Direct NMR and luminescence observation of water exchange at cationic ytterbium and europium centres

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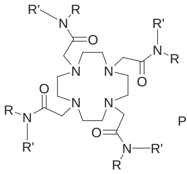
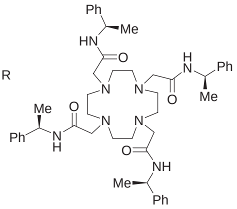
Cationic chiral Yb and Eu tetra-amide complexes, have been studied by VT NMR, luminescence and crystallography: the rate of dissociation of water is about 500 times faster at Yb than at the square antiprismatic Eu centre.

Dissociative water exchange at lanthanide ion centres has traditionally been considered to be fast, with rates of oxygen exchange of the order of $5 \times 10^6\ s^{-1}$ at 298 K for related nine-coordinate anionic complexes.[1] This rate is much slower for neutral[2] and cationic complexes[3] and mean water exchange rates of $5 \times 10^4\ s^{-1}$ occur for cationic tetra-amide complexes of gadolinium. With the europium complexes of the achiral ligands **1**–**3**, two major diastereoisomeric species exist in solution which interconvert by cooperative arm rotation (Δ/Λ conversion) and ring inversion (δ/λ exchange). For the corresponding complexes of the enantiopure ligand **4**, arm rotation is sterically inhibited and CD and NMR studies reveal that in D_2O and CD_3OD the complex exists as a single species, with average C_4 symmetry (⩾98%). Given that the rate of water exchange has now been shown to be markedly different for two isomers of the same complex[4] (twisted square antiprismatic *vs.* square-antiprismatic, Scheme 1), we set out to examine complexes[5] of the same ligand with Eu and Yb, which exist as different, single isomeric species in solution.



1 R= H = R'
2 R = Me, R' = H
3 R = Me = R'



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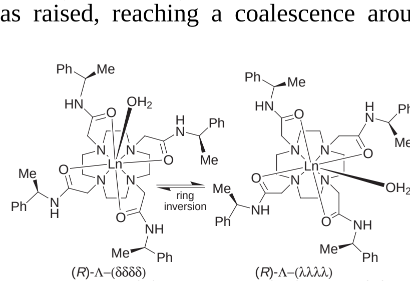
The solution and solid-state structures of $[Eu.\mathbf{4}]^{3+}(CF_3SO_3)_3$ revealed[5] a square-antiprismatic geometry about the metal centre: an (*R*) configuration at the carbon stereocentre gave rise to a left-handed (Λ) helicity with a δ configuration in each of the NCCN chelate rings. At −40 °C in CD_3CN, a resonance due to a bound water molecule was observed at δ +84.3 for $[Eu.\mathbf{4}](CF_3SO_3)_3$ (250 MHz, 10 mM complex, 80 mM H_2O) which moved to lower frequency and broadened at higher temperatures. The bound water signal could still be observed (δ_H = 60, $\omega_{1/2}$ = 750 Hz) at 295 K, while the signal for unbound water (δ *ca.* +2.5) broadened further as the temperature was raised, reaching a coalescence around 328 K, before sharpening again at temperatures in excess of 330 K. Variable temperature saturation transfer experiments at 400 MHz, allowed the rate of water exchange in the range 260–280 K to be measured. Standard ln *k vs.* $1/T$ analysis revealed that the rate at 298 K was 3600 ± 800 s^{-1}, with $\Delta G^{\ddagger}$ = 50.3 ± 2.7 kJ mol^{-1}.



Scheme 1

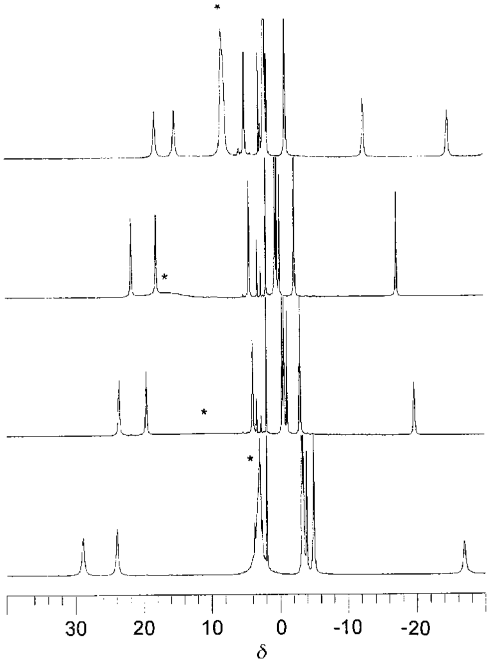
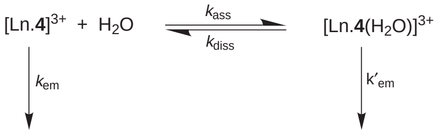


Fig. 1 Variable temperature 1H NMR spectra of $[Yb.\mathbf{4}(H_2O)][CF_3SO_3)_3$ in CD_3CN (10 mM complex, 80 mM H_2O, 300 MHz) at 345, 293, 273 and 233 K, highlighting water exchange (H_2O = *).

