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Positively Charged Gd^{III} Cryptates : Slow, Associative Water Exchange

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Equations:

EPR spectroscopy: Electron-spin relaxation of S=7/2 – ions is dominated by zero-field-splitting (ZFS) interaction. In the general case the relaxation is multi-exponential and can therefore not be described by single relaxation rates $1/T_{1e}$ and $1/T_{2e}$. Rast, Fries and Borel developed a description of electronic relaxation of paramagnetic metal ion complexes which takes the static zero field splitting into account [a) S. Rast, A. Borel, L. Helm, E. Belorizky, P. H. Fries, A. E. Merbach, *J. Am. Chem. Soc*. **2001**, *123*, 2637; b) S. Rast, P. H. Fries, E. Belorizky, A. Borel, L. Helm, A. E. Merbach, *J. Chem. Phys.* **2001**, *115*, 7554.]. This description allows calculation of the derivative of the ESR lineshape and therefore its peak-to-peak width ΔH_{pp} which is measured experimentally. The static ZFS has three components for order 2, 4 and 6 and therefore three parameters a_2, a_4, and a_6 have to be adjusted. The dynamic ZFS is described by the a_{2T} parameter.
It has been shown that the longitudinal relaxation of the electron spin can be adequately described by a single relaxation time T_{1e}. To describe the transverse relaxation of the electron spin magnetization four correlation functions with four characteristic times T_{2ek} and different intensities I_k have to be used.

$$g_e(t) = \sum_{k=1}^{4} I_k \exp\{-t/T_{2ek}\}$$

^{17}O NMR spectroscopy: The ^{17}O NMR measurements provide the relaxation rates and angular frequencies of the paramagnetic solutions, $1/T_1$, $1/T_2$ and ω, and of the acidified water reference, $1/T_{1A}$, $1/T_{2A}$ and ω_A. This allows the calculation of the reduced relaxation rates and chemical shift, $1/T_{1r}$, $1/T_{2r}$ and $\Delta\omega_r$.
The parameters $1/T_{1m}$ and $1/T_{2m}$ are the relaxation rates of the bound water and $\Delta\omega_m$ is the chemical shift difference between bound and bulk water in absence of exchange. The term τ_m is the mean residence time or the inverse of the water exchange rate, k_{ex}, and P_m is the mole fraction of the bound water.

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

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

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

Outer-sphere contributions to ^{17}O relaxation can in general be neglected for Gd^{3+} complexes. The temperature dependence of the water exchange rate is described by the Eyring equation where $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are the entropy and enthalpy of activation for the water exchange process, and k_{ex}^{298} is the water exchange rate at 298.15 K.

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

The ^{17}O transverse relaxation rates of the bound water, $1/T_{2m}$, are governed by scalar relaxation mechanism $1/T_{2sc}$ with $A/\hbar$ as the scalar coupling constant.

$$\frac{1}{\tau_{1s}} = \frac{1}{\tau_m} + \frac{1}{T_{1e}}; \qquad \frac{1}{\tau_{2sk}} = \frac{1}{\tau_m} + \frac{1}{T_{2ek}};$$

$$\frac{1}{T_{2sc}} = \left(\frac{A}{\hbar}\right)^2 \frac{S(S+1)}{3}\left[\tau_{1s} + \sum_{k=1}^{4} I_k \frac{\tau_{2sk}}{1+\omega^2\tau_{2sk}}\right]$$

The ^{17}O longitudinal relaxation rates of the bound water, $1/T_{1m}$, are the sum of dipolar and quadrupolar (in the approximation developed by Halle) contributions: γ_S and γ_I are the electron and nuclear gyromagnetic ratios, respectively (γ_S=1.76 × 10^{11} rad $s^{-1}T^{-1}$, γ_I=-3.626 × 10^7 rad $s^{-1}T^{-1}$), r_{GdO} is the effective distance between the Gd^{III}-electron spin and the ^{17}O nucleus, I is the nuclear spin (5/2 for ^{17}O), χ is the quadrupolar coupling constant and η is an asymmetry parameter.

$$\frac{1}{T_{1m}} = \frac{1}{T_{1dd}} + \frac{1}{T_{1q}}$$

$$\frac{1}{\tau_{1d}} = \frac{1}{\tau_m} + \frac{1}{\tau_R} + \frac{1}{T_{1e}}; \qquad \frac{1}{\tau_{2d}} = \frac{1}{\tau_m} + \frac{1}{\tau_R} + \frac{1}{T_{2ek}}$$

$$\frac{1}{T_{1dd}} = \frac{2}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2\gamma_I^2\gamma_S^2}{r_{GdO}^6} S(S+1)\left[3J(\omega_I;\tau_{d1}) + 7\sum_{k=1}^{4} I_k J(\omega_S;\tau_{d2k})\right]; \qquad J(\omega,\tau) = \frac{\tau}{1+\omega^2\tau^2}$$

$$\frac{1}{T_{1q}} = \frac{3\pi^2}{10}\frac{2I+3}{I^2(2I-1)}\chi^2\left(1+\eta^2/3\right)\left[0.2J_1(\omega_I) + 0.8J_2(\omega_I)\right]; \qquad J_n(\omega,\tau) = \frac{\tau}{1+n^2\omega^2\tau^2}$$

The chemical shift of the bound water molecule, $\Delta\omega_m$, depends on the hyperfine interaction between the Gd^{III} electron spin and the ^{17}O nucleus and is directly proportional to the scalar coupling constant, $A/\hbar$.

