Electronic Supplementary Information

A ^{13}C-NMR study of azacryptand complexes

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Fig. 1 Effect of 20 mM $ZnCl_2$ and temperature on the ^{13}C-NMR spectrum of 10 mM R3Bm.
Experimental details: 5 mm sample tubes were used. Acquisition parameters were: 16384 time domain data points; spectral width 220 ppm; acquisition time 0.295 s; 0.7 s relaxation delay time; 90 ^{o}C pulse angle; 2048 transients recorded per spectrum. Waltz-16 composite pulse ^{1}H decoupling of 0.4 W was used which was reduced to 0.006 W during the relaxation delay to minimize dielectric heating. All spectra were transformed with an exponential weighting factor of 4 Hz. Sample conditions were: 50% (v/v) d_6-DMSO, 50%(v/v) H_2O, 10 mM R_3Bm, 20 mM $ZnCl_2$. The pH values of samples (a), (b), (c), (d) and (e) were 9.91, 9.97, 9.97, 9.97 and 9.93 respectively.

Fig. 2 ^{13}C-NMR spectra of the reaction of $NaH^{13}CO_3$ with R3Bm**.**
Experimental details: 5 mm sample tubes were used. Acquisition parameters were: 32768 time domain data points; spectral width 237 ppm; acquisition time 0.551 s; 70s relaxation delay time; 90 ^{o}C pulse angle; 256 transients recorded per spectrum. ^{1}H decoupling was not used. All spectra were transformed with an exponential weighting factor of 10Hz.

The T_1 value in 50% d_6-DMSO and 50% H_2O for free bicarbonate at 159.6 ppm was 14.0 ± 0.6 s. The signals at 163.5 and 164.2 were clearly resolved in 20.9 mM $NaH^{13}CO_3$ (Fig 2b) and had T_1 values of 3.2 ± 0.3 s and 3.3 ± 0.3 s respectively. As there are no directly bonded protons in these species then proton decoupling did not significantly reduce line widths or increase signal intensities. Therefore as all the spectra in Fig. 2 were obtained without proton decoupling and with an inter-pulse delay of 70s the signals could be quantified by determining the area under each signal (Fig. 2). It was assumed that the signals at 163.3 and 163.6 (Fig. 2e,f) had T_1 values ≤ 14s.

Fig. 3 Titration of carbamylated R3Bm with zinc chloride.
Experimental details: 5 mm sample tubes were used. Acquisition parameters were as described in Fig.3. All spectra were transformed with an exponential weighting factor of 5 Hz. All samples were at 25˚C and contained 50% (v/v) d_6-DMSO, 50%(v/v) H_2O, 41.7 mM $NaH^{13}CO_3$ and 5.5 mM R3Bm. Sample conditions were: (a) 0.0 mM $ZnCl_2$, pH 9.98; (b) 2.5 mM $ZnCl_2$, pH 10.04; (c) 5.0 mM $ZnCl_2$, pH 10.0; (d) 7.6 mM $ZnCl_2$, pH 10.02; (d) 10.1 mM $ZnCl_2$, pH 10.05.

Fig. 4 Experimental and simulated ^{13}C-NMR spectra of the ^{13}C-enriched carbonate carbon of the R3Bm-$(Cd^{++})_2$-$^{13}CO_2$ complexes at different temperatures. Experimental details: 10 mm sample tubes were used. Acquisition parameters were: 32768 time domain data points; spectral width 237 ppm; acquisition time 0.551 s; 6.5 s relaxation delay time; 90 ^{o}C pulse angle; 256 transients recorded per spectrum. ^{1}H decoupling was not used. All spectra were transformed with an exponential weighting factor of 1 Hz. A 10 mm sample tube was used. The sample contained 50% (v/v) d_6-DMSO, 50%(v/v) H_2O, 20.21 mM $NaH^{13}CO_3$, 9.83 mM R3Bm and 19.6 mM $ZnCl_2$, pH 10.03. The sample temperature is given on the appropriate spectrum.

