ESI includes:

Figures 1 and 2:

Binding isotherms for titration of [Eu.2] with Tyr-OP and Ser-OP in the presence of 5mM sodium bicarbonate (pH 7.4, 0.1M MOPS)

Figure 3;

Job plot for addition of [Eu.1] to AMP (pH 5.4, 0.1 M MOPS); a similar plot with an inflection at 0.5 was obtained at pH 7.4

Table 1;

Summary of partial paramagnetic NMR data highlighting the mean shift data for the axial ring protons in Tm and Yb complexes of 4a/4b with various anions.

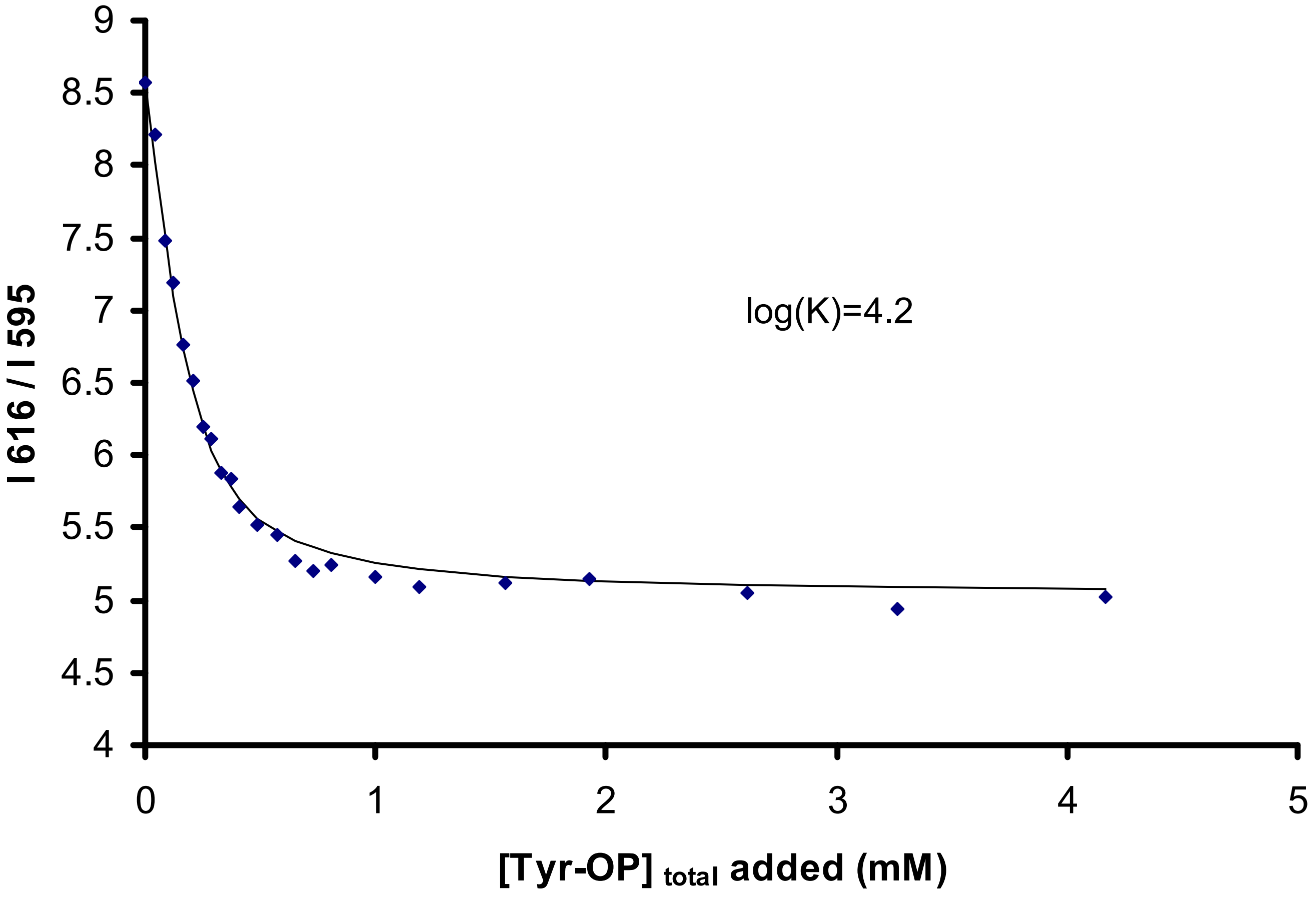
Figure 4

Correlation of Yb and Tm NMR shift data for complexes of [Ln.4a] showing the linear correlation consistent with presence of a purely pseudo-contact contribution for the mean chemical shift of the axial ring proton

