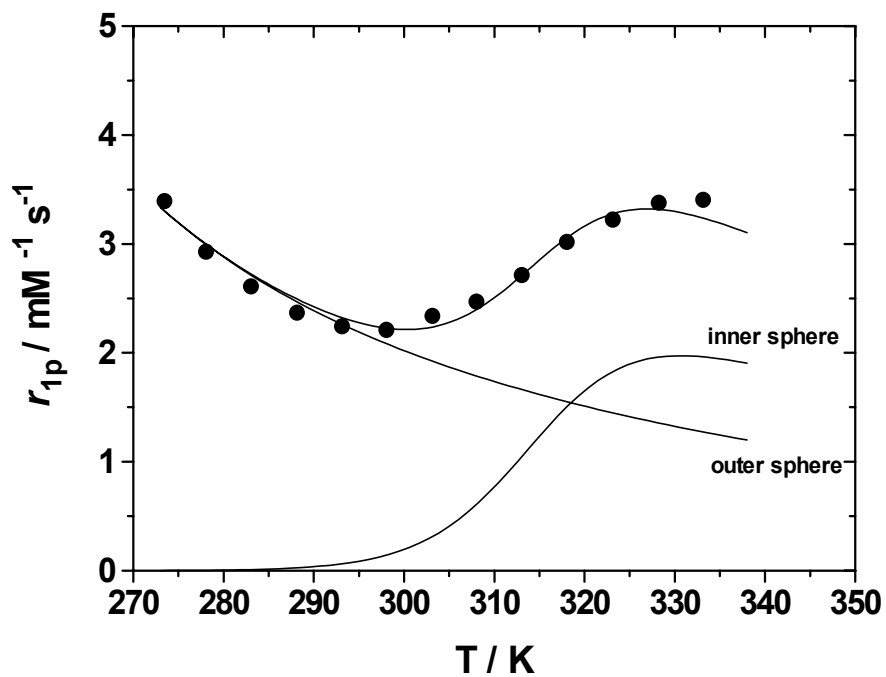


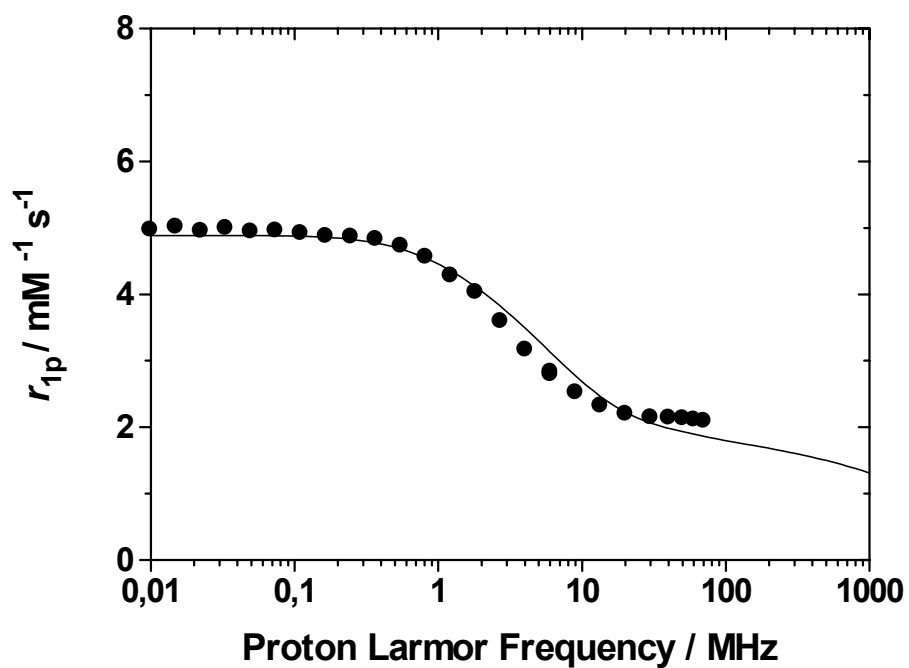
ESI Analyses of the T dependence of the relaxivity and (for selected complexes) the field dependence of the relaxivity for salts of  $[\text{Gd.2}]^{3+}$ .

