

Supporting Information for

Fine-tuning water exchange on Gd^{III} poly(amino carboxylates) by modulation of steric crowding

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Table S1. Variable temperature reduced transverse and longitudinal ¹⁷O relaxation rates and chemical shifts of [Gd(DTTA-Nprop)(H₂O)]²⁻ solution at 9.4T.

Table S2. Variable temperature reduced transverse and longitudinal ¹⁷O relaxation rates and chemical shifts of [Gd(EPTPA-BAA)(H₂O)] solution at 9.4T.

Table S3. Variable temperature reduced transverse and longitudinal ¹⁷O relaxation rates and chemical shifts of [Gd(DO3A-Nprop)(H₂O)] solution at 9.4T.

Table S4. EPR spectral data of [Gd(DTTA-Nprop)(H₂O)]²⁻ at X, Q and W band

Table S5. EPR spectral data of [Gd(EPTPA-BAA)(H₂O)] at X, Q and W band

Table S6. Proton relaxivities (r_1 ; mM⁻¹s⁻¹) of [Gd(DTTA-Nprop)(H₂O)]²⁻

Table S7. Proton relaxivities (r_1 ; mM⁻¹s⁻¹) of [Gd(EPTPA-BAA)(H₂O)]

Figure S1. Temperature dependence of reduced ¹⁷O transverse (●), longitudinal (■) relaxation rates (a), reduced chemical shifts (b) at 9.4 T; proton relaxivities at 5.1°C (▼), 25.0°C (●), 37.1 °C (■) and 49.7 °C (◆) (c); EPR peak-to-peak line widths (d) and the apparent g-factor (e) at 9.4 GHz (●), 35 GHz (■) and 94 GHz (▼-measured, ◆-calculated) for [Gd(EPTPA-BAA)(H₂O)].

Figure S2. Temperature dependence of reduced ¹⁷O transverse (●), longitudinal (■) relaxation rates (a) and reduced chemical shifts (b) at 9.4 T for [Gd(DO3A-Nprop)(H₂O)]

Appendix Equations used to analyse the ¹⁷O NMR, NMRD and EPR data.

Table S1. Variable temperature reduced transverse and longitudinal ^{17}O relaxation rates and chemical shifts of $[\text{Gd}(\text{DTTA-Nprop})(\text{H}_2\text{O})]^{2-}$ solution at 9.4T.

T/K	$1000/T/\text{K}^{-1}$	P_m	$T_1/\text{s}(\text{ref})$	T_1/s	$\ln(1/T_{1r})$	$T_2/\text{s}(\text{ref})$	T_2/s	$\ln(1/T_{2r})$	$\nu_{\text{ref}}/\text{Hz}$	$\nu_{\text{sample}}/\text{Hz}$	$\Delta\omega_r/\text{rad s}^{-1}$
277	3.61	8.12E-04	3.67E-03	3.14E-03	10.95	3.70E-03	7.10E-04	14.15	491.46	387.97	-8.01E+05
288	3.47	8.12E-04	5.47E-03	4.71E-03	10.50	5.53E-03	1.01E-03	13.81	462.27	350.82	-8.63E+05
300	3.33	8.12E-04	7.56E-03	6.62E-03	10.05	7.59E-03	1.46E-03	13.43	544.54	441.04	-8.01E+05
312	3.20	8.12E-04	1.00E-02	8.79E-03	9.76	1.00E-02	1.89E-03	13.18	515.35	414.5	-7.81E+05
324	3.08	8.12E-04	1.28E-02	1.13E-02	9.46	1.28E-02	2.42E-03	12.93	390.63	284.48	-8.22E+05
335	2.99	8.12E-04	1.56E-02	1.39E-02	9.18	1.56E-02	3.04E-03	12.69	364.09	263.25	-7.81E+05
346	2.89	8.12E-04	1.89E-02	1.68E-02	9.04	1.89E-02	4.00E-03	12.40	332.25	236.71	-7.40E+05
358	2.80	8.12E-04	2.25E-02	2.01E-02	8.78	2.24E-02	5.46E-03	12.05	303.06	212.83	-6.98E+05
371	2.70	8.12E-04	2.69E-02	2.42E-02	8.54	2.68E-02	7.85E-03	11.62	257.93	175.67	-6.37E+05

Table S2. Variable temperature reduced transverse and longitudinal ^{17}O relaxation rates and chemical shifts of $[\text{Gd}(\text{EPTPA-BAA})(\text{H}_2\text{O})]$ solution at 9.4T.