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

The isotopic Landé g factor is equal to 2.0 for Gd^{III}, B represents the magnetic field, and k_B is the Boltzmann constant. The outer-sphere contribution to the ^{17}O chemical shifts is set proportional to $\Delta\omega_m$, with C_{os} is an empirical constant.

$$\Delta\omega_{os} = C_{os}\Delta\omega_m$$

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^{1}H NMRD: The measured longitudinal proton relaxation rate, R_1^{obs}, is the sum of a paramagnetic, R_1^p, and a diamagnetic contribution, R_1^d. r_1 represents the proton relaxivity, normally expressed in $mM^{-1}\ s^{-1}$.

$$R_1^{obs} = R_1^d + R_1^p = R_1^d + r_1\left[Gd^{3+}\right]$$

The term r_1 can be decomposed into inner-sphere and outer-sphere contributions. q is the number of inner sphere water molecules and T_{1m}^H is the relaxation time of water proton directly bound to Gd^{III}.

$$r_1 = r_{1is} + r_{1os}$$

$$r_{1is} = \frac{1}{1000}\frac{q}{55.55}\frac{1}{T_{1m}^H + \tau_m}$$

The longitudinal relaxation rate of the inner-sphere protons, $1/T_{1m}^H$, is governed by dipolar interaction with the electron spin S, where r_{GdH} is the effective distance between the electron charge and the ^{1}H nucleus.

$$\frac{1}{T_{1m}^H} = \frac{2}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2\gamma_I^2\gamma_S^2}{r_{GdH}^6} S(S+1)\left[3J(\omega_I;\tau_{d1}) + 7\sum_{k=1}^{4} I_k J(\omega_S;\tau_{d2k})\right]$$

The outer-sphere contribution is estimated by Freed's model, where N_A is the Avogadro constant, a_{GdH} the closest approach distance of the water proton and the Gd^{III}, D_{GdH} is the mutual diffusion of bulk water and the complex, and τ_{GdH} is the correlation time for translational diffusion such that $\tau_{GdH}=a^2_{Gd}H/D_{GdH}$. The spectral densities, J_{os}, are from Freed's model.

$$r_{1os} = \frac{32N_A\pi}{405}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2\gamma_I^2\gamma_S^2}{a_{GdH}D_{GdH}} S(S+1)\left[3J_{os}(\omega_I;T_{1e}) + 7\sum_{k=1}^{4} I_k J_{os}(\omega_S;T_{2ek})\right]$$

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

The diffusion coefficient, D_{GdH}, is assumed to follow an Arrhenius law, with an activation energy E_{GdH}, and with D_{GdH}^{298} as the diffusion coefficient at 298.15 K.

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

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Tables:

Table S1. Variable temperature reduced transverse and longitudinal ^{17}O relaxation rates and chemical shifts of $[GdL^1(H_2O)_3]^{3+}$ solution at 9.4T.

Table S2. Proton relaxivities (r_1; $mM^{-1}s^{-1}$) of $[GdL^1(H_2O)_3]^{3+}$ solution

Table S3. The transverse electronic relaxation rates of $[GdL^1(H_2O)_3]^{3+}$ at variable temperature and field.

Table S4. Variable temperature reduced transverse and longitudinal ^{17}O relaxation rates and chemical shifts of $[GdL^2(H_2O)_3]^{3+}$ solution at a) 9.4 T and b) 14.1 T.

Table S5. Variable pressure reduced transverse ^{17}O relaxation rates of $[GdL^2(H_2O)_3]^{3+}$ solution at 298 K at 9.4 T.

Table S6. Proton relaxivities (r_1; $mM^{-1}s^{-1}$) of $[GdL^2(H_2O)_3]^{3+}$ solution.

Table S7. The transverse electronic relaxation rates of $[GdL^2(H_2O)_3]^{3+}$ at variable temperature and field.

Figures:

Fig. S1. a) $[GdL^1(H_2O)_3]^{3+}$ temperature dependence of reduced transverse /T_{2r} (○), longitudinal $1/T_{1r}$ (□) ^{17}O relaxation rates and chemical shifts $\Delta\omega_r$ (△) measured at 9.4 T.
b) $[GdL^1(H_2O)_3]^{3+}$ temperature dependence of EPR linewidths at 9.4 GHz (○), 35 GHz (△), 75 GHz (◇) and 225 GHz (□).
c) $[GdL^1(H_2O)_3]^{3+}$ ^1H NMRD profiles at 15°C (□), 25°C (○), 50°C (△) and 63°C (◇).
The lines represent results from the combined data analysis.

Fig. S2. ^1H NMR spectra of $[EuL^2(H_2O)_3]^{3+}$ in D_2O at different temperatures.

Fig. S3. ^1H NMR spectra of $[EuL^2(H_2O)_3]^{3+}$ in D_2O at different pDs.

Fig. S4. For $[Gd(DOTA)(H_2O)]^-$: temperature depence of reduced ^{17}O transverse (a), longitudinal relaxation rates (b) and reduced chemical shifts (c) at 9.4 T, 4.7 T and 1.4 T. Temperature depence of the EPR peak-to-peak line widths (d) and the apparent g-factor (e) at 9.4 GHz, 75 GHz, 150 GHz and 225 GHz. NMRD profiles (f) at 277.2 K, 283.2 K, 291.2 K, 298.2 K, 305.2 K and 312.2 K.

Fig. S5. For $[Gd(DTPA)(H_2O)]^{2-}$: temperature depence of reduced ^{17}O transverse (a), longitudinal relaxation rates (b) and reduced chemical shifts (c) at 9.4 T, 4.7 T and 1.4 T. Temperature depence of the EPR peak-to-peak line widths (d) at 9.4 GHz, 35 GHz and 125 GHz. NMRD profiles (e) at 278.2 K, 298.2 K and 308.2 K.