## Acetate

a) VT  $^1\text{H}$  - 20 MHz

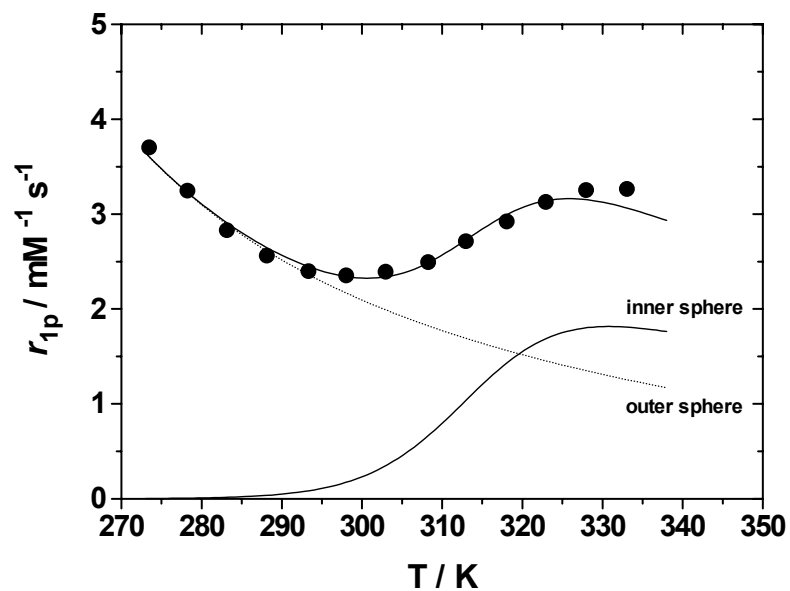


b) NMRD - 25°C, pH 6



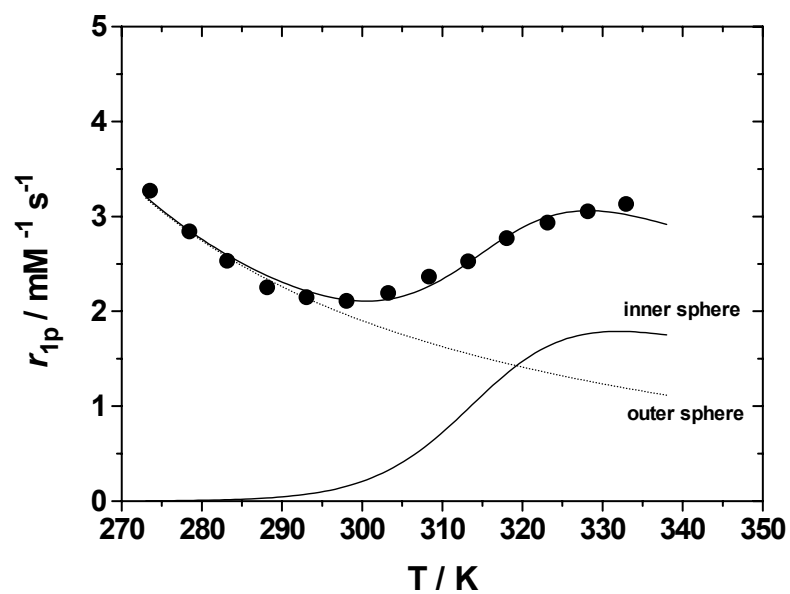
## Nitrate

VT  $^1\text{H}$  - 20 MHz



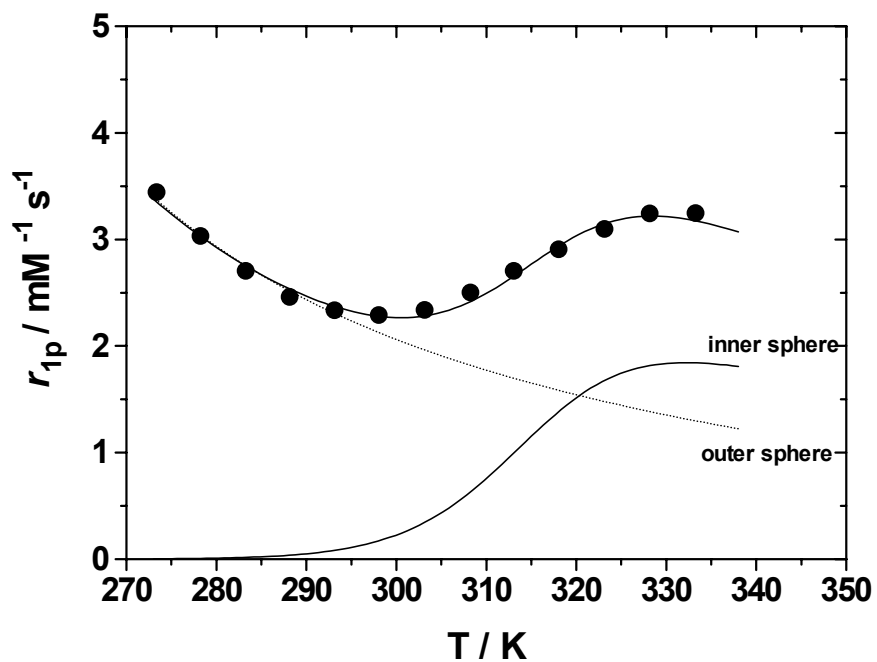
## Triflate

VT  $^1\text{H}$  - 20 MHz

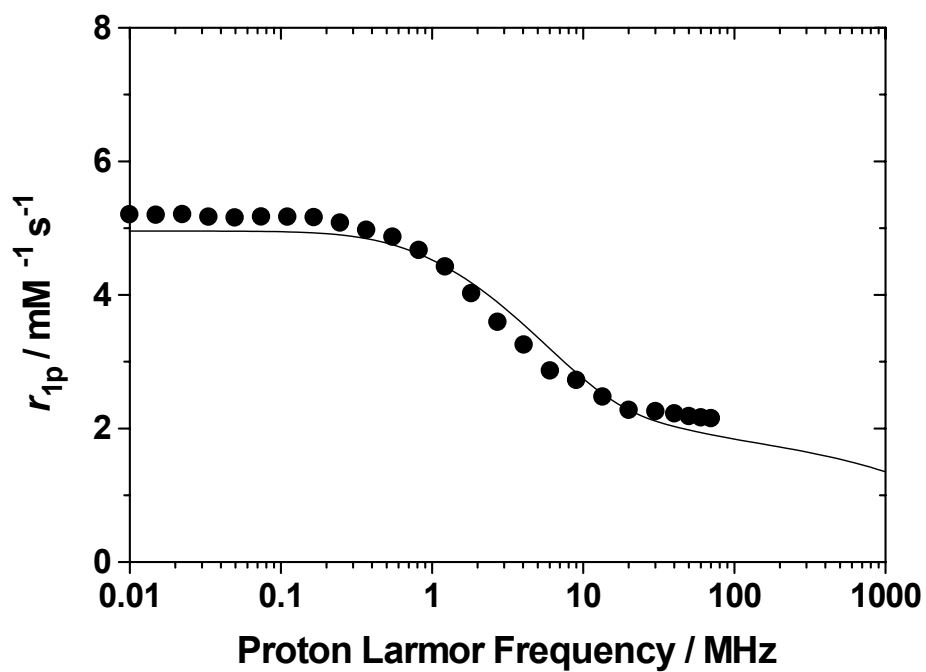


## Chloride

a) VT  $^1\text{H}$  - 20 MHz