T/K	$1000/T/\text{K}^{-1}$	P_m	$T_1/\text{s}(\text{ref})$	T_1/s	$\ln(1/T_{1r})$	$T_2/\text{s}(\text{ref})$	T_2/s	$\ln(1/T_{2r})$	$\nu_{\text{ref}}/\text{Hz}$	$\nu_{\text{sample}}/\text{Hz}$	$\Delta\omega_r/\text{rad s}^{-1}$
277	3.61	6.97E-04	3.67E-03	3.04E-03	11.30	3.70E-03	6.79E-04	14.36	491.46	407.81	-7.54E+05
288	3.47	6.97E-04	5.47E-03	4.65E-03	10.74	5.53E-03	8.64E-04	14.15	462.27	374.69	-7.90E+05
300	3.33	6.97E-04	7.56E-03	6.47E-03	10.38	7.59E-03	1.19E-03	13.83	544.54	449	-8.62E+05
312	3.20	6.97E-04	1.00E-02	8.63E-03	10.05	1.00E-02	1.66E-03	13.49	515.35	422.46	-8.38E+05
324	3.08	6.97E-04	1.28E-02	1.12E-02	9.69	1.28E-02	2.42E-03	13.08	390.63	297.74	-8.38E+05
335	2.99	6.97E-04	1.56E-02	1.38E-02	9.41	1.56E-02	3.47E-03	12.68	364.09	273.86	-8.14E+05
346	2.89	6.97E-04	1.89E-02	1.67E-02	9.21	1.89E-02	5.08E-03	12.24	332.25	247.32	-7.66E+05
358	2.80	6.97E-04	2.25E-02	2.01E-02	8.96	2.24E-02	7.27E-03	11.80	303.06	220.78	-7.42E+05
371	2.70	6.97E-04	2.69E-02	2.40E-02	8.77	2.68E-02	1.06E-02	11.31	257.93	183.63	-6.70E+05

Table S3. Variable temperature reduced transverse and longitudinal ^{17}O relaxation rates and chemical shifts of $[\text{Gd}(\text{DO3A-Nprop})(\text{H}_2\text{O})]^-$ solution at 9.4T.

T/K	$1000/T/\text{K}^{-1}$	P_m	$T_1/\text{s}(\text{ref})$	T_1/s	$\ln(1/T_{1r})$	$T_2/\text{s}(\text{ref})$	T_2/s	$\ln(1/T_{2r})$	$\nu_{\text{ref}}/\text{Hz}$	$\nu_{\text{sample}}/\text{Hz}$	$\Delta\omega_r/\text{rad s}^{-1}$
304	3.28	4.36E-04	8.24E-03	7.49E-03	10.23	8.54E-03	3.13E-03	13.05	454.5	403.2	-7.39E+05
318	3.14	4.36E-04	1.15E-02	1.07E-02	9.63	1.15E-02	4.81E-03	12.53	415.7	364.6	-7.36E+05
333	3.00	4.36E-04	1.50E-02	1.43E-02	8.93	1.53E-02	7.76E-03	11.89	377.0	330	-6.77E+05
362	2.76	4.36E-04	2.38E-02	2.25E-02	8.61	2.38E-02	1.62E-02	10.71	307.3	266.7	-5.85E+05
348	2.87	4.36E-04	2.05E-02	1.92E-02	8.93	1.94E-02	1.15E-02	11.31	341.0	296	-6.48E+05
274	3.65	4.36E-04	3.26E-03	3.01E-03	10.98	3.35E-03	1.17E-03	14.06	535.4	479	-8.12E+05
288	3.47	4.36E-04	5.40E-03	5.03E-03	10.35	5.45E-03	1.46E-03	13.95	492.1	434.25	-8.33E+05

Table S4. EPR spectral data of $[\text{Gd}(\text{DTTA-Nprop})(\text{H}_2\text{O})]^{2-}$ at X, Q and W band

