

Electronic Supplementary information for

Picture of a chelate in exchange: the crystal structure of NaHoDOTMA, a ‘semi’-hydrated chelate

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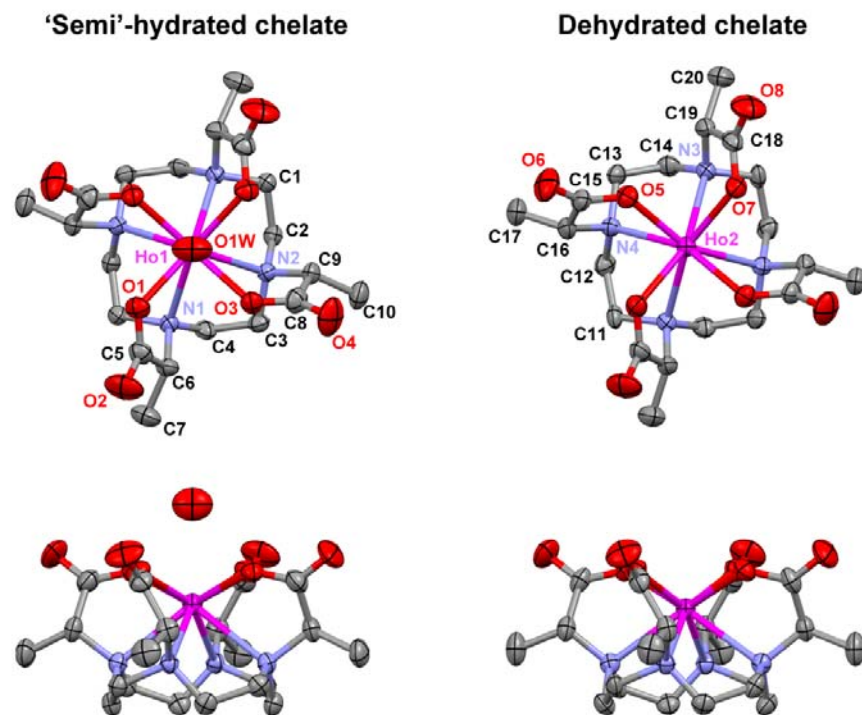
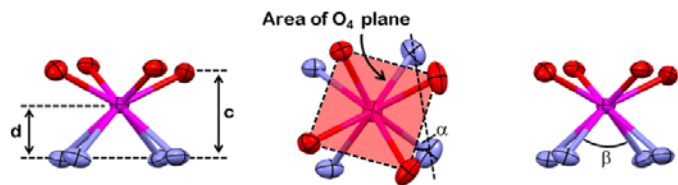


Fig S1. The structures of the two individual chelates in the unit cell of $(\text{NaHoDOMTA})_2 \cdot \text{NaCl} \cdot (\text{H}_2\text{O})_{16}$. Each chelate is in a TSAP ($\Lambda(\lambda\lambda\lambda\lambda)$) coordination geometry and diagonally C_2 symmetric. Protons have been omitted for clarity.

Table 1. Selected parameters from the crystal structure of $(\text{NaHoDOMTA})_2 \cdot \text{NaCl} \cdot (\text{H}_2\text{O})_{16}$. For comparative purposes the same parameters for HoDOTA (Aime *et al.*, *Acta. Cryst. C*) are shown.



	HoDOTMA		HoDOTA
	Semi-hydrated	Dehydrated	
Conformation	$\Lambda(\lambda\lambda\lambda\lambda)$	$\Lambda(\lambda\lambda\lambda\lambda)$	$\Delta(\lambda\lambda\lambda\lambda)/\Lambda(\delta\delta\delta\delta)$
Coord. Geom	TSAP	TSAP	SAP
Ho-OH ₂ (Å)	2.662	4.762	2.443
c (Å)	2.46	2.50	2.34
d (Å)	1.58	1.47	1.61
d/c ratio	0.64	0.59	0.69
α (°)	-24.9	-25.5	37.91
β (°)	135.3	127.2	144.6
β' (°)	135.4	127.3	142.6
Average N-C-C-N torsion angle (°)	-59.1	-59.0	59.2
Average N-C-C-O torsion angle (°)	-20.2	-23.2	-22.4
Area of O ₄ plane (Å ²)	9.14	8.51	9.78