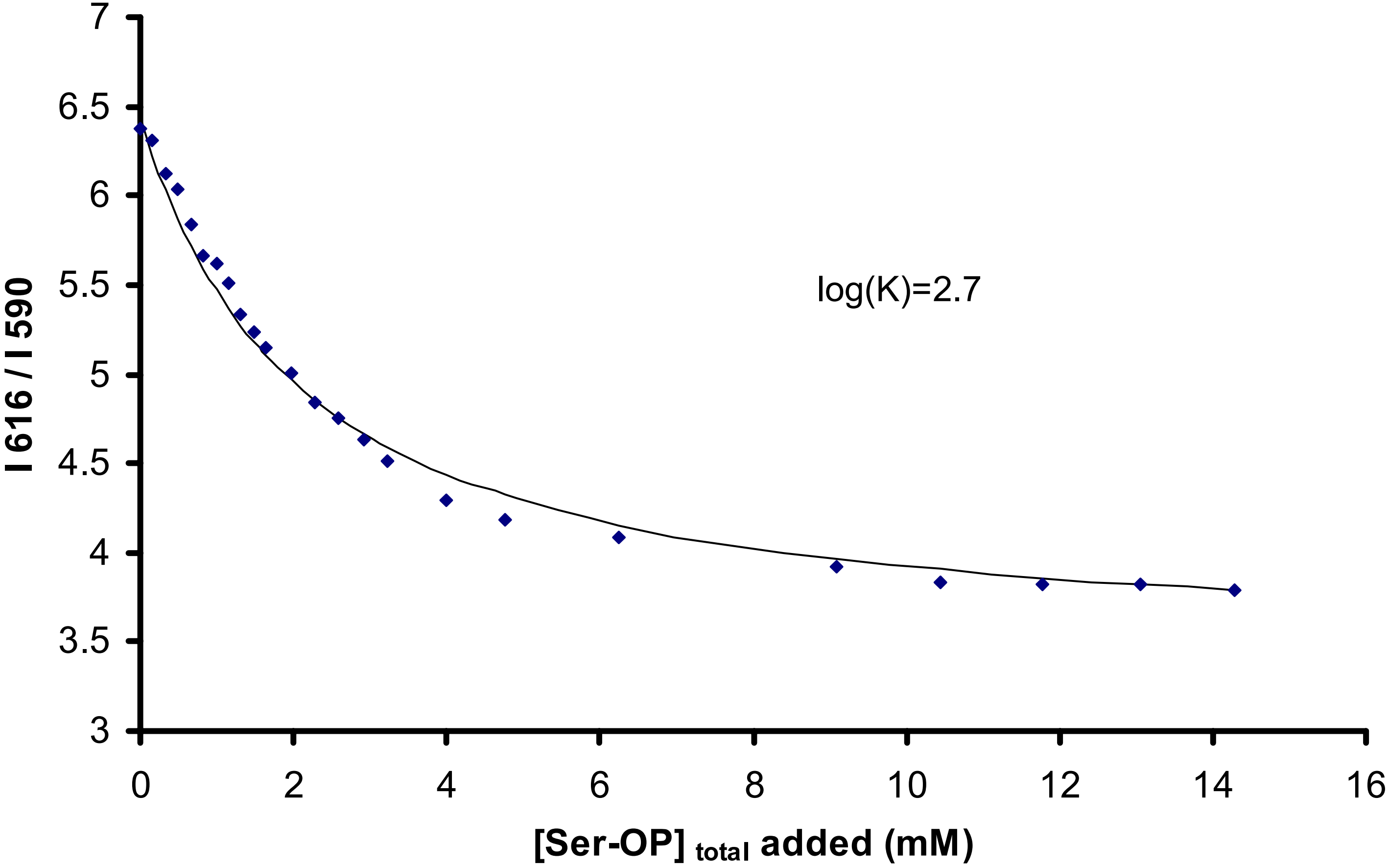
Figures and 6

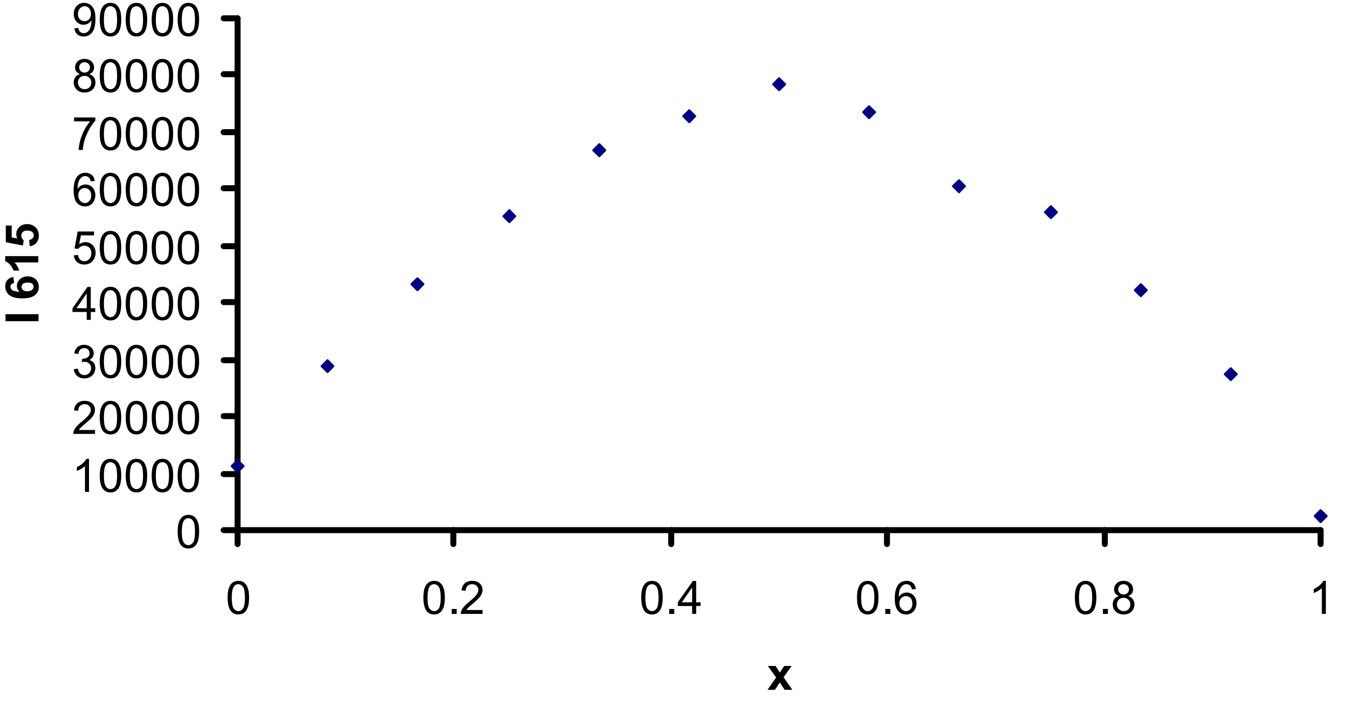
Partial 1-H NMR spectra (500MHz, 295K, 4mM complex 4-fold excess of added anion) for [Yb/Tm.4a], highlighting the sensitivity of the NMR spectral profile to the nature of the adduct.

Binding isotherm for titration of [Eu.**2**] with Tyr-OP in the presence of 5 mM HCO_3^- (pH=7.4, 0.1 M MOPS)



Binding isotherm for titration of [Eu.**2**] with Ser-OP in the presence of 5 mM HCO_3^- (pH=7.4, 0.1 M MOPS)



