



**Fig. S1** pH dependence of the relaxivity of [Gd.1a]Cl<sub>3</sub> (20 MHz, 298 K) showing the fit to the experimental data: the curve through the experimental data in Figure 1 is the result of the fitting to equation 1 (plus the contribution of the outer sphere term  $r_{1p}^{OS}$ ) which gives the value of  $T_{1M}$ . The value of  $T_{1M}$  thereby derived is in excellent agreement with that obtained from NMRD analysis on the same cationic complex (reference 16). The constant value of  $T_{1M}$  for the complexes with differing anions implies that their structure is very similar and supports the hypothesis that the differences in the  $k_{ex}$  values are due to the nature of the anion.