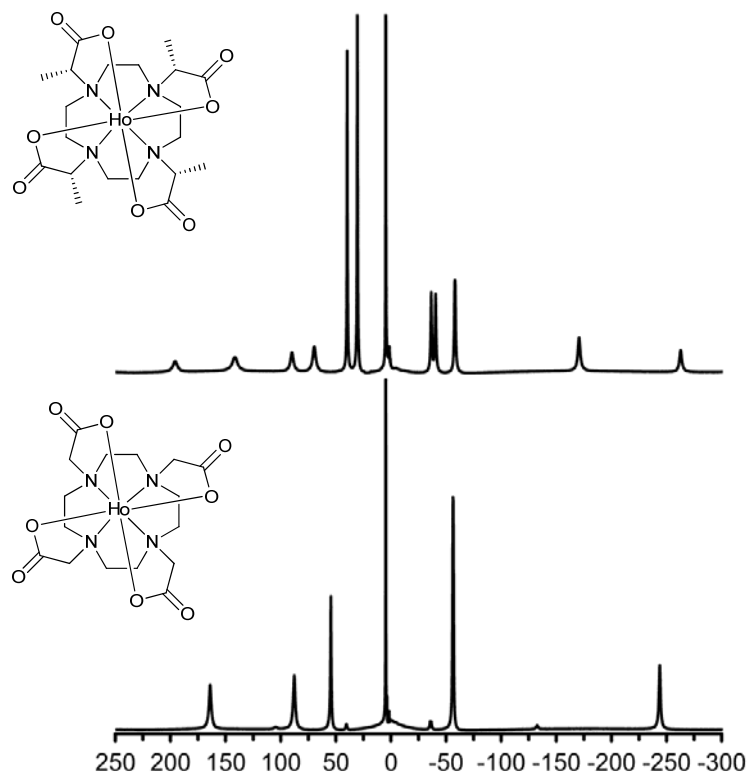


Fig S2. The ^1H NMR spectra of HoDOTMA (top) and HoDOTA (bottom) recorded at 298 K, 400 MHz and pD 5 in D_2O .