T/K	$1000/T/\text{K}^{-1}$	EPR freq. (GHz)	$\Delta H_{p/p}/\text{G}$	B_0/G
278.15	3.60	9.4365	196.8	3426.2
298.15	3.35	9.4345	171.0	3423.7
309.85	3.23	9.4340	174.0	3418.7
329.45	3.04	9.4336	190.2	3411.2
276.65	3.61	34.1870	54.7	12271.4
298.65	3.35	34.0990	53.8	12250.9
311.95	3.21	34.1860	52.8	12278.3
322.55	3.10	34.1850	51.7	12280.2
286.70	3.49	94.2027	26.9	33798.4

Table S5. EPR spectral data of $[\text{Gd}(\text{EPTPA-BAA})(\text{H}_2\text{O})]$ at X, Q and W band

T/K	$1000/T/\text{K}^{-1}$	EPR freq. (GHz)	$\Delta H_{p/p}/\text{G}$	B_0/G
278.15	3.60	9.4375	404.1	3426.2
298.15	3.35	9.4374	368.0	3418.0
309.85	3.23	9.4357	369.1	3406.3
329.45	3.04	9.4368	394.2	3393.8
276.65	3.61	34.1860	63.6	12284.1
298.65	3.35	34.0950	63.5	12263.6
311.95	3.21	34.1820	64.5	12292.9
322.55	3.10	34.1850	75.2	12292.9
286.70	3.49	94.1913	34.2	33811.1

Table S6. Proton relaxivities (r_1 ; mM⁻¹s⁻¹) of [Gd(DTTA-Nprop)(H₂O)]²⁻

Frequency / MHz	r_1 (mM ⁻¹ s ⁻¹) 278 K	Frequency / MHz	r_1 (mM ⁻¹ s ⁻¹) 298 K	Frequency / MHz	r_1 (mM ⁻¹ s ⁻¹) 310 K	Frequency / MHz	r_1 (mM ⁻¹ s ⁻¹) 323 K
200.0	7.69	200.0	4.78	200.0	3.68	200.0	2.84
100.0	8.32	100.0	4.83	100.0	3.73	100.0	2.87
60.0	8.71	60.0	5.01	60.0	3.81	60.0	2.92
50.0	8.11	50.0	5.05	50.0	3.93	50.0	3.05
40.0	8.57	40.0	5.18	40.0	3.92	40.0	3.12
30.0	8.44	30.0	5.22	30.0	4.04	30.0	3.27
19.9980	8.95	19.9980	5.41	19.9980	4.33	19.9980	3.63
18.0020	8.93	18.0020	5.54	18.0020	4.47	18.0020	3.80
15.9980	9.12	15.9980	5.62	15.9980	4.65	15.9980	3.93
13.9980	9.30	13.9980	5.78	13.9980	4.71	13.9980	4.08
12.0000	9.33	12.0000	6.27	12.0000	4.86	12.0000	4.36
10.0010	9.69	10.0010	6.58	10.0010	5.38	10.0010	4.67
6.9516	10.68	6.9516	7.21	6.9516	6.02	6.9516	5.18
4.8342	11.28	4.8342	7.89	4.8342	6.99	4.8342	5.92
3.3593	12.18	3.3593	8.44	3.3593	7.21	3.3593	6.05
2.3350	12.98	2.3350	8.95	2.3350	7.46	2.3350	6.37
1.6231	13.32	1.6231	9.12	1.6231	7.92	1.6231	6.58
1.1293	13.51	1.1293	9.52	1.1293	7.75	1.1293	6.60
0.7843	13.73	0.7843	9.45	0.7843	8.12	0.7843	6.64
0.5452	13.82	0.5452	9.56	0.5452	8.24	0.5452	6.84
0.3790	14.04	0.3790	9.59	0.3790	8.20	0.3790	6.76
0.2638	13.92	0.2638	9.78	0.2638	8.40	0.2638	6.74
0.1833	13.86	0.1833	9.77	0.1833	8.31	0.1833	6.66
0.1272	14.21	0.1272	9.53	0.1272	8.28	0.1272	6.69
0.0885	13.79	0.0885	9.82	0.0885	8.34	0.0885	6.60
0.0615	13.87	0.0615	9.82	0.0615	8.11	0.0615	6.76
0.0429	14.00	0.0429	9.72	0.0429	8.39	0.0429	6.80
0.0297	13.84	0.0297	9.84	0.0297	8.14	0.0297	6.74
0.0208	13.91	0.0208	9.73	0.0208	8.10	0.0208	6.97
0.0143	13.95	0.0143	9.89	0.0143	8.42	0.0143	6.86
0.0100	14.10	0.0100	9.89	0.0100	8.38	0.0100	6.89

