

Ln polyoxocations: Yttrium oxide solution speciation & solution deposited thin films

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General methods

All reagents were purchased from Sigma Aldrich or Strem Chemicals and used as received without further purification. NMR spectroscopy was performed on a Bruker Avance 600 MHz spectrometer equipped with a liquid He cooled cryoprobe. Raman spectroscopy was collected using an Alpha 300S confocal Raman microscope in a 180° backscattering configuration, averaging 20 scans with 5 s integration time per acquisition. Elemental analysis was obtained through Complete Analysis Laboratories, Inc. Thin films were spin-coated from 0.5 M solutions (per metal) in DMF at 3000 rpm for 60 s. The films were heated on a hot plate at 50°C for 2 min to drive off solvent, and then at 350°C for 10 min to anneal. Ellipsometry was performed using a Woollam M44 Spectroscopic Ellipsometer. SEM images were collected using a ZEISS Ultra-55 Scanning Electron Microscope at 5kV with a 20 μm aperture, and the sample was held at 45° to view both the top surface and the edge.

X-ray Crystallography.

Several attempts to determine the crystal structure of **Y₁₆** were made running data collections with different crystals on our Bruker Apex-II Duo system trying both the Mo and Cu sources. The final structure was checked in various different space groups in the tetragonal system and in lower symmetry systems well. We found that in all cases there are highly disordered groups in the structure and our attempts to find a complete solution for the disorder were unsuccessful. Importantly, while disorder prevented complete assignment of all solvent/ligands, the metal-oxo core of **Y₁₆** was determined precisely.

The main peaks on the residual density map are located in areas of disordered groups connected to the Y atoms. Even a rough treatment of these peaks in the residual density as possible N, O or C atoms reduces the R-factor and the max/min levels of the residual density map. Unfortunately, we could not find a solution to the disorder which acceptably convinced us that the model was any better than just assuming a chemical formula based on the other analytical data in hand. We did attempt some solutions that modelled the possible positions of disordered OSMe₂ and OCMe₂ solvent molecules and the NO₃⁻ counteranions. While such models could reduce the final R-factor and max/min levels of the residual density map, these models required strong restrictions on positions of these possible groups and their thermal parameters. In such a situation we decided that instead of modelling the disordered groups and refinement based on strong restrictions it is better to simply acknowledge that these solvents/counterions are highly disordered, and that a highly parameterized solution for this disorder does not really support analytical identification of the material any better. To be clear, while the final chemical formula determined by single crystal XRD may not verify the exact solvent and solvent-ligand content in this structure, the critical connectivity of this new hydroxo/aquo Y cluster is not in doubt. This structural information has been highly useful for understating the other complementary results reported in this manuscript; therefore, we think this structure, albeit imperfect, is useful to include herein (caveat emptor).

Diffraction intensities for **DWJ190** were collected at 173 K on a Bruker Apex2 CCD diffractometer with a MoKα source, λ = 0.71073 Å. Space group was determined based on systematic absences. Absorption correction was applied by SADABS.¹ The structure was solved by direct methods and Fourier techniques and refined on *F*² using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters, except for all atoms in disordered groups. Only the O atoms for some of the (NO₃)⁻ anions and/or acetone molecules coordinated to the Y atom (which shared the same positions and were highly disordered) were found. H atoms in the terminal Me groups were treated in calculated positions. H atoms in disordered solvent molecules and in terminal water molecule were not found and not taken into consideration. The -OSMe₂ groups were refined with restrictions; the standard S=O and S-C bond lengths were used in the refinement as the targets for the corresponding bonds. This ligand/solvent/counterion disorder and the resulting use of these parameters led to several level A and B alerts in the checkcif output; however, the connectivity of the key **Y₁₆** cluster core is not in doubt. All calculations were performed by the Bruker SHELXL-2014 package.²

Crystallographic Data for **Y₁₆** (variant 1, submitted to CCDC as 1517106): *M* = 132.16, 0.11 × 0.10 × 0.06 mm, *T* = 173 K, Tetragonal, space group *P-4n2*, *a* = *b* = 21.6421(17) Å, *c* = 19.6862(17) Å, *V* = 9220.6(17) Å³, *Z* = 2, *D_c* = 1.588 Mg/m³, μ(Cu) = 5.239 mm⁻¹, *F*(000) = 4372, 2θ_{max} = 56.0°, 107920 reflections, 8153 independent reflections [*R*_{int} = 0.1077], *R*1 = 0.1299, *wR*2 = 0.3596 and *GOF* = 1.088

for 4808 reflections (321 parameters) with $I > 2\sigma(I)$, $R_1 = 0.1954$, $wR_2 = 0.4274$ and $GOF = 1.087$ for all reflections, $Flack = 0.052(11)$, max/min residual electron density $+4.680/-0.918 \text{ e}\text{\AA}^{-3}$.