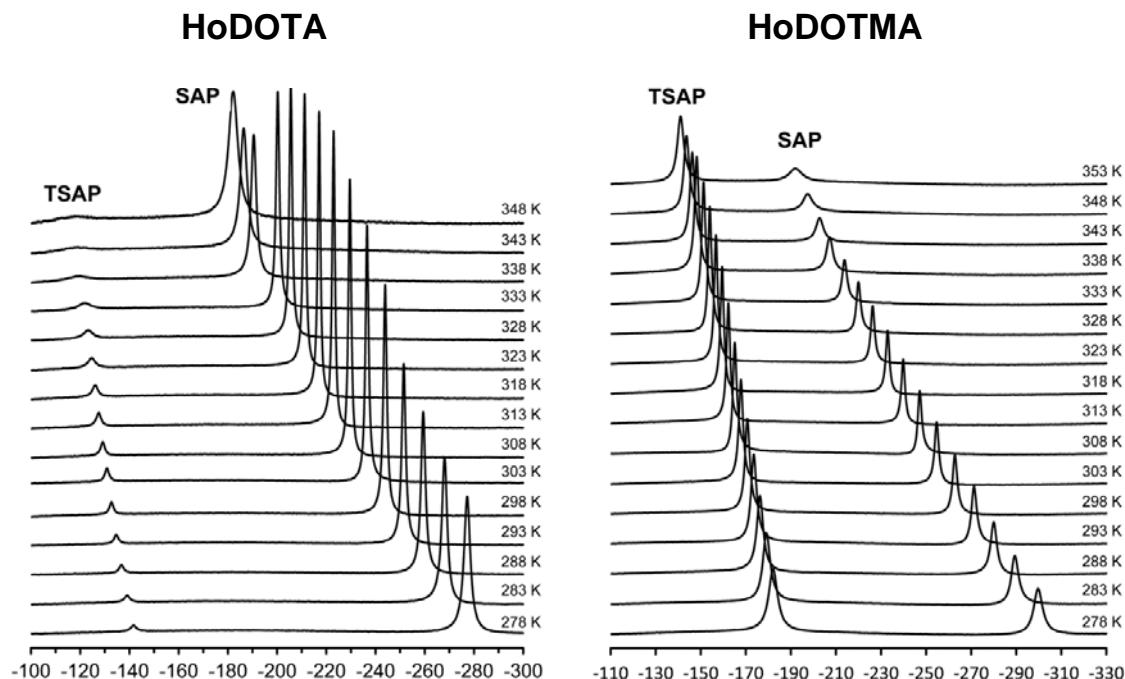


Fig S3. The ^1H NMR spectrum, expanded to show just the ax^S macrocyclic protons of the SAP and TSAP isomers, of HoDOTA (left) and HoDOTMA (right) shown as a function of temperature. It is notable that the hyperfine shifts of all resonances decrease as the temperature is increased, consistent with the known inverse relationships between temperature and the dipolar and contact contributions to the hyperfine shift. However, it is important to note that shifts of the SAP and TSAP isomers also move together as the temperature increases. This is the result of the interchange process between the two coordination isomers. As the temperature increases so does the rate of interchange, and while the two coordination isomers remain in the slow exchange regime ($k_{\text{ex}} < \Delta\omega$), the accelerated rate of exchange brings the shifts of the isomers closer together. This has an important consequence; according to an analysis of the HoDOTMA structure the shifts of the ax^S protons should experience a slightly larger dipolar contribution to the hyperfine shift as water exchange is increased. In these systems this change in shift cannot be detected because it is rather small and is swamped by the much larger changes in shift resulting from interconversion of coordination isomers. Another phenomenon is worthy of note. As the temperature increases the line width of all resonances begin to sharpen and then broaden again, creating the illusion that maximum intensity is achieved in the middle of the temperature range. In all cases the intensity of a resonance was determined by using the line-fitting routine in the NUTS (NMR Utility Transform Software, Acorn NMR Inc) software.

Crystallographic Details

The diffraction pattern: pseudo-four-fold symmetry but no tetragonal lattice, is consistent with the C-centering. A model was developed from a triclinic solution using SHELXS-86¹ in a cell with $a = b = 13.14440(10)$ Å, and $c = 18.9992(4)$ Å. This model could be described better by transposing to the orthorhombic system, space group C222 (#20) with $a = 18.5845(3)$ Å, $b = 18.6061(6)$ Å, $c = 18.9964(4)$ Å. The Ho³⁺ ions lay on the two-fold axes. A model was obtained by transposing the holmium coordinates to k special positions and extending the initial structure with cycles of difference Fourier calculations. Complex ions are pairs in the asymmetric unit. For these, one Ho ion is in effect nine-coordinate with an octadentate DOTMA anion while the other is eight-coordinate without a coordinated water. Refinements were performed using SHELXL-97.² A single chloride (also in a k special position) was located, requiring 3 sodium ions for charge balance. Sodium ion locations were found to be disordered in the region of the carboxylates between the “halves” of the dimeric complex. These were modeled with partial occupancy (general) Na positions and water oxygens. All non-H atoms were refined and with anisotropic vibrational factors. H-atoms were observable in difference electron density maps, and placed in idealized positions, again, with the exception of those on waters were not found (though the H's on the coordinated O1W are just apparent at the end of the refinement but would have required restraints to refine, and added little to the result). H's were assigned as riding atoms with relative isotropic displacement parameters of 120% of the $U(\text{eq})$ of the attached atom. The correct absolute configuration was determined from the known chirality of the ligand, and by refinement of the Flack parameter, +0.014(13). The final full-matrix least-squares refinement converged to $R_1 = 0.0384$ (7976 reflections, F^2 , $I > 2\sigma(I)$); $R_1 = 0.0484$ and $wR_2 = 0.0991$ for all 9231 data, 452 parameters, 0 restraints, goodness-of-fit (S) 1.147, and no extinction. The larger difference peaks at the end of the refinement are in the vicinity of the Ho³⁺ ions.

- 1 SHELXS86 - G. M. Sheldrick, In "Crystallographic Computing 3", Ed. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press. pp. 175-189, 1985, 2c; G. M. Sheldrick, Acta Crystallogr. A64, 112-122 (2008). SHELXS86 - Program for Crystal Structure solution. G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1986
- 2 SHELX97 [Includes SHELXS97, SHELXL97, CIFTAB] - Programs for Crystal Structure Analysis (Release 97-2). G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.