For $[Yb.\mathbf{4}][CF_3(SO_3)_3]$, ^1H NMR analysis (293 K, CD_3OD, 65.3 and 300 MHz) gave shifts for the ring axial protons of δ 108.0 and −35.5 (δ 20.5/16.8 for the related 'equatorial' pair). Proton NMR chemical shifts for Yb complexes are determined primarily by the dipolar contribution and the observed shift values for the (12)ane$[N_4]$ ring protons are entirely consistent with those obtained for tetraphosphinate complexes of 1,4,7,10-tetraazacyclododecane,[6] which exist in solution only as a *twisted* square-antiprismatic isomer (Scheme 1). The ^1H NMR spectra recorded in CD_3CN at −40 °C, ([Yb.**4**] = 10 mM, $[H_2O]_{tot}$ = 90 mM, 65.3 MHz) revealed a broad resonance (2H, $\omega_{1/2} \approx 2800$ Hz) at δ 325 consistent with an Yb-bound water molecule. On raising the temperature to 238 K, this signal broadened further ($\omega_{1/2} \approx$ 4000 Hz) and above 240 K, the resonance was too broad to be observed. The 'unbound' water signal resonated as a relatively sharp signal at temperatures in excess of 300 K. On lowering the temperature it broadened and shifted to higher frequency, with maximal line-broadening and positive shift (δ_{H_2O} 26) around 260 K (65.6 MHz), before the signal sharpened again and resonated at δ 6 at 233 K (slow-exchange limit). An independent VT NMR study at 300 MHz (Fig. 1) gave maximal exchange-broadening and positive shift



Scheme 2

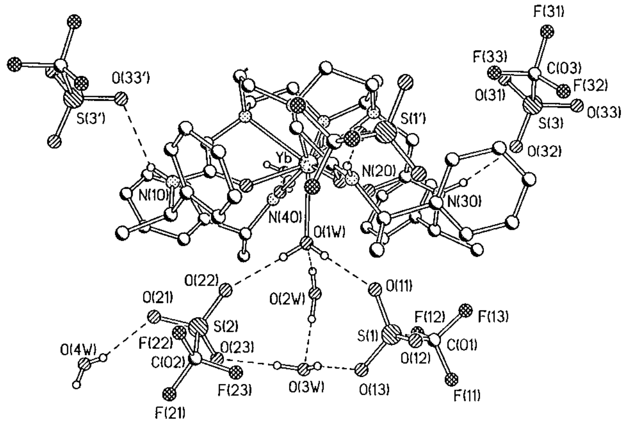


Fig. 2 View of the molecular structure of (R)-Λ-[Yb.**4**(H_2O)](CF_3SO_3)$_3$·$3H_2O$ at 120 K, showing the hydrogen bonding of the inner and second sphere water molecules.

for the water signal at 283 K. Line-shape analysis for the water signal in the temperature range 293–343 K correcting for the predominant dipolar T^{-2} dependence of the chemical shift,[7] allowed the rate of water proton exchange to be measured ($\Delta\nu = 9.6 \times 10^4$ Hz at 233 K, 6.2×10^4 Hz at 283 K; $p^{\mathrm{Yb}}_{\mathrm{H_2O}} = 0.11$, $p^{\mathrm{free}}_{\mathrm{H_2O}} = 0.89$). At 298 K, the forward rate of association (Scheme 2) was 2.5×10^5 s^{-1}, and the rate of dissociation from ytterbium was $1.9 \pm 0.7 \times 10^6$ s^{-1} with a free energy of activation of 34.6 ± 2.6 kJ mol^{-1}.