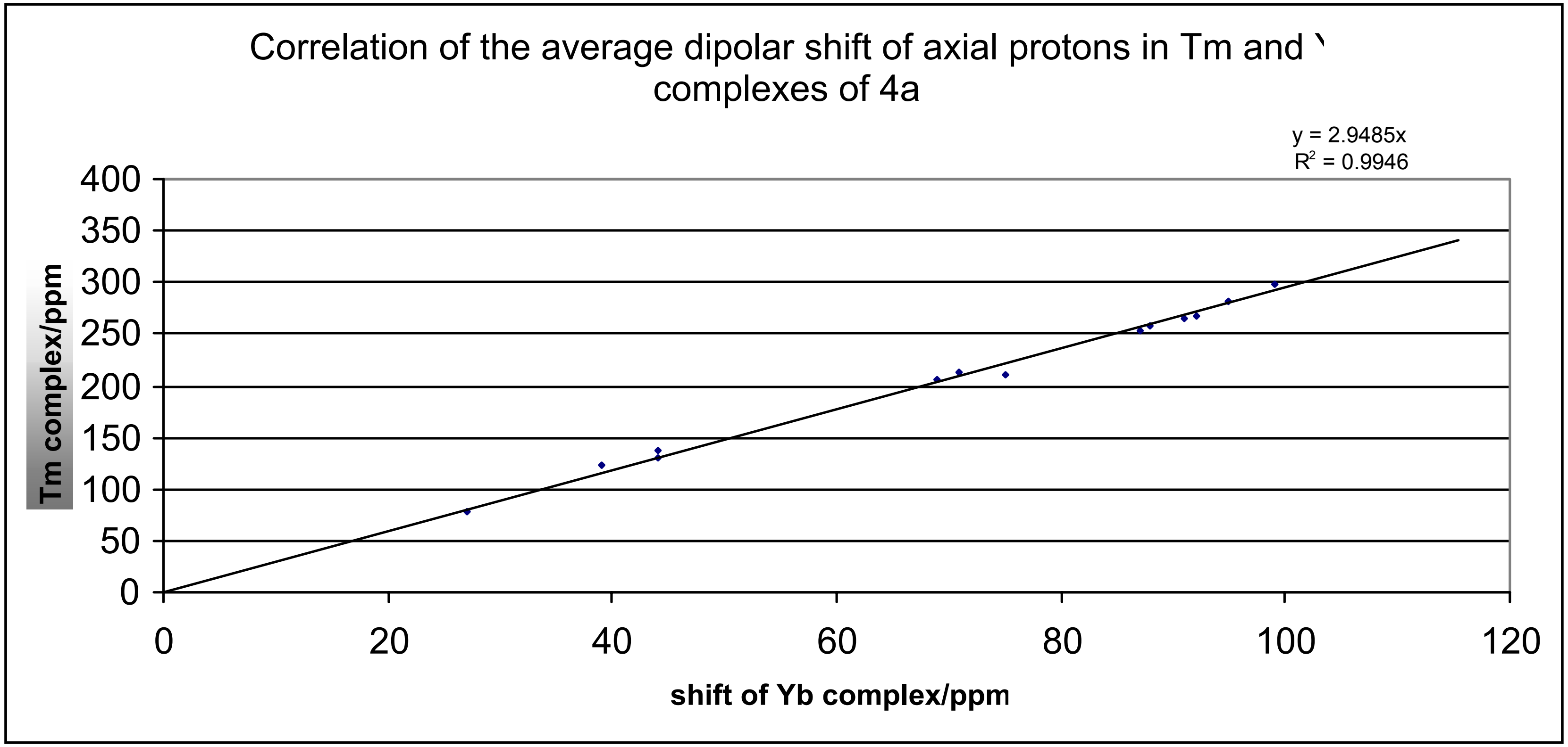


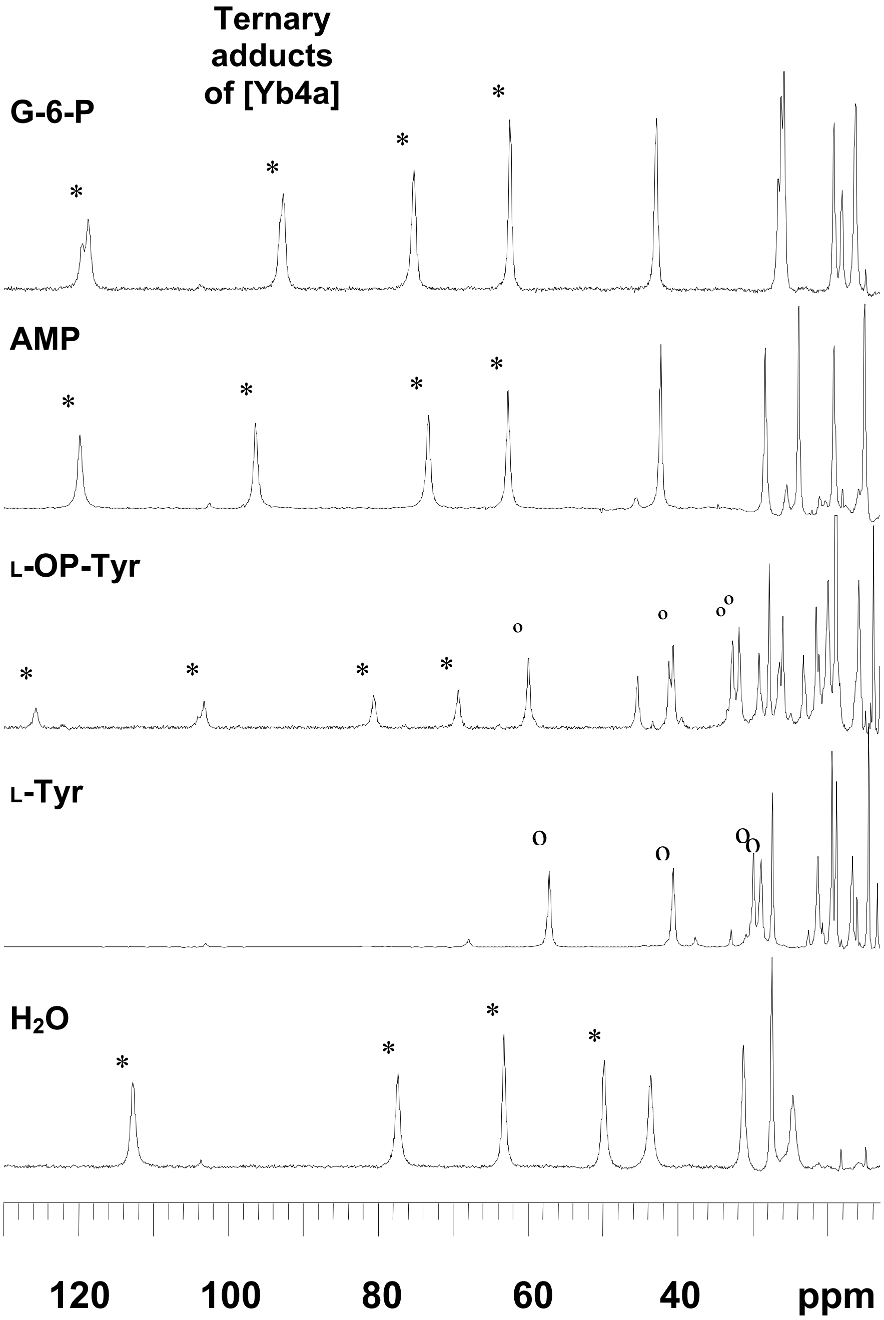
[Eu.1] + AMP

pH=5.4, 0.1 M MOPS

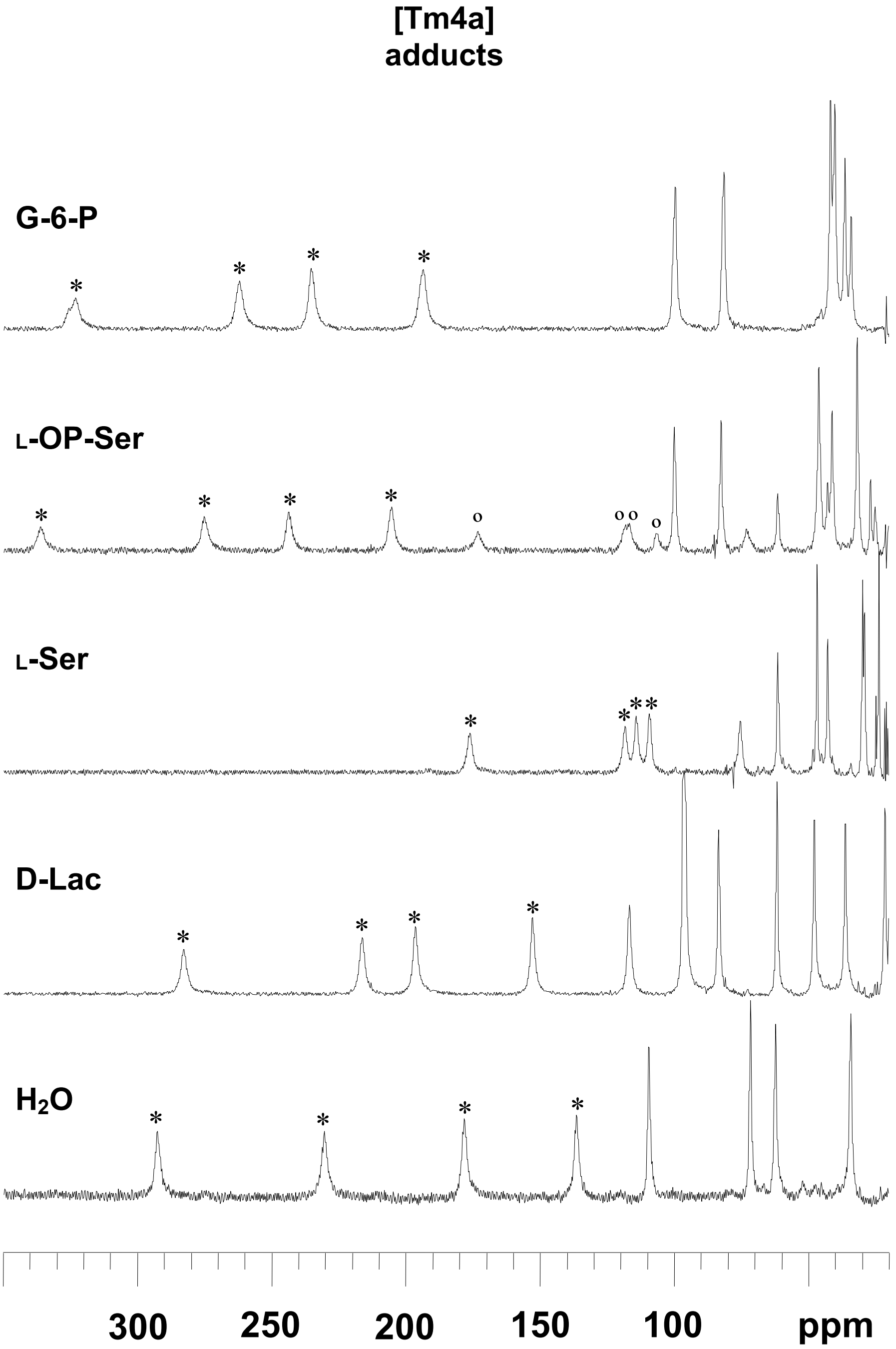
	Average dipolar shift of axial ring protons / δ			
Anion	[Yb.4a]	[Yb.4b]	[Tm.4a]	[Tm.4b]
None (H_2O)	75	101	210	313
Hydrogen carbonate	27	32	78	94
L-Serine	44	55	130	165
L-Threonine	44	58	137	171
L-Tyrosine	39	51	122	152
D-Lactate	71	89	212	265
Acetate	69	76	207	231
Hydrogen phosphate	100	100	247	349
Phospho-L-Serine	91	54 (107)	265	161 (360)
Phospho-L-Threonine	92	57 (109)	268	171 (365)
Phospho-L-Tyrosine	95	53	281	158 (373)
Glucose-6-Phosphate	87	105	254	356
AMP	88	108	258	362
F^-	99	114	299	430