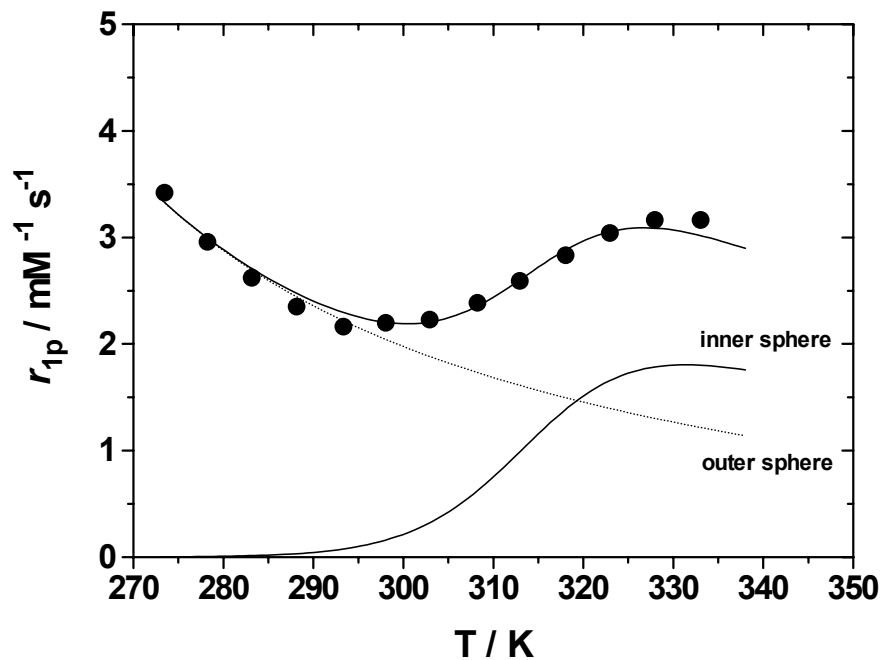


b) NMRD - 25°C, pH 6

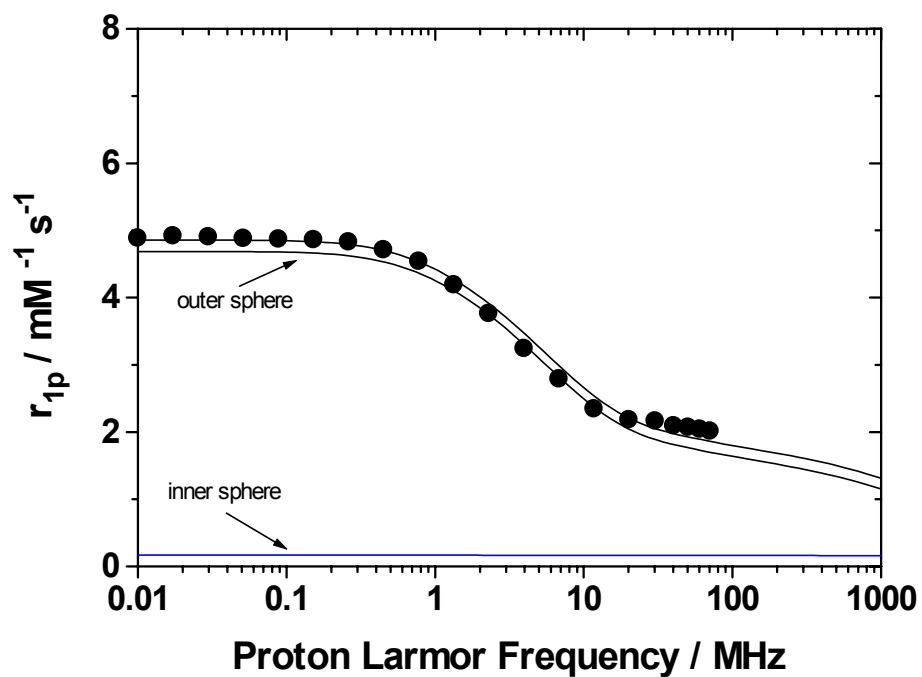


## Bromide

a) VT  $^1\text{H}$  - 20 MHz

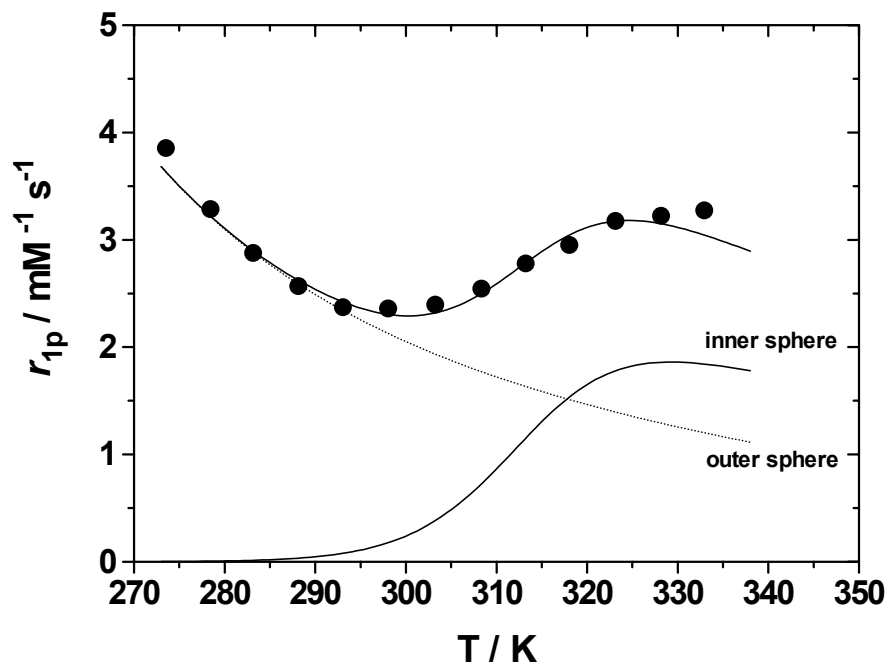


b) NMRD - 25°C, pH 6

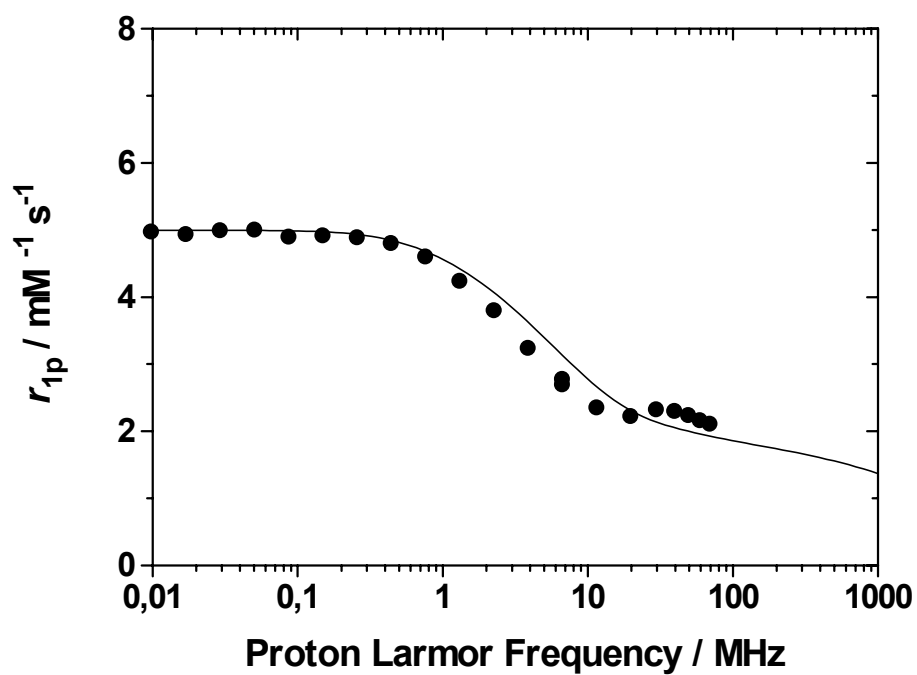


## Iodide

a) VT 1H - 20 MHz



b) NMRD - 25°C, pH 6



**Table:** Relaxation parameters for [Gd.2] salts (298 K)

	Acetate	Nitrate	Triflate	Chloride	Bromide	Iodide