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Table 1. Variable temperature reduced transverse and longitudinal ^{17}O relaxation rates and chemical shifts of $[GdL^1(H_2O)_3]^{3+}$ solution at 9.4T. (c=0.0127 mol kg^{-1}, pH=3.0)

T/K	1000/T	P_m	$T_1/s(H_2O)$	T_1/s	$\ln(1/T_{1r})$	$T_2/s(H_2O)$	T_2/s	$\ln(1/T_{2r})$	ν_{ref}/Hz	ν_{sample}/Hz	$\Delta\omega_r$/rad s^{-1}
299.2	3.34	6.86E-04	7.31E-03	6.70E-03	9.80	7.42E-03	9.42E-04	14.12	-396.6	-412.5	-1.46E+05
312.2	3.20	6.86E-04	9.68E-03	8.76E-03	9.67	9.75E-03	7.77E-04	14.36	-423.1	-455.0	-2.92E+05
336.2	2.97	6.86E-04	1.51E-02	1.37E-02	9.17	1.58E-02	7.89E-04	14.38	-486.8	-545.0	-5.33E+05
299.3	3.34	6.86E-04	7.31E-03	6.66E-03	9.87	7.42E-03	9.31E-04	14.13	-396.6	-412.5	-1.46E+05
288.2	3.47	6.86E-04	5.53E-03	5.14E-03	9.91	5.60E-03	1.21E-03	13.76	-375.6	-383.8	-7.73E+04
276.8	3.61	6.86E-04	3.97E-03	3.64E-03	10.4	3.91E-03	1.56E-03	13.24	-338.2	-343.5	-4.85E+04
323.5	3.09	6.86E-04	1.22E-02	1.12E-02	9.25	1.27E-02	7.30E-04	14.45	-449.7	-502.7	-4.86E+05
347.9	2.87	6.86E-04	1.81E-02	1.71E-02	8.51	1.86E-02	9.18E-04	14.23	-505.23	-576.7	-6.54E+05
299.3	3.34	6.86E-04	7.31E-03	6.70E-03	9.82	7.40E-03	9.56E-04	14.10	-390.9	-401.5	-9.70E+04
359.7	2.78	6.86E-04	2.17E-02	2.03E-02	8.43	2.23E-02	1.08E-03	14.07	-544.6	-616.0	-6.54E+05

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Table 2. Proton relaxivities (r_1; $mM^{-1}s^{-1}$) of $[GdL^1(H_2O)_3]^{3+}$ solution

ν /MHz	B / T	15 °C	25 °C	37 °C	50 °C	63 °C	75 °C
20.00	0.470	12.60	9.79	7.95	6.02	5.53	4.85
16.00	0.376	12.81	10.09	8.19	6.23	5.61	4.92
12.00	0.282	13.09	10.60	8.61	7.18	6.26	5.54
9.998	0.235	13.29	11.18	8.98	7.84	6.41	5.77
5.999	0.141	14.42	12.89	10.99	9.30	7.95	7.11
3.598	0.08456	15.71	15.45	12.68	11.08	9.20	8.06
2.159	0.05074	17.15	16.55	14.09	12.12	10.15	8.97
1.296	0.03046	18.50	18.19	15.42	12.54	10.58	9.26
0.7781	0.01829	19.24	18.37	15.74	13.08	10.93	9.68
0.4669	0.01097	20.07	18.46	15.84	13.29	10.85	9.53
0.2800	0.006580	20.08	18.68	16.17	13.19	11.29	9.58
0.1680	0.003948	19.28	18.37	15.83	12.97	10.95	9.62
0.1008	0.002369	19.96	18.44	16.10	12.99	10.93	9.63
0.0605	0.001422	19.88	18.72	16.08	12.92	11.08	9.73
0.0362	0.0008507	19.21	18.59	15.78	13.01	11.18	9.73
0.0217	0.0005099	19.70	18.69	15.95	13.20	11.24	9.87

Table 3. The transverse electronic relaxation rates of $[GdL^1(H_2O)_3]^{3+}$ at variable temperature and field. (c=0.008 mol kg^{-1})

B/T	T/K	1000/T	W/Gauss	$\Delta H_{p/p}$ /Gauss	$1/T_{2e}$	$\ln(1/T_{2e})$
0.34	277.00	3.61	204.40	236.0	3.75E+09	22.04
0.34	298.00	3.36	207.80	239.9	3.81E+09	22.06
0.34	316.00	3.16	193.10	223.0	3.54E+09	21.99
0.34	336.00	2.98	178.40	206.0	3.27E+09	21.91
0.34	358.00	2.79	170.61	197.0	3.13E+09	21.86
1.28	277.00	3.61	51.44	59.4	9.43E+08	20.66
1.28	298.00	3.36	67.44	77.9	1.24E+09	20.94
1.28	316.00	3.16	70.02	80.9	1.28E+09	20.97
1.28	336.00	2.98	76.45	88.3	1.40E+09	21.06
1.28	358.00	2.79	80.85	93.4	1.48E+09	21.12
2.71	277.00	3.61	22.06	25.5	4.04E+08	19.82
2.71	298.00	3.36	25.02	28.9	4.59E+08	19.94
2.71	316.00	3.16	31.02	35.8	5.69E+08	20.16
2.71	336.00	2.98	34.43	39.8	6.31E+08	20.26
2.71	358.00	2.79	39.65	45.8	7.27E+08	20.40
8.12	277.00	3.61	10.25	11.8	1.88E+08	19.05
8.12	298.00	3.36	11.11	12.8	2.04E+08	19.13
8.12	316.00	3.16	12.88	14.9	2.36E+08	19.28
8.12	336.00	2.98	14.11	16.3	2.59E+08	19.37
8.12	358.00	2.79	15.83	18.3	2.90E+08	19.49