Table S7. Proton relaxivities (r_1 ; $\text{mM}^{-1}\text{s}^{-1}$) of $[\text{Gd}(\text{EPTPA-BAA})(\text{H}_2\text{O})]$

Frequency / MHz	r_1 ($\text{mM}^{-1}\text{s}^{-1}$) 278 K	Frequency / MHz	r_1 ($\text{mM}^{-1}\text{s}^{-1}$) 298 K	Frequency / MHz	r_1 ($\text{mM}^{-1}\text{s}^{-1}$) 310 K	Frequency / MHz	r_1 ($\text{mM}^{-1}\text{s}^{-1}$) 323 K
200.0	10.17	200.0	6.08	200.0	4.59	200.0	3.38
100.0	11.54	100.0	6.20	100.0	4.65	100.0	3.50
60.0	12.15	60.0	6.48	60.0	4.72	60.0	3.57
50.0	11.50	50.0	6.51	50.0	4.79	50.0	3.66
40.0	12.31	40.0	6.67	40.0	4.84	40.0	3.75
30.0	11.86	30.0	6.68	30.0	4.94	30.0	3.86
19.9980	12.11	19.9980	6.65	19.9980	4.91	19.9980	4.09
18.0020	12.08	18.0020	6.68	18.0020	5.08	18.0020	4.16
15.9980	12.19	15.9980	6.85	15.9980	5.12	15.9980	4.24
13.9980	12.28	13.9980	6.88	13.9980	5.42	13.9980	4.42
12.0000	12.51	12.0000	7.16	12.0000	5.57	12.0000	4.64
10.0010	12.65	10.0010	7.34	10.0010	5.81	10.0010	4.97
6.9516	13.04	6.9516	7.66	6.9516	6.26	6.9516	5.74
4.8342	14.59	4.8342	8.54	4.8342	6.82	4.8342	6.42
3.3593	14.77	3.3593	10.08	3.3593	7.04	3.3593	6.81
2.3350	15.38	2.3350	10.52	2.3350	7.28	2.3350	7.29
1.6231	16.85	1.6231	11.42	1.6231	7.99	1.6231	7.71
1.1293	17.57	1.1293	11.64	1.1293	7.57	1.1293	7.78
0.7843	17.67	0.7843	11.98	0.7843	7.92	0.7843	7.91
0.5452	18.01	0.5452	12.02	0.5452	8.04	0.5452	7.89
0.3790	18.43	0.3790	12.05	0.3790	8.00	0.3790	8.07
0.2638	17.97	0.2638	12.04	0.2638	8.20	0.2638	8.04
0.1833	18.32	0.1833	12.33	0.1833	8.11	0.1833	8.02
0.1272	18.25	0.1272	12.25	0.1272	8.08	0.1272	8.12
0.0885	18.37	0.0885	12.15	0.0885	8.14	0.0885	8.10
0.0615	18.34	0.0615	12.11	0.0615	7.92	0.0615	8.01
0.0429	18.24	0.0429	12.16	0.0429	8.18	0.0429	8.19
0.0297	18.04	0.0297	12.23	0.0297	7.94	0.0297	7.99
0.0208	18.27	0.0208	12.12	0.0208	7.91	0.0208	8.21
0.0143	18.17	0.0143	12.11	0.0143	8.22	0.0143	8.08
0.0100	18.01	0.0100	12.19	0.0100	8.18	0.0100	8.06