An alternate modelling of the possible ligand disorder surrounding of the \mathbf{Y}_{16} core was also performed (variant 2). In this model the 26 coordination positions in the two outer \mathbf{Y}_6 units are fully or partially occupied by heavily restrained DMSO solvent molecules and four terminal/capping positions in the cluster are occupied by solvent water molecules with occupation factor 0.5. The 10 additional NO_3^- ligands needed for charge balance are not coordinated to the Y atoms in this model and assumed to be disordered in the lattice. These disordered nitrates and likely additional disordered, non-coordinating solvent molecules were treated by SQUEEZE. The correction of the X-ray data by SQUEEZE was 496 electron/cell. This is consistent with 10 nitrates (310 electrons) and 2-3 DMSO solvates. Both variants yield the same \mathbf{Y}_{16} cluster core.

Crystallographic Data for \mathbf{Y}_{16} (variant 2, cif included as additional supporting information but not submitted to CCDC): $\text{C}_{52}\text{H}_{156}\text{N}_8\text{O}_{79}\text{S}_{26}\text{Y}_{16}$, $M_r = 4413.96$, tetragonal, $P-4n2$ (No. 118), $a = 21.6421(17) \text{ \AA}$, $b = 21.6421(17) \text{ \AA}$, $c = 19.6862(17) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 9220.6(17) \text{ \AA}^3$, $T = 173(2) \text{ K}$, $Z = 2$, $Z' = 0.25$, $\mu(\text{MoK}\alpha) = 5.337$, 107920 reflections measured, 8153 unique ($R_{int} = 0.2074$) which were used in all calculations. The final wR_2 was 0.2375 (all data) and R_1 was 0.0780 ($I > 2(I)$), $Flack = 0.055(10)$, max/min residual electron density $+0.5973/-0.7457 \text{ e}\text{\AA}^{-3}$.

Small Angle X-ray Scattering

Small angle x-ray scattering data was collected at Oregon State University on an Anton Paar SAXSess instrument using Cu K α radiation (1.54 \AA) and line collimation. Solutions of \mathbf{Ln}_6 were prepared by dissolution of the pure crystalline product (84 mg/ mL) in N,N-dimethylformamide (Anhydrous, 99.8% min) and contained in 1.5 mm diameter quartz capillary tube (Hampton Research) for SAXS measurements. Solvent background was collected for every sample. Scattering was measured for 30 min. SAXSQUANT software was used for data collection and treatment (normalization, primary beam removal, background subtraction, desmearing, and smoothing to remove extra noise created by the desmearing routine). Data was analyzed to determine radius of gyration (R_g), size, structure factors and pair distance distribution function (PDDF) using IRENA macros within IgorPro.³ Simulated scattering data from crystal structures was obtained using SolX software.^{4,5}

Synthesis of $[\text{Ln}_6(\text{O})(\text{OH})_8(\text{H}_2\text{O})_{12}(\text{NO}_3)_6](\text{NO}_3)_2$ (\mathbf{Ln}_6)

The same procedure was applied to synthesis of \mathbf{Y}_6 , \mathbf{Gd}_6 , \mathbf{Er}_6 , and \mathbf{Ho}_6 ; described below is the method for \mathbf{Y}_6 as an example. $\text{Y}(\text{NO}_3)_3$ (5.76 g, 15.00 mmol) was dissolved in 15 mL water to make a $\sim 1\text{M}$ solution. Zn powder (99 mg, 1.50 mmol, 0.1 equivalent) was added all at once with rapid stirring. The reaction mixture was allowed to stir at room temperature for 60 minutes. Over time the solution became turbid as the Zn reacted and dissolved. Aliquots (3 mL) were taken at various times and filtered through a syringe filter (0.2 μm) into a scintillation vial. The clear solutions were stored at 0°C until crystals formed (2-3 days). The supernatant was decanted and the crystals were isolated and washed with acetone. The yields varied for each aliquot and are summarized in figure 1 in the manuscript. \mathbf{Eu}_6 and \mathbf{Sm}_6 were synthesized by the prior reported method.⁶ The redox activity of these metals is incompatible with the zinc dissolution synthesis method.