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Table 4a. Variable temperature reduced transverse and longitudinal ^{17}O relaxation rates and chemical shifts of $[GdL^2(H_2O)_3]^{3+}$ solution at 9.4 T. (c=0.010 mol kg^{-1}, pH=2.5)

T/K	1000/T	P_m	$T_1/s(H_2O)$	T_1/s	$\ln(1/T_{1r})$	$T_2/s(H_2O)$	T_2/s	$\ln(1/T_{2r})$	ν_{ref}/Hz	ν_{sample}/Hz	$\Delta\omega_r$/rad s^{-1}
299.20	3.34	5.40E-04	7.31E-03	6.59E-03	10.2	7.42E-03	1.88E-03	13.51	-396.6	-412.5	-1.85E+05
312.15	3.20	5.40E-04	9.68E-03	8.91E-03	9.71	9.75E-03	1.46E-03	13.89	-423.1	-444.35	-2.47E+05
336.15	2.97	5.40E-04	1.51E-02	1.37E-02	9.41	1.58E-02	1.04E-03	14.33	-486.8	-523.0	-4.21E+05
299.30	3.34	5.40E-04	7.31E-03	6.69E-03	10.1	7.42E-03	1.85E-03	13.53	-396.6	-407.2	-1.23E+05
288.15	3.47	5.40E-04	5.53E-03	5.11E-03	10.2	5.60E-03	2.33E-03	13.05	-375.3	-386.0	-1.24E+05
275.75	3.63	5.40E-04	3.97E-03	3.75E-03	10.2	3.91E-03	2.45E-03	12.55	-338.2	-343.5	-6.17E+04
323.45	3.09	5.40E-04	1.22E-02	1.11E-02	9.59	1.27E-02	1.19E-03	14.16	-449.6	-476.0	-3.06E+05
347.85	2.87	5.40E-04	1.81E-02	1.70E-02	8.78	1.86E-02	1.07E-03	14.31	-505.2	-551.7	-5.40E+05
299.30	3.34	5.40E-04	7.31E-03	6.76E-03	9.94	7.40E-03	1.93E-03	13.47	-390.9	-406.9	-1.86E+05
359.65	2.78	5.40E-04	2.17E-02	2.02E-02	8.72	2.23E-02	1.12E-03	14.26	-544.5	-601.4	-6.61E+05

Table 4b. Variable temperature reduced transverse and longitudinal ^{17}O relaxation rates and chemical shifts of $[GdL^2(H_2O)_3]^{3+}$ solution at 14.1 T. (c=0.0074 mol kg^{-1}, pH=2.6)

T/K	1000/T	P_m	$T_1/s(H_2O)$	T_1/s	$\ln(1/T_{1r})$	$T_2/s(H_2O)$	T_2/s	$\ln(1/T_{2r})$	ν_{ref}/Hz	ν_{sample}/Hz	$\Delta\omega_r$/rad s^{-1}
298.0	3.36	4.00E-04	7.14E-03	6.71E-03	10.0	7.10E-03	2.40E-03	13.44	-2066.5	-2075.5	-1.41E+05
322.1	3.11	4.00E-04	1.26E-02	1.19E-02	9.39	1.24E-02	1.42E-03	14.26	-2162.9	-2183.7	-3.26E+05
286.3	3.49	4.00E-04	5.08E-03	4.73E-03	10.5	5.07E-03	2.79E-03	12.91	-2021.5	-2029.9	-1.33E+05
276.0	3.62	4.00E-04	3.66E-03	3.43E-03	10.7	3.77E-03	2.62E-03	12.59	-1986.2	-1993.0	-1.07E+05
347.8	2.88	4.00E-04	1.98E-02	1.86E-02	9.01	1.95E-02	1.23E-03	14.46	-2263.3	-2307.6	-6.97E+05
310.3	3.22	4.00E-04	9.61E-03	9.04E-03	9.71	9.46E-03	1.80E-03	13.93	-2112.6	-2123.3	-1.67E+05
368.7	2.71	4.00E-04	2.55E-02	2.42E-02	8.60	2.52E-02	1.53E-03	14.24	-2331.5	-2389.0	-9.04E+05
357.8	2.80	4.00E-04	2.21E-02	2.10E-02	8.73	2.18E-02	1.31E-03	14.40	-2290.1	-2343.0	-8.31E+05
335.8	2.98	4.00E-04	1.61E-02	1.52E-02	9.13	1.60E-02	1.23E-03	14.45	-2211.8	-2246.0	-5.37E+05

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Table 5. Variable pressure reduced transverse ^{17}O relaxation rates of $[GdL^2(H_2O)_3]^{3+}$ solution at 298 K at 9.4 T (c=0.00778 mol kg^{-1}, pH=2.5)

P/Mpa	P_m	T_2/s(H2O)	T_2/s	$\ln(1/T_{2r})$
0.1	4.20E-04	7.42E-03	2.38E-03	13.43
24.5	4.20E-04	7.42E-03	2.33E-03	13.46
50.0	4.20E-04	7.42E-03	2.28E-03	13.49
100.3	4.20E-04	7.42E-03	2.18E-03	13.55
148.0	4.20E-04	7.42E-03	2.14E-03	13.58
193.0	4.20E-04	7.42E-03	2.08E-03	13.62
168.8	4.20E-04	7.42E-03	2.13E-03	13.59
125.0	4.20E-04	7.42E-03	2.18E-03	13.56
75.9	4.20E-04	7.42E-03	2.25E-03	13.51

Table 6. Proton relaxivities (r_1; $mM^{-1}s^{-1}$) of $[GdL^2(H_2O)_3]^{3+}$ solution.