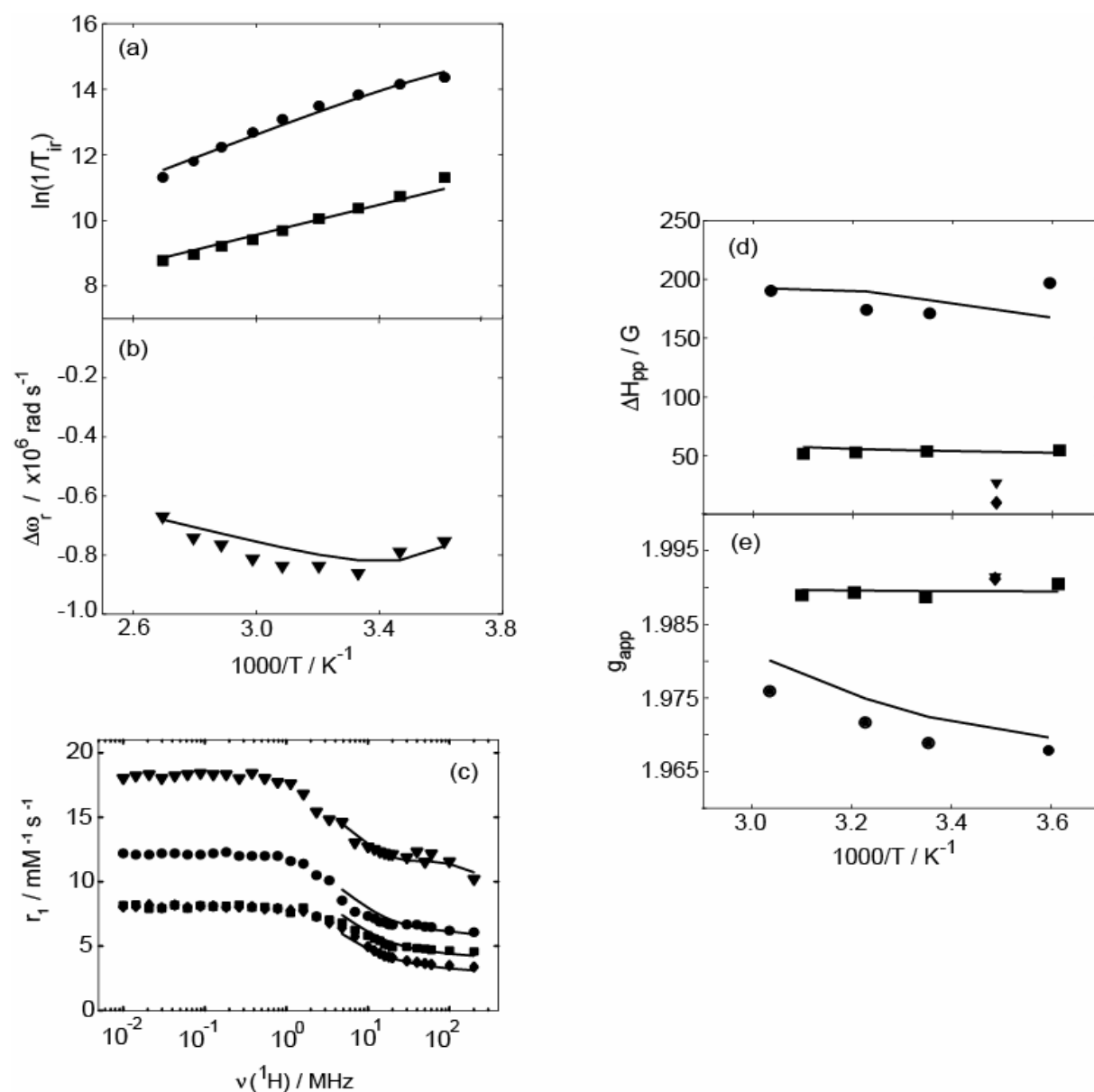


Figure S1. Temperature dependence of reduced ¹⁷O transverse (●), longitudinal (■) relaxation rates (a), reduced chemical shifts (b) at 9.4 T; proton relaxivities at 5.1°C (▼), 25.0°C (●), 37.1 °C (■) and 49.7 °C (◆) (c); EPR peak-to-peak line widths (d) and the apparent g-factor (e) at 9.4 GHz (●), 35 GHz (■) and 94 GHz (▼-measured, ◆-calculated) for [Gd(EPTPA-BAA)(H₂O)].

