

**VT  $^{17}\text{O}$  relaxation measurements:** Variable-temperature  $^{17}\text{O}$  NMR data were recorded on JEOL EX-90 (2.1 T) and EX-400 (9.4 T) spectrometers, equipped with a 5 mm probe, by using a  $\text{D}_2\text{O}$  external lock (2.1 T). Experimental settings were: spectral width 10000 Hz,  $90^\circ$  pulse width, acquisition time 10 ms, 1000 scans and no sample spinning. Aqueous solutions of the paramagnetic complexes (pH=5.5-7) containing 2.6% of  $^{17}\text{O}$  isotope (Yeda, Israel) were used. The observed transverse relaxation rates ( $R_2$ ) were calculated from the signal width at half height.

The experimental conditions employed for the gadolinium complexes with different anions are listed in the following table.

Table S1: Composition of the aqueous solutions used in the VT  $^{17}\text{O}$  NMR experiments

Anion	Magnetic field strength (T)	$[\text{Gd}^{3+}]$ (mmol $\text{L}^{-1}$ )	pH
acetate	2.1	58	7.0
bromide	2.1	12	5.5
chloride	2.1	48	5.9
iodide	9.4	9	6.0
nitrate	2.1	28	5.5
sulfate	2.1	37	6.4
triflate	2.1	50	5.5
trifluoroacetate	2.1	47	6.2

The residence lifetime of a water molecule directly coordinated to a paramagnetic metal ion ( $\tau_{\text{M}}^{\text{O}}$ ) may be evaluated by measuring the temperature dependence of the paramagnetic contribution ( $R_{2p}^{\text{O}}$ ) to the observed  $^{17}\text{O}$  water solvent transverse relaxation rate:

$$R_{2p}^{\text{O}} = R_{2\text{obs}}^{\text{O}} - R_{2d}^{\text{O}} \quad (1)$$

where the diamagnetic term  $R_{2d}^O$  is measured on a solution containing a diamagnetic analogue of the chelate of interest.  $R_{2p}^O$  is related to  $\tau_M^O$  through the values of  $\Delta\omega_M^O$  (which is the  $^{17}\text{O}$  chemical shift difference between coordinated and bulk water molecule) and  $R_{2M}^O$  (which is the transverse relaxation rate of the coordinated water oxygen):

$$R_{2p}^O = \frac{qC}{55.6} \tau_M^{O-1} \frac{R_{2M}^O{}^2 + \tau_M^{O-1} R_{2M}^O + \Delta\omega_M^O{}^2}{(R_{2M}^O + \tau_M^{O-1})^2 + \Delta\omega_M^O{}^2} \quad (2)$$

The temperature dependence of  $\Delta\omega_M^O$  is described by the following equation:

$$\Delta\omega_M^O = \frac{g e \mu_B S(S+1) B_0}{3 k_B T} \frac{A}{\hbar} \quad (3)$$

where  $B_0$  is the magnetic field strength (2.11 T in this work) and  $A/\hbar$  is the Gd- $^{17}\text{O}$  scalar coupling constant (whose value was fixed to  $-3.8 \cdot 10^6 \text{ rad s}^{-1}$ , a standard value for polyaminocarboxylate  $\text{Gd}^{3+}$  complexes. For relatively small-sized  $\text{Gd}^{3+}$  chelate  $R_{2M}^O$  is dominated by the electron-nucleus scalar interaction:

$$R_{2M}^O = \frac{1}{3} \left( \frac{A}{\hbar} \right)^2 S(S+1) \left( \tau_{E1} + \frac{\tau_{E2}}{1 + \omega_s^2 \tau_{E2}^2} \right) \quad (4)$$

$$\tau_{Ei}^{-1} = T_{iE}^{-1} + (\tau_M^O)^{-1} \quad (5)$$

For  $\text{Gd}^{3+}$  complexes  $T_{iE}$  are related to the modulation of the zero field splitting (ZFS) of the electronic spin states due to the dynamic distortions of the ligand field interaction and, according to the Blombergen-Morgan theory, their magnetic field dependence is given by the following equations:

$$T_{1E}^{-1} = \frac{1}{25} \Delta^2 \tau_v [4S(S+1) - 3] \left( \frac{1}{1 + \omega_s^2 \tau_v^2} + \frac{4}{1 + 4\omega_s^2 \tau_v^2} \right) \quad (6)$$

$$T_{2E}^{-1} = \frac{1}{50} \Delta^2 \tau_v [4S(S+1) - 3] \left( 3 + \frac{5}{1 + \omega_s^2 \tau_v^2} + \frac{2}{1 + 4\omega_s^2 \tau_v^2} \right) \quad (7)$$

where  $\Delta^2$  is the trace of the square of the transient ZFS tensor and  $\tau_v$  is the correlation time related to its modulation. Finally, the temperature dependence of  $R_{2p}^O$  is expressed in terms of the Eyring relationship for  $\tau_M^O$  and  $\tau_v$  :

$$(\tau_j)_T^{-1} = \frac{(\tau_j^{-1})^{298,15} T}{298.15} \exp\left[\frac{\Delta H_j}{R} \left(\frac{1}{298.15} - \frac{1}{T}\right)\right] \quad (8)$$

where  $j$  refers to the two different dynamic processes involved ( $j = v, M$ ) and  $\Delta H_j$  is the corresponding activation enthalpy.

In the analysis, for all the cationic gadolinium complexes with the different anions the  $q$  value was set to 1 and very similar values were found for the parameters characterizing the electronic relaxation.