ν /MHz	B / T	15 °C	25 °C	37 °C	50 °C	63 °C	75 °C
200.1	4.70	12.11	11.20	9.73	7.43	5.87	4.74
60.00	1.410	13.43	11.56	9.80	8.01	6.20	5.47
20.00	0.470	12.38	11.18	9.55	7.65	6.42	5.54
16.00	0.376	12.58	11.53	9.62	8.18	6.98	6.02
12.00	0.282	12.25	11.72	10.52	8.56	7.32	6.51
9.998	0.235	12.65	12.13	10.76	9.11	7.81	7.03
5.999	0.141	13.95	13.60	12.38	10.22	8.90	9.02
3.598	0.08456	14.76	15.50	13.20	12.30	10.66	9.89
2.159	0.05074	15.47	16.53	15.85	13.92	11.42	10.70
1.296	0.03046	16.81	17.48	16.81	14.62	11.97	10.96
0.7781	0.01829	16.96	17.56	17.23	14.74	12.49	11.30
0.4669	0.01097	16.79	17.89	17.27	14.84	12.88	11.39
0.28	0.006580	16.84	17.93	16.21	14.80	12.87	11.35
0.168	0.003948	16.57	17.91	17.01	15.04	12.37	11.49
0.1008	0.002369	16.95	18.07	16.43	15.18	12.50	11.39
0.0605	0.001422	16.51	18.13	16.96	15.28	12.23	11.64
0.0362	0.0008507	16.84	18.23	17.24	15.08	12.55	11.49
0.0217	0.0005099	16.81	18.09	17.53	15.36	12.58	11.35

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Table 7. The transverse electronic relaxation rates of $[GdL^2(H_2O)_3]^{3+}$ at variable temperature and field. (c=0.010 mol kg^{-1})

B/T	T/K	1000/T	W/Gauss	$\Delta H_{p/p}$ /Gauss	1/T2e	ln(1/T2e)
0.34	277.00	3.61	256.30	295.9	4.70E+09	22.27
0.34	298.00	3.36	245.10	283.0	4.49E+09	22.23
0.34	316.00	3.16	233.80	270.0	4.29E+09	22.18
0.34	336.00	2.98	219.10	253.0	4.02E+09	22.11
0.34	358.00	2.79	200.00	230.9	3.67E+09	22.02
1.28	277.00	3.61	48.32	55.8	8.86E+08	20.60
1.28	298.00	3.36	62.38	72.0	1.14E+09	20.86
1.28	316.00	3.16	81.93	94.6	1.50E+09	21.13
1.28	336.00	2.98	85.14	98.3	1.56E+09	21.17
1.28	358.00	2.79	92.50	106.8	1.70E+09	21.25
2.71	277.00	3.61	20.17	23.3	3.70E+08	19.73
2.71	298.00	3.36	25.53	29.5	4.68E+08	19.96
2.71	316.00	3.16	27.84	32.1	5.10E+08	20.05
2.71	336.00	2.98	35.91	41.5	6.58E+08	20.31
2.71	358.00	2.79	36.07	41.7	6.61E+08	20.31
8.12	277.00	3.61	8.69	10.0	1.59E+08	18.89
8.12	298.00	3.36	11.09	12.8	2.03E+08	19.13
8.12	316.00	3.16	11.48	13.3	2.11E+08	19.17
8.12	336.00	2.98	13.32	15.4	2.44E+08	19.31
8.12	358.00	2.79	14.23	16.4	2.61E+08	19.38

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Fig. S1. top) $[GdL^1(H_2O)_3]^{3+}$ temperature dependence of reduced transverse $/T_{2r}$ (○), longitudinal $1/T_{1r}$ (□) ^{17}O relaxation rates and chemical shifts $\Delta\omega_r$ (△) measured at 9.4 T.
middle) $[GdL^1(H_2O)_3]^{3+}$ temperature dependence of EPR linewidths at 9.4 GHz (○), 35 GHz (△), 75 GHz (◊) and 225 GHz (□).
bottom) $[GdL^1(H_2O)_3]^{3+}$ ^1H NMRD profiles at 15°C (□), 25°C (○), 50°C (△) and 63°C (◊).
The lines represent results from the combined data analysis.

