ESI b818445c

Variation of water exchange dynamics with ligand structure and stereochemistry in lanthanide complexes based on 1,4-diazepine derivatives

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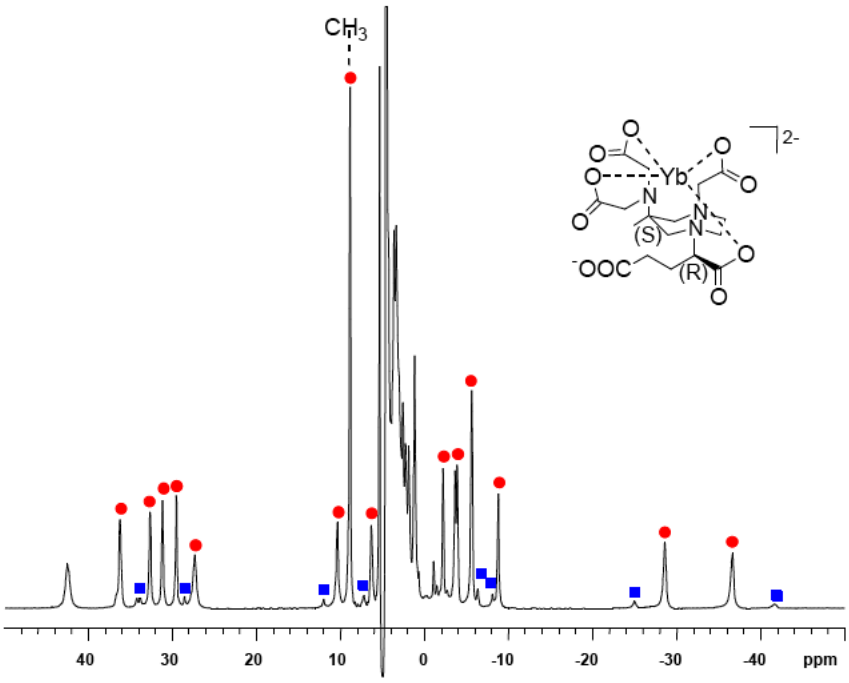
1. **Selected 1-H NMR spectra of complexes and NMRD profile of $[Gd.L^5]^{2-}$ at 298K and 310K, showing data fitting.**

