

Appendix A. Supplementary material

Table A1. Variable-temperature ^{17}O NMR Data for Cryptate **1** and Sr^{2+} analogue of **1** in the presence of albumin:

Temperature ($^{\circ}\text{C}$)	Linewidth of $^{17}\text{OH}_2$ (Hz)	
	Sr^{2+} analogue of 1 -HSA	1 -HSA
50	57.85	60.44
45	65.03	68.09
40	73.78	77.40
35	84.57	89.24
30	96.26	102.35
25	111.44	119.16
15	151.97	160.28

Parameters

		Value	Standard Error
1overT2P	T1e298	2.44399E-8	1.75994E-9
	taum298	3.9744E-8	6.85832E-9
	deltaH	61984.56106	8163.02663
	deltaE	2.5E-11	0
	q	1	0
	Eu	1E-3	0

Iterations Performed = 4
 Total Iterations in Session = 4
 Fit converged - Chi-sqr no longer changed.
 Some parameter values were fixed.

Statistics

	1overT2P
Number of Points	7
Degrees of Freedom	4
Reduced Chi-Sqr	1.4706
Residual Sum of Squares	5.88242
Adj. R-Square	0.97113
Fit Status	Succeeded(101)

Fit Status Code :
 101 : Fit converged

Fitted Curves Plot

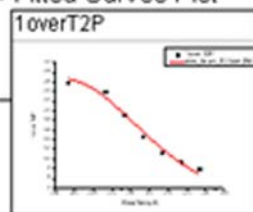


Fig A1. Variable-temperature ^{17}O NMR Fittings for Cryptate **1** in the presence of albumin.

Pertinent equations:

$$\text{relaxivity} = \frac{1}{T_1} = \frac{q}{1000c} = \frac{q}{55} \cdot 5 \left(\frac{1}{T_{1m} + \tau_m} \right)$$

$$\frac{1}{T_{1m}} = \frac{1}{T_1^{DD}} + \frac{1}{T_1^{SC}} \quad \text{note: } \frac{1}{T_1^{SC}} \text{ goes to zero at frequencies above 10 MHz}$$

$$\frac{1}{T_1^{DD}} = \frac{2}{15} \left(\frac{\gamma^2 g^2 \mu_B^2}{r_{2NH}^6} \right) S(S+1) \left(\frac{\mu_0}{4\pi} \right)^2 \left(7 \frac{\tau_{CS}}{1 + \omega_S^2 \tau_{CS}^2} + 3 \frac{\tau_{CI}}{1 + \omega_I^2 \tau_{CI}^2} \right)$$

$$\frac{1}{\tau_{CI}} = \frac{1}{\tau_R} + \frac{1}{T_{1e}} + \frac{1}{\tau_m}$$

$$\frac{1}{\tau_{CS}} = \frac{1}{\tau_R} + \frac{1}{T_{2e}} + \frac{1}{\tau_m}$$

$$\frac{1}{T_{1e}} = 2C \left(\frac{1}{1 + \omega_S^2 \tau_{1e}^2} + \frac{4}{1 + \omega_I^2 \tau_{1e}^2} \right)$$

$$\frac{1}{T_{2e}} = C \left(\frac{5}{1 + \omega_S^2 \tau_{2e}^2} + \frac{2}{1 + \omega_I^2 \tau_{2e}^2} + 3 \right)$$

$$C = \frac{1}{50} \Delta^2 \tau_v [4S(S+1) - 3]$$

$$\omega_S = \gamma_S B$$

$$\omega_I = \gamma_I B$$

The calculated relaxivity decreases from 1.4 T to 11.7 T (Table 1). Assumptions made in the calculations are that the electronic parameters, ν and Δ^2 , do not change with magnetic field and that the values of ν and Δ^2 that were measured at 0.34 T are valid at higher field strengths. It was also assumed that the τ_R for the biphenyl-modified cryptate in the presence of HSA is the same as that of MS-325 in the presence of HSA at 37 °C.

Constants	References	
m	4.0×10^{-8}	this work
q	1	this work
γ_I	2.67×10^8	http://physics.nist.gov/cgi-bin/cuu/Value?gammap
g	2	http://physics.nist.gov/cgi-bin/cuu/Value?gem search_for=all!
μ_B	9.27×10^{-24}	http://physics.nist.gov/cgi-bin/cuu/Value?mub
$r_{\text{Eu-H}}$	3.22×10^{-10}	L. Burai, É. Tóth, S. Seibig, R. Scopelliti, A. E. Merbach, Chem. Eur. J. 6 (2000) 3761–3770.
μ_o	1.00×10^{-7}	http://physics.nist.gov/cgi-bin/cuu/Value?mu0
γ_S	1.76×10^{11}	L. Burai, É. Tóth, S. Seibig, R. Scopelliti, A. E. Merbach, Chem. Eur. J. 6 (2000) 3761–3770.
R	1.33×10^{-8}	MS-325 with HSA from P. Caravan, N. J. Cloutier, M. T. Greenfield, S. A. McDermid, S. U. Dunham, J. W. M. Bulte, J. C. Amedio, Jr., R. J. Looby, R. M. Supkowski, W. DeW. Horrocks, Jr., T. J. McMurry, R. B. Lauffer, J. Am. Chem. Soc. 124 (2002) 3152–3162.
Δ^2	2.10×10^{19}	Eu ²⁺ [2.2.2]cryptate from L. Burai, R. Scopelliti, É. Tóth, Chem. Commun. (2002) 2366–2367.
ν	1.70×10^{-11}	Eu ²⁺ [2.2.2]cryptate from L. Burai, R. Scopelliti, É. Tóth, Chem. Commun. (2002) 2366–2367.

Table A2. Calculated relaxivity values of **1** in the presence of HSA at different field strengths at 37 °C.

Field Strength (T)	Relaxivity (mM ⁻¹ s ⁻¹)
1.4	16.10
3	3.80
7	0.71
9.4	0.40
11.7	0.26