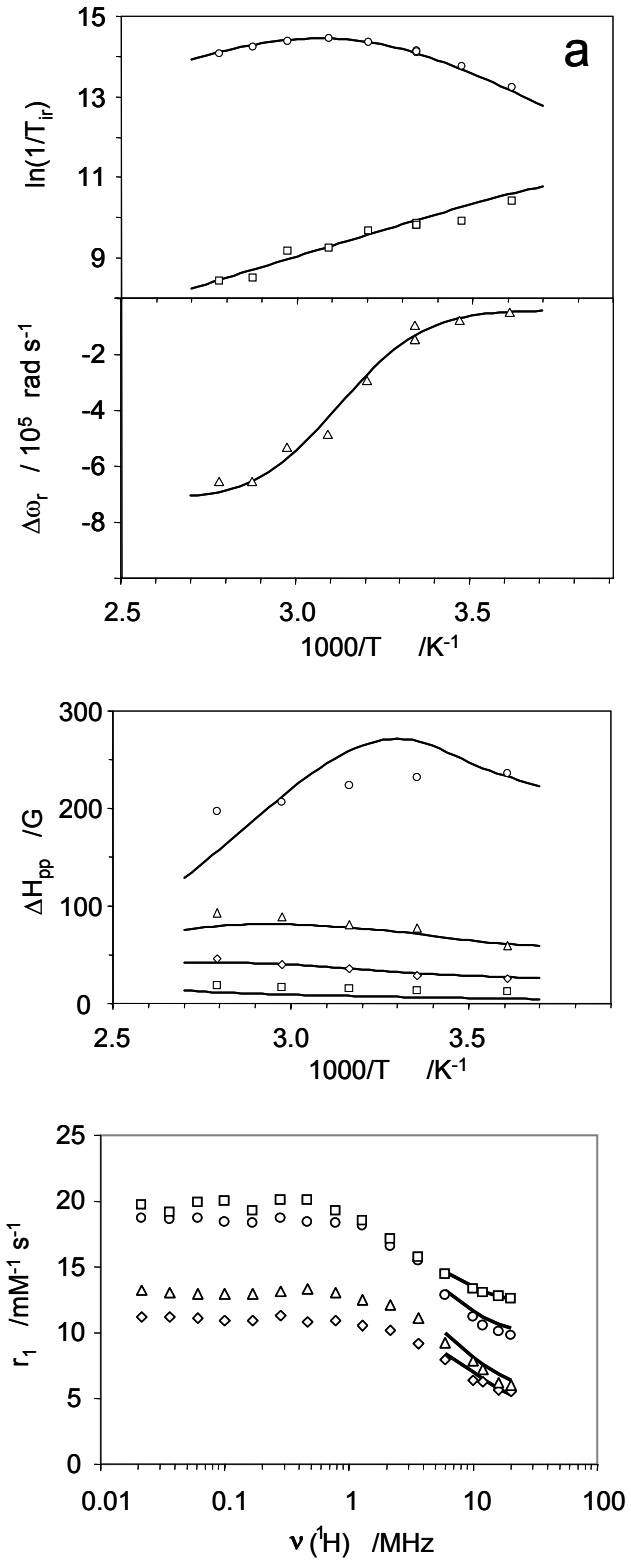

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Fig. S2. ^{1}H NMR spectra of $[EuL^{2}(H_2O)_3]^{3+}$ in D_2O at different temperatures.

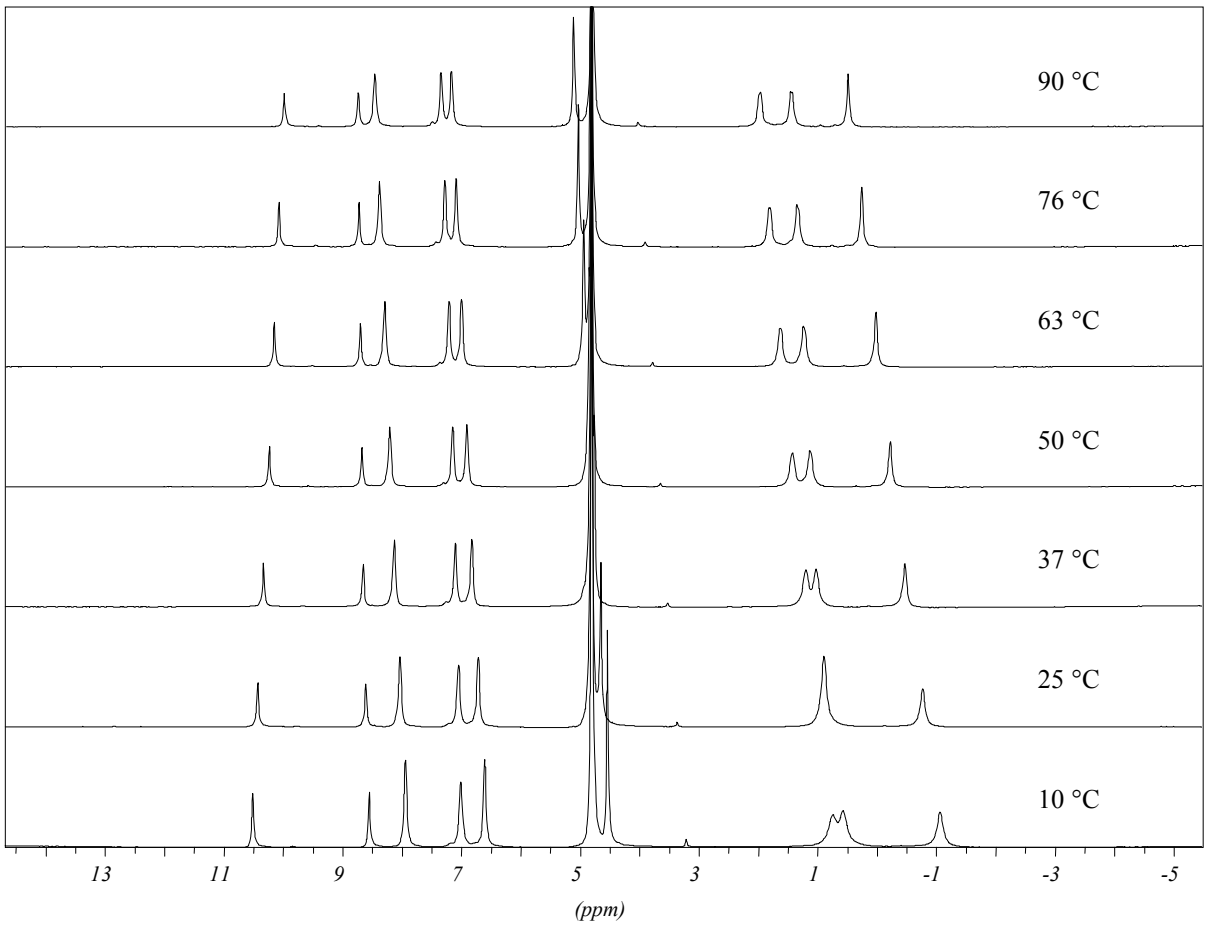

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Fig. S3. ^{1}H NMR spectra of $[EuL^{2}(H_2O)_3]^{3+}$ in D_2O at different pDs.

