III) complexes determined by Evans method. *Complexes causing a nondistinguishable chemical shift of *tert*-butanol signal. **treatment with sodium dithionite.

	magnetic moment / B.M.	
complex	Co(III)	reduction**
Co-acacen	diamagnetic*	4.74 ± 0.07
Co-TPA	diamagnetic*	4.27 ± 0.05



Figure S1 Instability of **Co(II)acacen** (100 μ M) after reduction with excess sodium dithionite (10 mM) in 0.15 M NaCl 0.1 M Tris buffer pH 7.4 (a) UV-visible spectra of **Co-acacen** and **acacen** ligand alone; (b) reduction in absorbance at 375 nm consistent with breakdown of **Co(II)acacen** over time.



Figure S2 Paramagnetic region of ¹H-NMR spectra of Co-acacen (6 mM) after reduction by *N*-acetyl cysteine in deoxygenated 10% D_2O in H_2O , 0.15 M NaCl 0.1 M Tris buffer pH 7.4



Figure S3 Magnetic moment of Co(III)acacen (6 mM) in deoxygenated solution in the presence of *N*-acetyl cysteine and sodium dithionite in 10% D_2O in H_2O , 0.15 M NaCl 0.1 M Tris buffer pH 7.4



Figure S4 Cyclic voltammetry of [Co(III)acacen]²⁺ (2 mM) at scan rate of 100 mV in deoxygenated 0.15 M NaCl, 0.1 M Tris buffer, pH 7.4, 300 K. The arrow indicates the start of the cycle with an initial positive scan direction.



Figure S5 Paramagnetic ¹H-NMR shifts of **Co(II)TPA** (6 mM) in aqueous solution, 0.15 M NaCl, 0.1 M Tris buffer, pH 7.4, 300 K generated from **Co(III)TPA** by reduction with excess sodium dithionite (60 mM) under atmospheric conditions (a) and independently-synthesised Co(II)TPACl in deoxygenated solution (b) and after 3 days (c).



Figure S6 Diamagnetic regions of ¹H-NMR spectra of acetylacetone, Co(II)TPA and Co(III)TPA. All spectra were collected with 6 mM analyte concentration in 0.15 M NaCl, 0.1 M Tris buffer, pH 7.4, 300 K, under atmospheric conditions with Co(II)TPA and acetylacetone solution additionally containing excess sodium dithionite reducing agent (60 mM). (*) denotes free acetylacetone, (**) corresponds to coordinated acac.



Figure S7 Magnetic moment upon redox cycling by addition of sodium dithionite (50 mM) to [Co(III)TPAacac]⁺ (5.14 mM) and subsequent exposure to atmospheric conditions, calculated from *tert*-butanol chemical shift from coaxial inner tube standard containing 10% D_2O in H_2O , 0.15 M NaCl 0.1 M Tris buffer pH 7.4 with sodium dithionite (50 mM) and 5% v/v *tert*-butanol measured at 9.4 T and 310K. (*) Denotes diamagnetism as indicated by a negligible chemical shift from coaxial standard (less than 1 Hz). Black bar corresponds to magnetic moment of Co(II)TPACI in the same conditions.



Figure S8 Cyclic voltammetry of [Co(III)TPA(acac)]²⁺ (2 mM) at a scan rate of 100 mV in deoxygenated 0.15 M NaCl, 0.1 M Tris buffer, pH 7.4, 300 K. Arrow indicates the start of the cycle and scan direction.



Figure S9 Plot of peak current versus square root of scan rate for the voltammetric reduction of **Co(III)TPA** (2 mM) in deoxygenated 0.15 M NaCl, 0.1 M Tris buffer, pH 7.4, 300 K.



Figure S10: Cyclic voltammograms for **Co(III)TPA** (2 mM) at various scan rates in deoxygenated 0.15 M NaCl, 0.1 M Tris buffer, pH 7.4, 300 K. The scan rates were: (a) 0.05, (b) 0.10, (c) 0.15, (d) 0.20, (e) 0.30 and (f) 0.40 Vs⁻¹, initial potential (*) with a negative scanning direction.



Figure S11 Dependence of relaxation rate with concentration, measured at 310K at 9.4 T in deoxygenated 10% D_2O in H_2O , 0.15 M NaCl 0.1 M Tris buffer pH 7.4 with excess sodium dithionite (10 equivalents) used as reducing agent. (a) Inverse longitudinal relaxation times of non-reduced **Co(III)TPA** (\bullet); and reduced form **Co(II)TPA** (\bullet). (b) Inverse transverse relaxation times of non-reduced **Co(III)TPA** (\bullet); and reduced form **Co(II)TPA** (\bullet). r_1 and r_2 relaxivity values were determined from the gradient, by linear regression (see Table S2).

Table S2 Relaxivity of $[CoTPA(acac)]^{2+}$ complex in Co(II) and Co(III) oxidation states measured at 310K at 9.4 T in deoxygenated 10% D₂O in H₂O, 0.15 M NaCl 0.1 M Tris buffer pH 7.4 (mean ± error, n = 9). Relaxivity values were calculated by linear regression of $1/T_{1,2}$ experimental values from Figure S2. ^aValues of $[Co(III)TPA(acac)]^{2+}$ are within error of diamagnetic buffer measurement.

Complex	<i>r</i> ¹ relaxivity (mM ⁻¹ s ⁻¹)	<i>r</i> ² relaxivity (mM ⁻¹ s ⁻¹)
Co(III)TPA(acac)	0ª	0 ^a
Co(II)TPA	0.0607 ± 0.0009	0.239 ± 0.034