$r_{1p}$ (mM <sup>-1</sup> s <sup>-1</sup> ) <sup>a</sup>	2.20	2.34	2.10	2.28	2.19	2.35
$\Delta^2$ (s <sup>-1</sup> ; $\times 10^{19}$ ) <sup>b</sup>	1.5	1.5	1.5	1.5	1.5	1.5
$\tau_V$ (ps) <sup>b</sup>	8.0	8.0	8.0	8.0	8.0	8.0
$\Delta H_V$ (kJ) <sup>c</sup>	5.0	5.0	5.0	5.0	5.0	5.0
$\tau_R$ (ps)	100	90	98	100	90	103
$\Delta H_R$ (kJ) <sup>b</sup>	14	14	14	14	14	14
$\tau_M$ ( $\mu$ s)	119.6	96.6	95	100	105	101
$\Delta H_M$ (kJ)	122	114	110	106.9	114	117
$q$ <sup>c</sup>	1	1	1	1	1	1
$r$ (Å) <sup>c</sup>	3.0	3.0	3.0	3.0	3.0	3.0
$a$ (Å)	4.25	4.15	4.40	4.22	4.30	4.20
$D$ (cm <sup>2</sup> s <sup>-1</sup> ; $\times 10^{-5}$ ) <sup>c</sup>	2.24	2.24	2.24	2.24	2.24	2.24
$\Delta H_D$ (kJ)	-21	-23	-22	-21	-22	-25