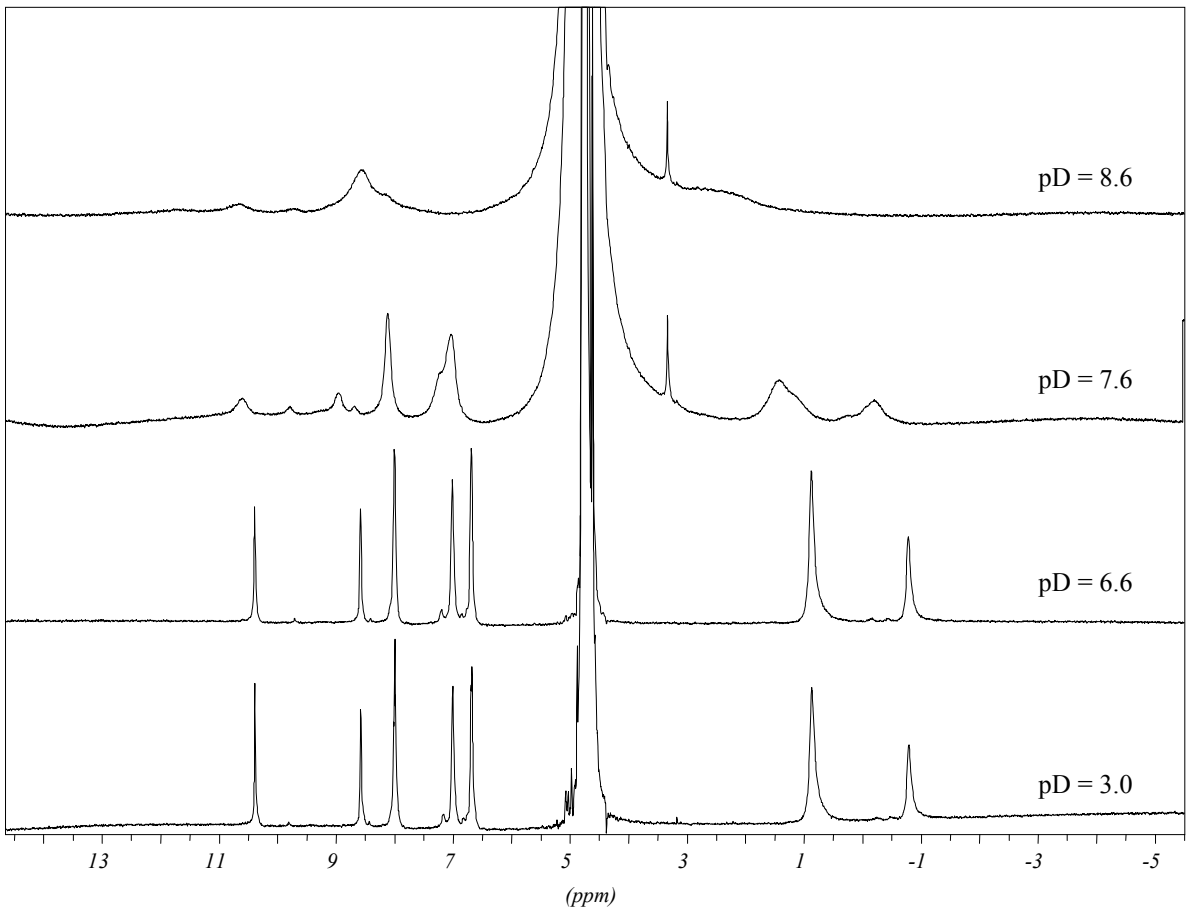

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Fig. S4. For $[Gd(DOTA)(H_2O)]^-$ temperature depence of reduced ^{17}O transverse (a), longitudinal relaxation rates (b) and reduced chemical shifts (c) at 9.4 T (▼), 4.7 T (■) and 1.4 T (●). Temperature depence of the EPR peak-to-peak line widths (d) and the apparent g-factor (e) at 9.4 GHz (●), 75 GHz (■), 150 GHz (▼) and 225 GHz (♦). NMRD profiles (f) at 277.2 K (■), 283.2 K (▼), 291.2 K (♦), 298.2 K (●), 305.2 K (✳) and 312.2 K (▲).