Figure S1

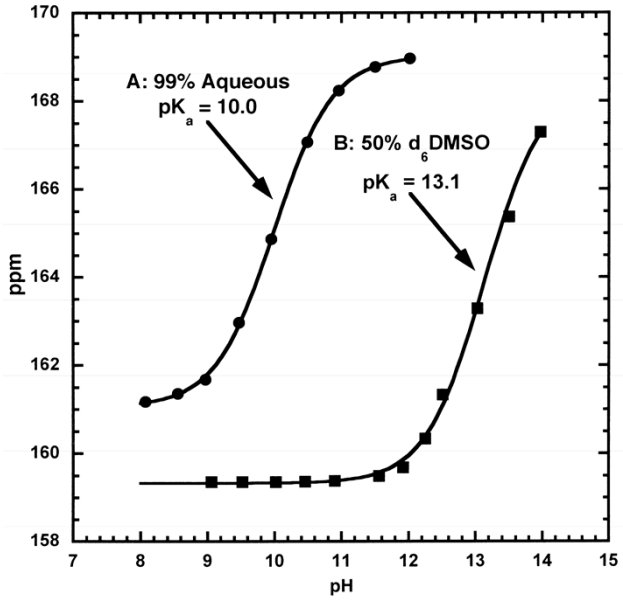

Fig. S1 pH titration of R3Bm in 99% aqueous solution and in 50% (v/v) d_6-DMSO. Line A: 89%(v/v) H_2O, 10%(v/v) ^2H_2O, 1% (v/v) dioxane and 20 mM $NaH^{13}CO_3$;Line B 50% (v/v) d_6-DMSO, 40%(v/v) H_2O,10%(v/v) ^2H_2O and 5.0 mM $NaHCO_3$. All samples were at 25˚C and in 10mm sample tubes. Lines A and B were calculated using the equation $S_{obs} = S_1/(1+[H]/K_a) + S_2/(1+ K_a/[H])$. For Line A the fitted parameters were: pKa = 9.99 ± 0.01, S_1 = 161.06 ± 0.03 ppm, S_2 =169.02 ± 0.03 ppm. For Line B the fitted parameters were: pKa = 13.13 ± 0.03, S_1 = 159.33 ± 0.04 ppm, S_2 =168.41 ± 0.16 ppm. For line A dioxane at 67.4 ppm was used as a secondary reference. For line B d_6-DMSO at 38.7 ppm was used as a secondary reference.

Figure S2

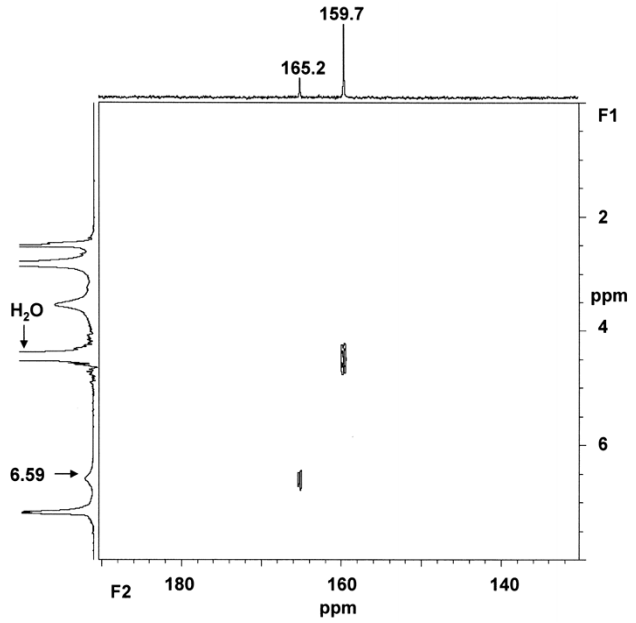

Fig.S2 HOESY spectrum of the carbonate-$(Zn^{++})_2$-R3Bm complex
For the HOESY spectra F2 was ^{13}C. Acquisition parameters were: 512 time domain data points; spectral width 130-190 ppm; acquisition time 0.034 s; 6s relaxation delay time; 90 ^{o}C pulse angle; 16 dummy scans per spectrum; 256 transients recorded per spectrum. Waltz-16 composite pulse ^{1}H decoupling was used. F1 was ^{1}H. Acquisition parameters were: 64 time domain data points; spectral width 0-8 ppm; acquisition time 0.008 s; 90 ^{o}C pulse angle. A 10 mm sample tube was used. The sample was at 25˚C and pH 9.99. It contained 50% (v/v) d_6-DMSO, 50%(v/v) $^{2}H_2O$, 38.8 mM $NaH^{13}CO_3$,10.0 mM R3Bm and 19.5 mM $ZnCl_2$.

Table S1 Stoichiometry of the carbamoylation of R3Bm when the concentration of sodium bicarbonate is increased at pH 10.

	% Molarity of ^{13}C signals				
$NaH^{13}CO_3$ [mM]	164.2 [ppm]	163.6 [ppm]	163.5 [ppm]	163.3 [ppm]	Total
10.4	42.5		17.2		59.7
20.9	56.5		41.8		98.3
41.7	50.6	12.8	40.6	32.1	136.1
79.0	31.5	42.9	44.0	64.4	182.9

The amount of each NMR signal is expressed as its % Molarity of the R3Bm (5.5 mM) present.

Table S2 Effect of temperature on the ^{13}C-NMR

signals at 160 and 165 ppm

˚C	Linewidth of signals 160 ppm Hz	 165 ppm Hz
5.5	31.82 ± 0.33	51.37 ± 4.56
25.3	40.68 ± 0.13	7.25 ± 0.13
40.4	57.84 ± 0.89	4.42 ± 0.11