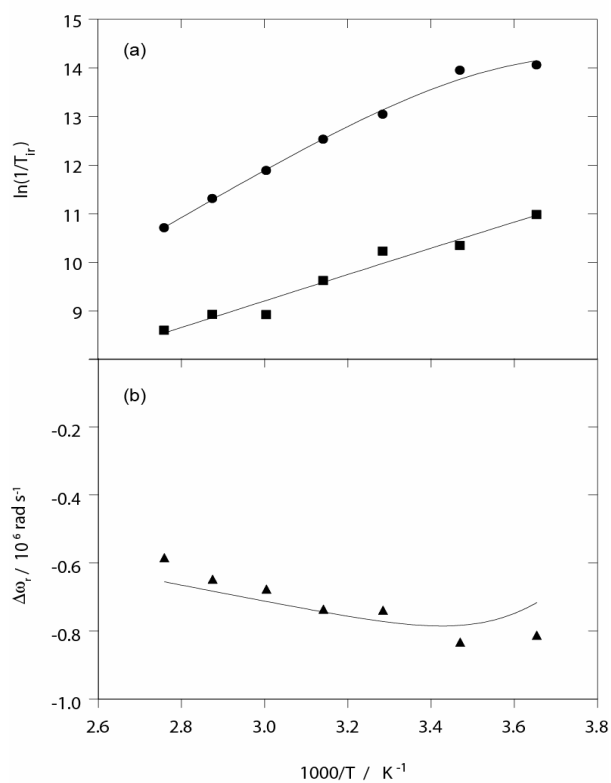


Figure S2. Temperature dependence of reduced ^{17}O transverse (●), longitudinal (■) relaxation rates (a) and reduced chemical shifts (b) at 9.4 T for $[\text{Gd}(\text{DO3A-Nprop})(\text{H}_2\text{O})]$

Appendix

Solomon-Bloembergen-Morgan theory of paramagnetic relaxation enhancement

¹⁷O NMR. From the measured ¹⁷O NMR relaxation rates and angular frequencies of the paramagnetic solutions, $1/T_1$, $1/T_2$ and ω , and of the reference, $1/T_{1A}$, $1/T_{2A}$ and ω_A , one can calculate the reduced relaxation rates and chemical shift, $1/T_{1r}$, $1/T_{2r}$ and ω_r , (Equations (1-3)), where P_m is the molar fraction of bound water, $1/T_{1m}$, $1/T_{2m}$ are the relaxation rates of the bound water and $\Delta\omega_m$ is the chemical shift difference between bound and bulk water.

$$\frac{1}{T_{1r}} = \frac{1}{P_m} \left[\frac{1}{T_1} - \frac{1}{T_{1A}} \right] = \frac{1}{T_{1m} + \tau_m} \quad (1)$$

$$\frac{1}{T_{2r}} = \frac{1}{P_m} \left[\frac{1}{T_2} - \frac{1}{T_{2A}} \right] = \frac{1}{\tau_m} \frac{T_{2m}^{-2} + \tau_m^{-1} T_{2m}^{-1} + \Delta\omega_m^2}{(\tau_m^{-1} + T_{2m}^{-1})^2 + \Delta\omega_m^2} \quad (2)$$

$$\Delta\omega_r = \frac{1}{P_m} (\omega - \omega_A) = \frac{\Delta\omega_m}{(1 + \tau_m T_{2m}^{-1})^2 + \tau_m^2 \Delta\omega_m^2} + \Delta\omega_{os} \quad (3)$$

$\Delta\omega_m$ is determined by the hyperfine or scalar coupling constant, A/\hbar , (Equation (4)), where B represents the magnetic field, S is the electron spin and g_L is the isotropic Landé g factor.