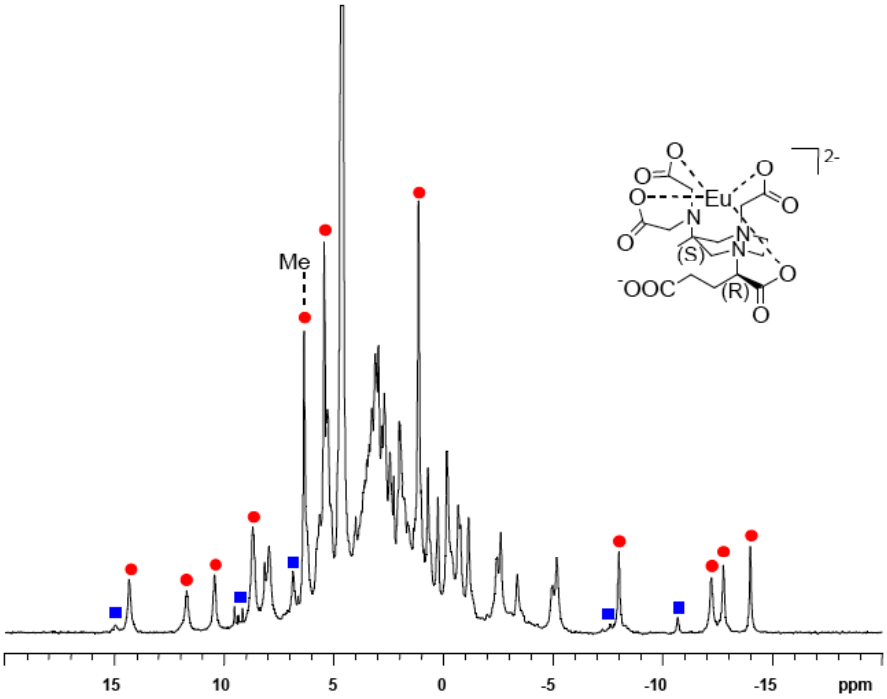
2. **HPLC Methods of Analysis**

1 Selected 1-H NMR spectra of complexes

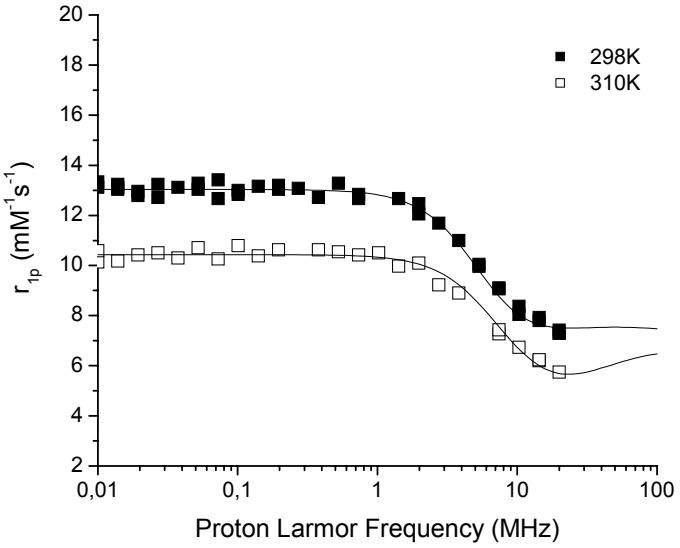
b) 1-H NMR spectrum of $[YbL^5]^{2-}$ showing major (red circles) and minor (blue squares) isomeric species (2OO MHz, D_2O, pD 5.4)



b) 1-H NMR spectrum of $[EuL^5]^{2-}$ showing major (red circles) and minor (blue squares) isomeric species (5OO MHz, D_2O, pD 5.4); this sample contains some free ligand; note the absence of correlation of the most shifted resonances with those of the Yb complex above)



c) Proton NMRD profile for (*RR*)-$[GdL^5]^{2-}$ at 298K and 310K (lower), showing the fit (line) to the experimental data.



2. HPLC Methods of Analysis

method A1 **:** Perkin Elmer Series 200 Pump
Perkin Elmer Series 200 Autosampler
Perkin Elmer Series 200 Diode array detector

Column: Phenomenex Synergi 4µ Fusion-RP 80 ; dimensions: 150*4.6 mm

Particle size: 4 µm ; flow rate: 1 ml/min; detection (UV): 210 nm, 254 nm.

Injection volume: 100 µl. Mobile phase: A: H_2O; B: Acetonitrile
Programme A1:

Time (min)	Solvent A (%)	Solvent B (%)	Gradient
0	100	0	0
10	100	0	0
20	0	100	1
22	0	100	0
24	100	0	-3
28	100	0	0

method A2 **:** stationary phase:Lichrosorb 60 RP-Select B 5 μm; 75 x 4 mm column; temperature:45 °C; mobile phase, gradient elution

A = 0.01 M KH_2PO_4 and 0.017 M H_3PO_4 in water

B = CH_3CN

Gradient timetable:	min	% A	% B
	0	95	5
	15	20	80
	20	20	80

Flow rate:1 mL min^{-1}; detection (UV):210 nm; injection:10 μL; sample conc. 1 mg mL^{-1} . Instrumentation :VWR Elite LaChrom- Hitachi high pressure gradient pump system (L-2100), VWR Elite LaChrom - Hitachi L-2200 autosampler, VWR Elite LaChrom - Hitachi L 2300 column oven, VWR Elite LaChrom - Hitachi L 2400 UV detector.