A single crystal X-ray diffraction analysis of (R)-[Yb-.**4**(H_2O)]CF_3SO_3·$3H_2O$ at 120 K revealed a nine-coordinate complex (Fig. 2)[8] with ligand Yb–N and Yb–O distances averaging 2.62 and 2.28 Å, some 0.08 Å longer than in the related europium complex.[4] The Yb–OH_2 distance of 2.44 Å was 0.01 Å longer than in the Eu analogue, but is similar to the only other Yb–water bond length reported for a nine-coordinate species.[10] The N–C–C–N and N–C–C–O torsional angles averaged +59.0 and −28.9°, consistent with a Λ(δδδδ) configuration. The twist of the N_4/O_4 planes about the C_4 axis was −39.7°, typical of a *regular* square-antiprismatic geometry at the metal centre. The selective crystallisation from water of this *minor* solution isomer at 293 K may seem surprising, but related square-antiprismatic complexes also crystallise preferentially.[9]

Luminescence from the $^2F_{5/2}$ and $^5D_0$ excited states of the Yb and Eu ions occurs on the micro- and milli-second timescale, respectively. The slowness of water exchange suggested that measurements of the rate constant for decay of the luminescent lanthanide excited state might allow simultaneous observation of decay from the shorter-lived nine-coordinate (Ln·OH_2) species (in which vibrational quenching to OH oscillators occurs) and from the eight-coordinate lanthanide species. The rate constant for decay of Yb luminescence in [Yb.**4**]$^{3+}$ was 1.6×10^5 s^{-1} at 295 K in D_2O, and a single exponential decay curve was observed. In H_2O, $k_{\mathrm{obs}} = 1.4 \times 10^6$ s^{-1} at 295 K, but bi-exponential decay was apparent at temperatures below 280 K. In D_2O there are no OH (or NH) oscillators available to quench the luminescence and a single exponential decay is observed: in H_2O the faster decay may be ascribed to the nine-coordinate monohydrated species, while the slower process occurs from the short-lived eight-coordinate intermediate. The rate of decay of europium emission from [Eu.**4**]$^{3+}$ was characterised by a single exponential decay profile, both in water ($k_{\mathrm{H_2O}} = 1.72 \times 10^3$ s^{-1}) and in dry acetonitrile ($k_{\mathrm{MeCN}} = 0.76 \times 10^3$ s^{-1} 293 K). The observed mono-exponential decay rate in MeCN increased as a function of added water and from a titration measuring k_{obs} as a function of added water concentration, the equilibrium constant for dissociation of water from the hydrated species was assessed to be $K_d = 42 \pm 5$ mM (298 K). Between −40 and 0 °C the rate of water exchange was sufficiently slow that independent (bi-exponential) decay was observed from the eight- and nine-coordinate species, under conditions where sufficient H_2O had been added to allow each species to be significantly populated. The proportion of the shorter-lived component (*i.e.* the species with water bound to Eu) in the bi-exponential decay increased as the temperature was lowered.

Taken together, this information is consistent with rate-limiting dissociative water exchange which occurs *ca.* 500 times faster at ambient temperature at Yb, in a twisted square-antiprismatic isomer, than at Eu in the related square-antiprismatic complex. The experiments also suggest that water (proton) exchange may be amenable to analysis by variable temperature luminescence measurements.

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7 The T^{-2} temperature dependence of the chemical shift of the bound water resonance (2.9 Å from Yb) is an approximation, as it assumes that the contact shift (varying as T^{-1}) is not significant. Earlier work has shown that a T^{-2} dependence represents a good approximation (valid to ±10%) for the dipolar term: B. McGarvey, *J. Magn. Reson.*, 1979, **33**, 445 and references therein. The most shifted axial ring proton (3.5 Å from the Yb centre), resonating at δ 108 at 293 K (CD_3OD), showed a T^{-2} dependence of its chemical shift.

8 Crystal data for $C_{46}H_{66}N_8O_5Yb(CF_3SO_3)_3.3H_2O$: $M = 1509.29$, monoclinic, space group $P2_1$; $a = 14.390(1)$, $b = 11.928(1)$, $c = 19.300(1)$ Å; $\beta = 102.67°$, $U = 3232.1(4)$ Å^3, $D_c = 1.551$ g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, $Z = 2$, $\mu = 1.640$ mm^{-1}. Data were collected on a SMART at 120(2) K. Refinement of 999 parameters by full matrix least squares on F^2 (SHELX96) converged at $R = 0.021$, $wR_2 = 0.051$ for 16442 observed reflections with $I > 2\sigma(I)$. The disordered phenyl ring in the structure was isotropically refined with two sets of partially occupied atoms. CCDC 182/1231. See http://www.rsc.org/suppdata/cc/1999/1011/ for crystallographic files in .cif format.

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