<sup>a</sup> 20 MHz, 298 K; <sup>b</sup> adjusted for bromide and fixed for the other salts; <sup>c</sup> fixed in the fitting procedure

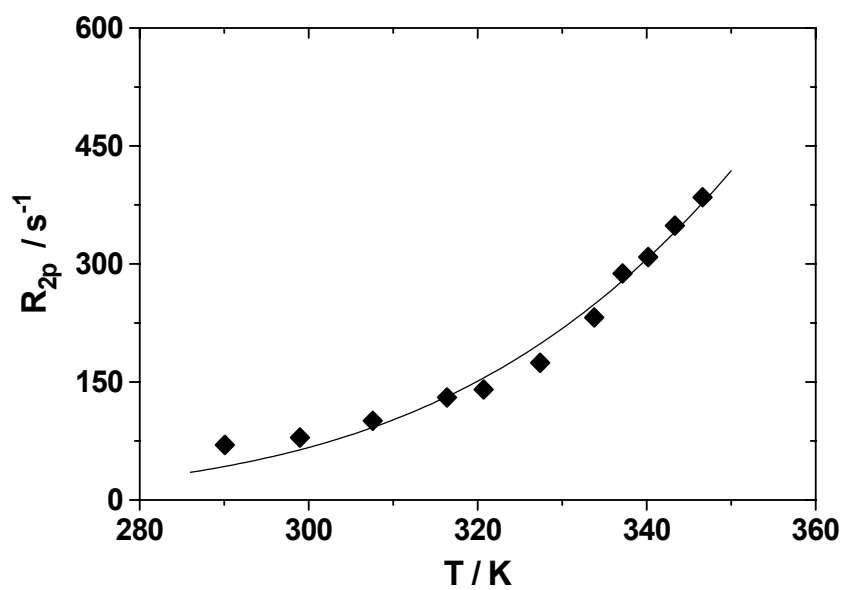


Figure A Variable temperature  $^{17}\text{O}$  NMR measurements of the transverse relaxation rate  $R_{2p}$  for  $[\text{Gd}.1]\text{Cl}_3$  (2.1 T, 47 mM, pH 5.5) showing the fit to the observed data

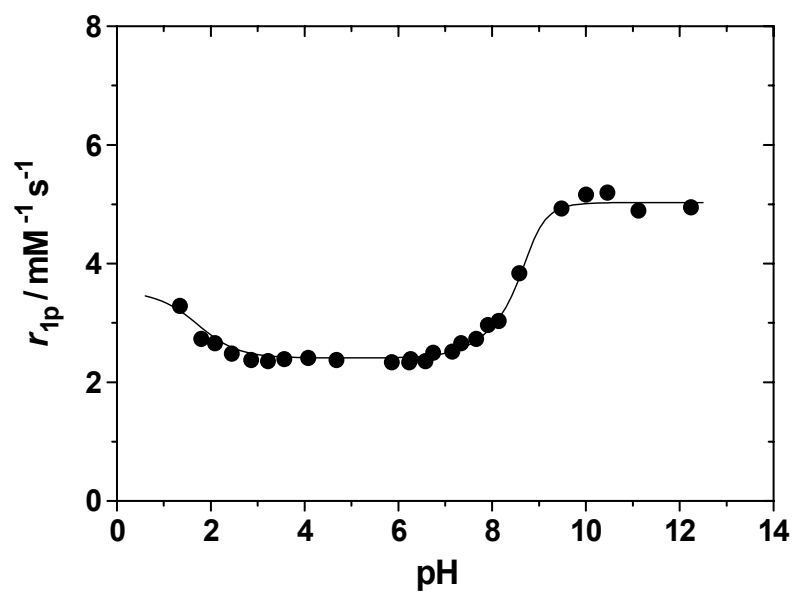


Figure B Variation of the proton relaxivity of  $[\text{Gd.1}]\text{Cl}_3$  with pH (298K, 20MHz), showing the fit to the observed data (ref. 21b for details of the fitting process)