$$\Delta\omega_m = \frac{g_L \mu_B S(S+1) B A}{3k_B T \hbar} \quad (4)$$

The outer sphere contribution to the chemical shift is assumed to be linearly related to $\Delta\omega_m$ by a constant C_{os} (Eq. (5))

$$\Delta\omega_{os} = C_{os} \Delta\omega_m \quad (5)$$

The ¹⁷O longitudinal relaxation rates are given by Equation (6), where γ_S is the electron and γ_I is the nuclear gyromagnetic ratio ($\gamma_S = 1.76 \times 10^{11} \text{ rad s}^{-1} \text{ T}^{-1}$, $\gamma_I = -3.626 \times 10^7 \text{ rad s}^{-1} \text{ T}^{-1}$), r is the effective distance between the electron charge and the ¹⁷O nucleus, I is the nuclear spin (5/2 for ¹⁷O), χ is the quadrupolar coupling constant and η is an asymmetry parameter:

$$\frac{1}{T_{1m}} = \left[\frac{1}{15} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma_I^2 \gamma_S^2}{r_{GdO}^6} S(S+1) \right] \times \left[6\tau_{d1} + 14 \frac{\tau_{d2}}{1 + \omega_S^2 \tau_{d2}^2} \right] + \frac{3\pi^2}{10} \frac{2I+3}{I^2(2I-1)} \chi^2 (1 + \eta^2/3) \tau_{RO} \quad (6)$$

$$\frac{1}{\tau_{di}} = \frac{1}{\tau_m} + \frac{1}{\tau_{RO}} + \frac{1}{T_{ie}} \quad i = 1, 2 \quad (7)$$

The τ_{RO} overall rotational correlation time is assumed to have a simple exponential temperature dependence with an E_R activation energy as follows:

$$\tau_{RO} = \tau_{RO}^{298} \exp\left\{\frac{E_R}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right\} \quad (8)$$

In the transverse relaxation the scalar contribution, $1/T_{2sc}$, is the most important [Eq. (9)]. $1/\tau_{s1}$ is the sum of the exchange rate constant and the electron spin relaxation rate.

$$\frac{1}{T_{2m}} \cong \frac{1}{T_{2sc}} = \frac{S(S+1)}{3} \left(\frac{A}{\hbar}\right)^2 \tau_{s1} \quad (9)$$

$$\frac{1}{\tau_{s1}} = \frac{1}{\tau_m} + \frac{1}{T_{1e}} \quad (10)$$

The inverse binding time (or exchange rate, k_{ex}) of water molecules in the inner sphere is assumed to obey the Eyring equation [Eq. (11)], where ΔS^\ddagger and ΔH^\ddagger are the entropy and enthalpy of activation for the exchange, and k_{ex}^{298} is the exchange rate at 298.15 K.

$$\frac{1}{\tau_m} = k_{ex} = \frac{k_B T}{h} \exp\left\{\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}\right\} = \frac{k_{ex}^{298} T}{298.15} \exp\left\{\frac{\Delta H^\ddagger}{R}\left(\frac{1}{298.15} - \frac{1}{T}\right)\right\} \quad (11)$$

In the fit of ^{17}O NMR data on $[Gd(DO3A-Nprop)(H_2O)]^-$, the electron spin relaxation has been described as in the traditional SBM theory. Here, the electron spin relaxation rates, $1/T_{1e}$ and $1/T_{2e}$ for metal ions in solution with $S > 1/2$ are mainly governed by a transient zero-field-splitting mechanism (ZFS). The ZFS term is expressed by Equations (12) and (13), where Δ^2 is the trace of the square of the transient zero-field-splitting tensor, τ_v is the correlation time for the modulation of the ZFS with the activation energy E_v , and ω_s is the Larmor frequency of the electron spin:

$$\left(\frac{1}{T_{1e}}\right)^{ZFS} = \frac{1}{25} \Delta^2 \tau_v \{4S(S+1) - 3\} \left(\frac{1}{1 + \omega_s^2 \tau_v^2} + \frac{4}{1 + 4\omega_s^2 \tau_v^2}\right) \quad (12)$$

$$\left(\frac{1}{T_{2e}}\right)^{ZFS} = \Delta^2 \tau_v \left[\frac{5.26}{1 + 0.372\omega_s^2 \tau_v^2} + \frac{7.18}{1 + 1.24\omega_s^2 \tau_v^2}\right] \quad (13)$$

$$\tau_v = \tau_v^{298} \exp\left\{\frac{E_v}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right\} \quad (14)$$