Data above relate to the mean dipolar shift of the most paramagnetically shifted ring proton resonance (pseudo-contact shift dominant) , i.e. the axial proton nearest the Ln centre within the McConnell cone. Values in parentheses for phosphorylated amino-acids refer to the O-phosphate bound species , compared to the amino-acid chelate to lower frequency. Data were measured at 500MHz and 295K in D_2O with 4mM solutions of complex and a 5-fold excess of added anion. Independent titration had revealed that under these conditions the ternary adducts were not only in slow exchange with the aqua precursor (triflate anion) on the NMR timescale, but were fully bound and the shifts given are therefore limiting shifts for the ternary complex. In the case of glucose-6-phosphate, the resolved resonances (see figure 5 ESI) may relate to the glucofuranose and glucopyranose adducts.


Correlation of the average dipolar shift of axial protons in Tm and Y
complexes of 4a
y = 2.9485x
R^2 = 0.9946
Tm complex/ppm
400
350
300
250
200
150
100
50
0
0
20
40
60
80
100
120
shift of Yb complex/ppm



Starred resonances show the most shifted axial ring protons in each of the 4 5-membered NCCN chelate rings of the 12-N-4 ring. For Tyr-OP and Tyr, the circled resonances show the amino-acid chelate


[Tm4a]
adducts
G-6-P
L-OP-Ser
L-Ser
D-Lac
H₂O
300
250
200
150
100
ppm