Synthesis of $\text{Ln}_{16}\text{O}_3(\text{OH})_{24}(\text{DMSO})_{16}(\text{NO}_3)_{18}(\text{H}_2\text{O})_4(\text{acetone})_2$ (\mathbf{Ln}_{16})

Crystals of \mathbf{Ln}_{16} were obtained by dissolving \mathbf{Ln}_6 in DMSO and layering with acetone. Briefly for yttrium, 43 mg of \mathbf{Y}_6 was dissolved in 0.5 mL DMSO with sonication and this solution was carefully pipetted into the bottom of a test tube containing acetone, and the two layers were left undisturbed to allow for slow mixing and crystallization. After 1 day, colorless crystals of \mathbf{Y}_{16} began to form on the sides of the test tube, and were collected after 2 days (41 mg, 78% yield). Anal calc. for $\text{Y}_{16}\text{O}_3(\text{OH})_{24}(\text{NO}_3)_{18}(\text{DMSO})_{17}(\text{H}_2\text{O})_{14}$: C, 8.93; H, 3.39; N, 5.51; Found: C, 8.84; H, 3.01; N, 5.26. (While the disordered crystal structure and symmetry perhaps suggests the composition of the title \mathbf{Y}_{16} compound, elemental analysis fits better for a solvated structure with only water and DMSO ligands/co-crystallized solvent. The core structure and counterions, based on charge balance, are not in doubt.)

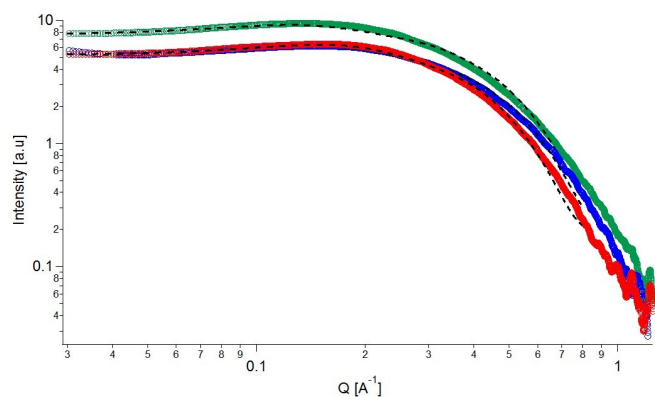


Figure S1. SAXS scattering curves for Ln_6 crystals dissolved in DMF (84 mg / mL). Er_6 (green), Ho_6 (blue) and Y_6 (red). Dotted black lines are curve fits to a model that assumes spherical particles and includes a structure factor due to inter-particle interactions

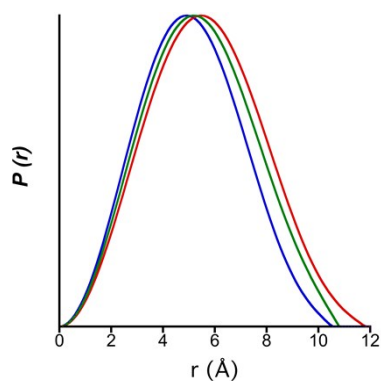


Figure S2. Pair Distance Distribution Function (PDDF) analysis of Ln_6 SAXS data; Er_6 (green), Y_6 (red) and Ho_6 (blue).

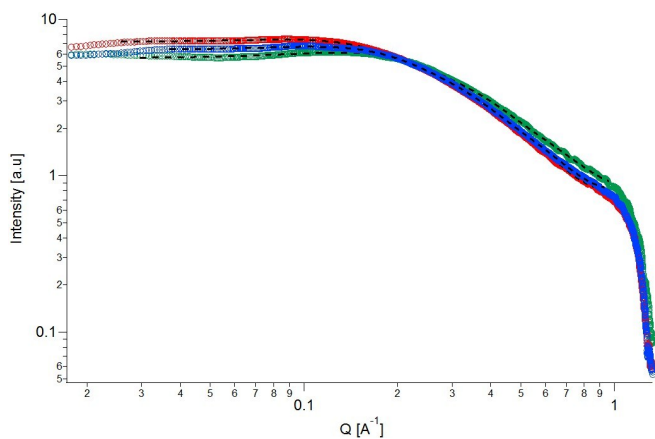


Figure S3. SAXS scattering curves for Ln_6 crystals dissolved in DMF (84 mg / mL). Gd_6 (green), Eu_6 (blue) and Sm_6 (red). Dotted black lines are curve fits to a model that assumes cylindrical particles and includes a structure factor due to inter-particle interactions.

Table S1. Calculated Form and Structural Factor Parameters from SAXS data of Ln_6 crystals dissolved in DMF

	Radius from cylindrical fit (\AA)	length from cylindrical fit (\AA)	η (distance between clusters, \AA)	φ (number of clusters in nearest neighbor sphere)
Gd_6	3.2	14.4	29.1	0.3
Eu_6	3.5	16.35	32.7	0.24
Sm_6	3.6	18.1	39	0.18