In the fit of ^{17}O NMR, EPR and NMRD data on $[\text{Gd}(\text{DTTA-Nprop})(\text{H}_2\text{O})]^{2-}$ and $[\text{Gd}(\text{EPTPA-BBA})(\text{H}_2\text{O})]$, the electron spin relaxation has been described by the Rast-Borel theory. Details of this have been published in Alain Borel, Lothar Helm, André E. Merbach, *Molecular Dynamics of Gd(III) Complexes in Aqueous Solution by HF EPR in Very High Frequency (VHF) ESR/EPR Biological Magnetic Resonance*, Chapter 6, Vol. 22, pp 207-247, Ed. L.J. Berliner, Plenum Press, New York, 2002.

NMRD. The measured proton relaxivities (normalized to 1 mM Gd^{3+} concentration) contain both inner and outer sphere contributions:

$$r_1 = r_{\text{is}} + r_{\text{os}} \quad (15)$$

The inner sphere term is given by Equation (16), where q is the number of inner sphere water molecules.

$$r_{\text{is}} = \frac{1}{1000} \times \frac{q}{55.55} \times \frac{1}{T_{1\text{m}}^{\text{H}} + \tau_{\text{m}}} \quad (16)$$

The longitudinal relaxation rate of inner sphere protons, $1/T_{1\text{m}}^{\text{H}}$ is expressed:

$$\frac{1}{T_{1\text{m}}^{\text{H}}} = \frac{2}{15} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma_{\text{S}}^2 \gamma_{\text{I}}^2}{r_{\text{GdH}}^6} S(S+1) \left[\frac{3\tau_{\text{d1H}}}{1 + \omega_1^2 \tau_{\text{d1H}}^2} + \frac{7\tau_{\text{d2H}}}{1 + \omega_{\text{S}}^2 \tau_{\text{d2H}}^2} \right] \quad (17)$$

Here r_{GdH} is the effective distance between the Gd^{3+} electron spin and the water protons, ω_1 is the proton resonance frequency and τ_{d1H} is given by Equation (18), where τ_{RH} is the rotational correlation time of the Gd^{3+} - H_{water} vector:

$$\frac{1}{\tau_{\text{d1H}}} = \frac{1}{\tau_{\text{m}}} + \frac{1}{\tau_{\text{RH}}} + \frac{1}{T_{\text{ie}}} \quad i = 1, 2 \quad (18)$$

The outer sphere contribution is described by Equation (19), where N_{A} is the Avogadro constant, and J_{os} is a spectral density function.

$$r_{\text{os}} = \frac{32 N_{\text{A}} \pi}{405} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma_{\text{S}}^2 \gamma_{\text{I}}^2}{a_{\text{GdH}} D_{\text{GdH}}} S(S+1) [3J_{\text{os}}(\omega_1, T_{1\text{e}}) + 7J_{\text{os}}(\omega_{\text{S}}, T_{2\text{e}})] \quad (19)$$

$$J_{\text{os}}(\omega, T_{\text{je}}) = \text{Re} \left[\frac{1 + \frac{1}{4} \left(i\omega\tau_{\text{GdH}} + \frac{\tau_{\text{GdH}}}{T_{\text{je}}} \right)^{1/2}}{\left[1 + \left(i\omega\tau_{\text{GdH}} + \frac{\tau_{\text{GdH}}}{T_{\text{je}}} \right)^{1/2} \right]^2 + \frac{4}{9} \left(i\omega\tau_{\text{GdH}} + \frac{\tau_{\text{GdH}}}{T_{\text{je}}} \right) + \frac{1}{9} \left(i\omega\tau_{\text{GdH}} + \frac{\tau_{\text{GdH}}}{T_{\text{je}}} \right)^{3/2}} \right] \quad (20)$$

$j = 1, 2$

For the temperature dependence of the diffusion coefficient for the diffusion of a water proton away from a Gd^{3+} complex, D_{GdH} , we assume an exponential temperature dependence, with an activation energy E_{DGdH} :

$$D_{\text{GdH}} = D_{\text{GdH}}^{298} \exp\left\{\frac{E_{\text{DGdH}}}{R} \left(\frac{1}{T} - \frac{1}{298.15}\right)\right\} \quad (2)$$