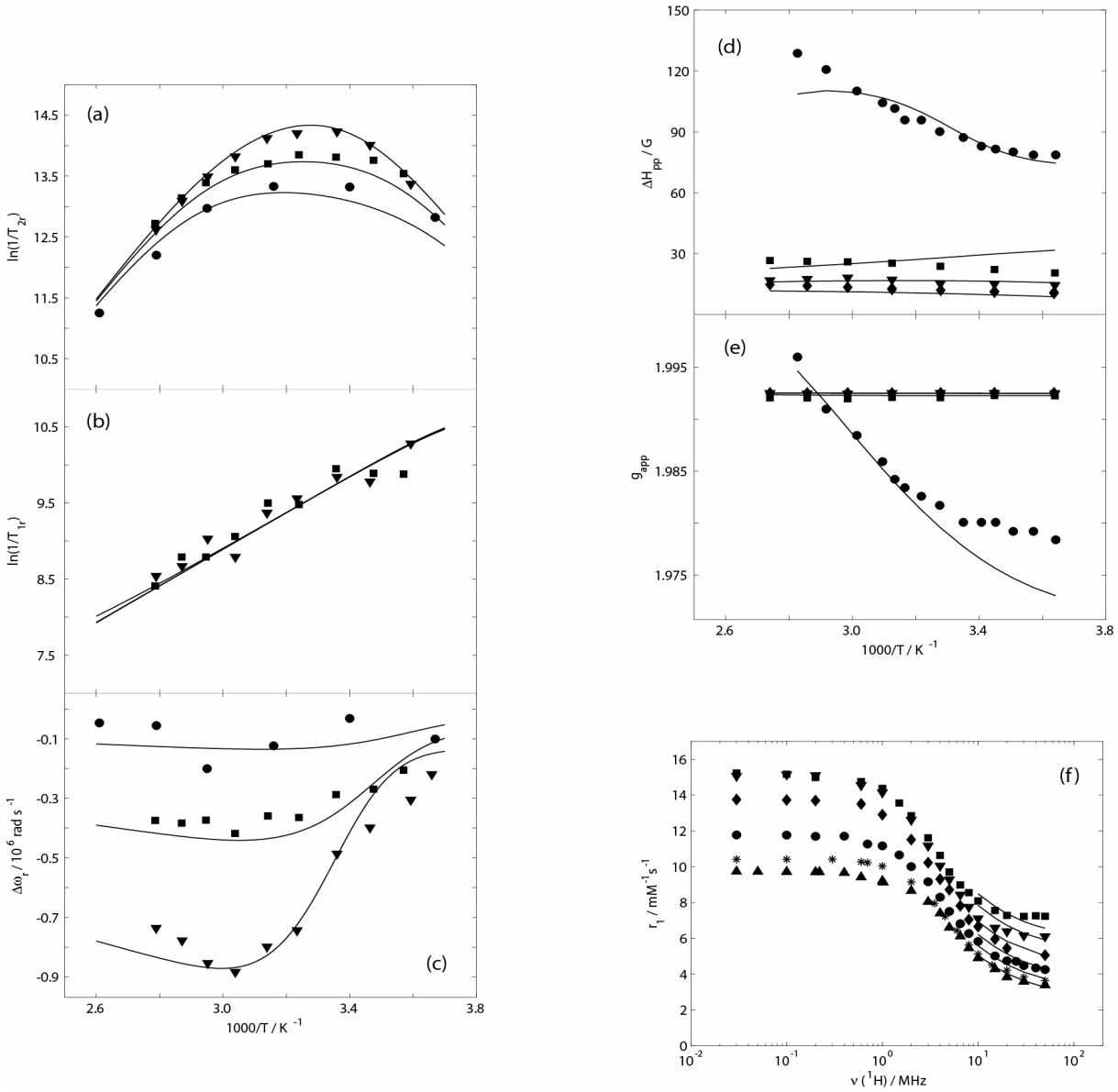
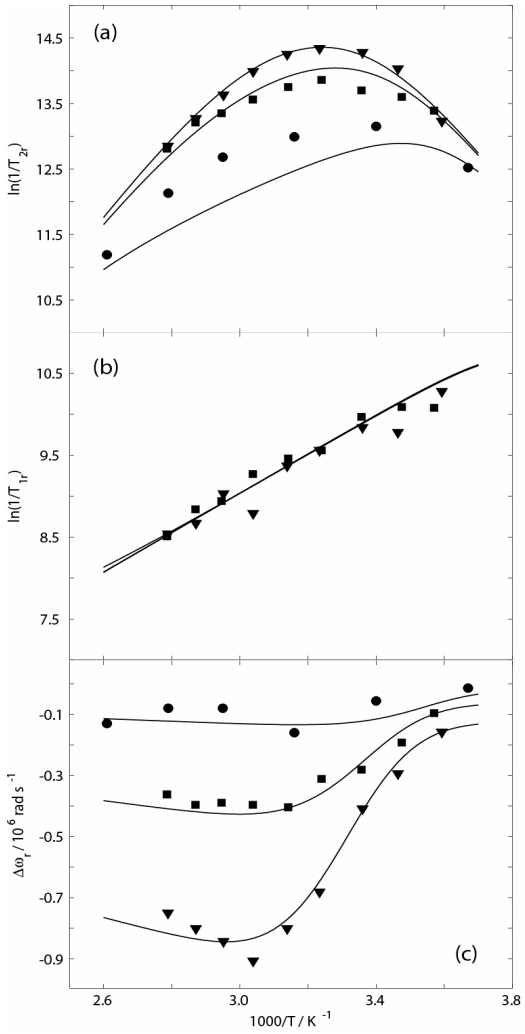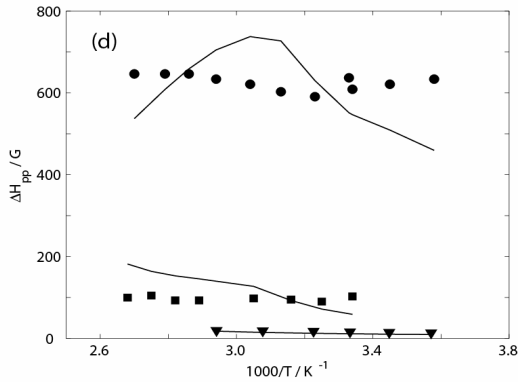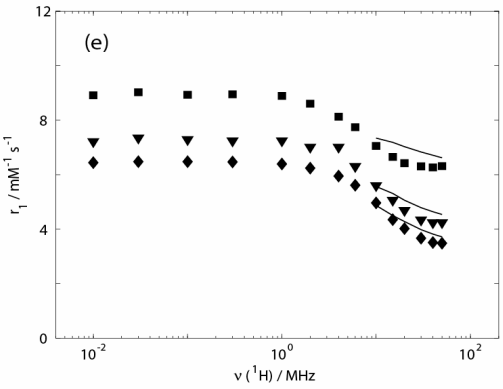
Fig. S5. For $[Gd(DTPA)(H_2O)]^{2-}$ temperature depence of reduced ^{17}O transverse (a), longitudinal relaxation rates (b) and reduced chemical shifts (c) at 9.4 T (▼), 4.7 T (■) and 1.4 T (●). Temperature depence of the EPR peak-to-peak line widths (d) at 9.4 GHz (●), 35 GHz (■) and 125 GHz (▼). NMRD profiles (e) at 278.2 K (■), 298.2 K (▼) and 308.2 K (♦).