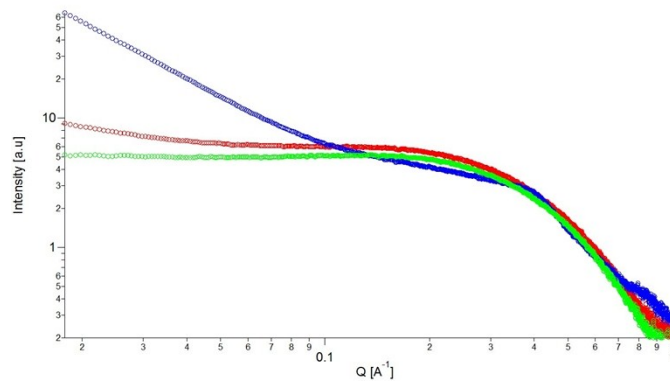


Figure S4. SAXS scattering curves of Y_6 crystals dissolved in DMF / H_2O mixtures (84 mg / mL). 0 % H_2O (green), 1 % H_2O (red) and 10 % H_2O (blue).

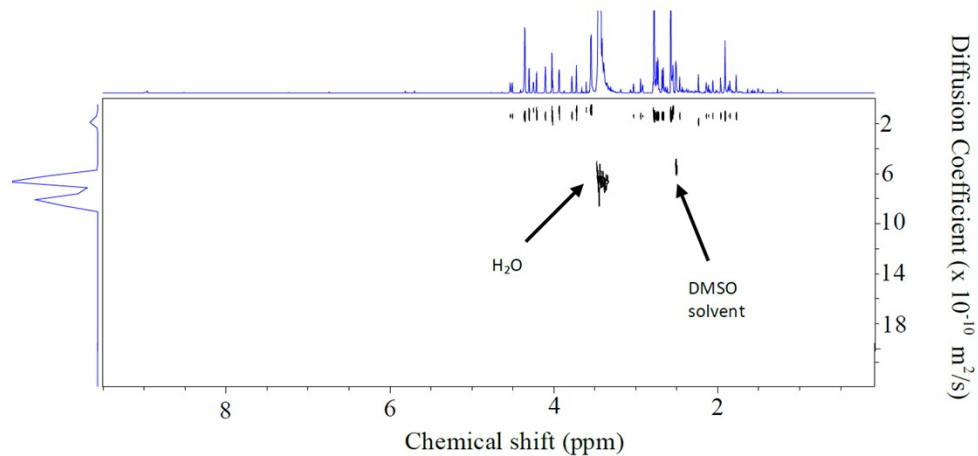


Figure S5. ^1H DOSY NMR of Y_6 immediately after dissolution, showing that all peaks have the same diffusion coefficient. The diffusion coefficient was calculated to be $8.47 \times 10^{-11} \pm 2.2 \times 10^{-11} \text{ m}^2/\text{s}$.

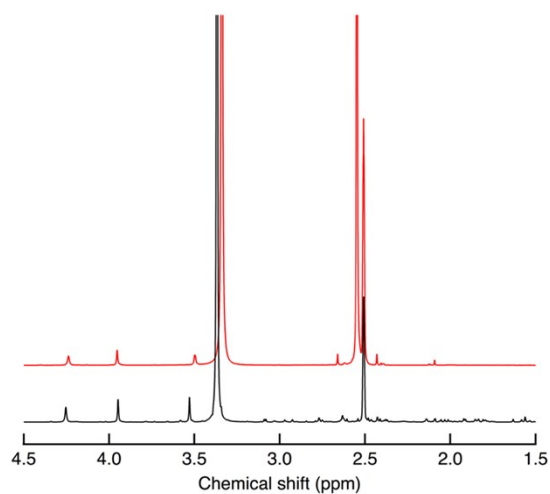


Figure S6. ^1H NMR spectra of solid Y_6 dissolved in DMSO-d_6 after 26 days (black) compared to the initial spectrum for Y_{16} (red) confirming that Y_6 , once dissolved in DMSO , converts to the previously unknown Y_{16} cluster.

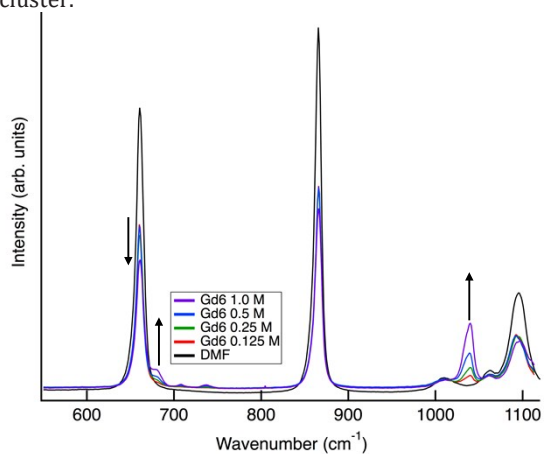


Figure S7. Solution-state Raman spectroscopy of Gd_6 in DMF , with the arrow direction corresponding to an increase in Gd_6 concentration.

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