

¹⁵N NMR spectrum

The measurement was performed with 0.7 ml of a saturated solution of **3** in DMSO, to which 70 mg of nearly isotopically pure (¹⁵NH₄)Br (98%) was added. The solvent was chosen because the interpretation of the spectra in water would otherwise have been more difficult due to an increased H⁺ exchange. The gradient selected ¹⁵N-HSQC spectrum was measured with the sensitivity enhanced version of the pulse sequence on a Bruker AVANCE 400 spectrometer, adjusted to a ¹H-¹⁵N coupling constant of 75 Hz. The measurement time was 14 h with 64 scans and 256 increments (see also: L. E. Kay, P. Keifer and T. Saarinen, *J. Amer. Chem. Soc.*, 1992, **114**, 10663-10665).

IR and Raman spectra

Compound 2

IR bands: ν/cm^{-1} (KBr pellet, some characteristic bands for 1700-500 cm^{-1}), $\approx 1737\text{sh}$, $\approx 1707\text{sh}$, $\approx 1681\text{sh}$ [$\nu_{\text{a}}(\text{C}=\text{O})$]; 1633s [$\delta(\text{H}_2\text{O})$]; 1400s [$\delta(\text{NH}_4)$]; 1327w, 1248w [$\nu_{\text{s}}(\text{C}-\text{O})$]; 974s, 943w [$\nu(\text{Mo}=\text{O})$]; 858m, 800s, 729s, 634w, 572s.

Characteristic Raman bands: ν/cm^{-1} (solid state, KBr dilution, $\lambda_{\text{e}} = 1064 \text{ nm}$): 944m [$\nu(\text{Mo}=\text{O})$]; 879s [$\nu_{\text{s}}(\text{O}_{\text{bri}} - \text{breathing}/\text{A}_{1\text{g}})$]; 374m; 309w.

Compound 3

IR bands: ν/cm^{-1} (KBr pellet, some characteristic bands for 1700-500 cm^{-1}); $\approx 1735\text{sh}$, $\approx 1705\text{sh}$, $\approx 1682\text{sh}$ [$\nu_{\text{a}}(\text{C}=\text{O})$]; 1622m [$\delta(\text{H}_2\text{O})$]; 1400s [$\delta(\text{NH}_4)$]; 1327w, 1269w [$\nu_{\text{s}}(\text{C}-\text{O})$]; 974s, 941w [$\nu(\text{Mo}=\text{O})$]; 856m, 802s, 729s, 634w, 572s.

Characteristic Raman bands: ν/cm^{-1} (solid state, KBr dilution, $\lambda_{\text{e}} = 1064 \text{ nm}$): 944m [$\nu(\text{Mo}=\text{O})$]; 879s [$\nu_{\text{s}}(\text{O}_{\text{bri}} - \text{breathing}/\text{A}_{1\text{g}})$]; 375m; 310w.

X-ray crystallography

Crystal data for 2: C₆₄ H₉₄₆ Mo₁₃₂ N₄₂ O₈₇₂, $M = 28926.7 \text{ g mol}^{-1}$, rhombohedral, space group $R\bar{3}$, $a = 32.6802(8)$, $c = 73.440(2) \text{ \AA}$, $V = 67926(3) \text{ \AA}^3$, $Z = 3$, $\rho = 2.121 \text{ g/cm}^3$, $\mu = 1.884 \text{ mm}^{-1}$, $F(000) = 42432$, crystal size = $0.20 \times 0.20 \times 0.12 \text{ mm}^3$. Crystals of **2** were removed from the mother liquor and immediately cooled to 188(2) K on a Bruker AXS SMART diffractometer (three circle goniometer with 1K CCD detector, Mo-K α radiation, graphite

monochromator; hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435 and 230 frames ($\phi = 0, 88$ and 180°) at a detector distance of 5.00 cm). A total of 136068 reflections ($1.66 < \theta < 26.99^\circ$) were collected of which 32868 reflections were unique ($R(\text{int}) = 0.0310$). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.10. The structure was solved with the program SHELXS-97 and refined using SHELXL-97 to $R = 0.0453$ for 26266 reflections with $I > 2\sigma(I)$, $R = 0.0614$ for all reflections; max./min. residual electron density 1.98 and $-1.19 \text{ e } \text{\AA}^{-3}$.

Crystal data for 3: $\text{C}_{48}\text{H}_{984}\text{Mo}_{132}\text{N}_{52}\text{O}_{852}$, $M = 28592.9 \text{ g mol}^{-1}$, rhombohedral, space group $R\bar{3}$, $a = 32.6616(8)$, $c = 73.307(3) \text{ \AA}$, $V = 67725(3) \text{ \AA}^3$, $Z = 3$, $\rho = 2.103 \text{ g/cm}^3$, $\mu = 1.886 \text{ mm}^{-1}$, $F(000) = 41988$, crystal size = $0.50 \times 0.40 \times 0.40 \text{ mm}^3$. Crystals of **3** were removed from the mother liquor and immediately cooled to $183(2) \text{ K}$ on a Bruker AXS SMART diffractometer (three circle goniometer with 1K CCD detector, Mo- K_α radiation, graphite monochromator; hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435 and 230 frames ($\phi = 0, 88$ and 180°) at a detector distance of 5.00 cm). A total of 111107 reflections ($1.47 < \theta < 27.00^\circ$) were collected of which 31558 reflections were unique ($R(\text{int}) = 0.0354$). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.10. The structure was solved with the program SHELXS-97 and refined using SHELXL-97 to $R = 0.0475$ for 25654 reflections with $I > 2\sigma(I)$, $R = 0.0641$ for all reflections; max./min. residual electron density 1.23 and $-0.96 \text{ e } \text{\AA}^{-3}$.

(SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen, 1997/2003; structure graphics with DIAMOND 2.1/3.0, <http://www.crystalimpact.com/> and with POV-Ray™ 3.6, <http://www.povray.org/>).

CCDC 297963 and 277334 contain the supplementary crystallographic data for **2** and **3** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

Analytical details

The chemical formulae of **2** and **3** refer to the maximum possible number of water molecules and are calculated from the respective cell volumes and the sum of volumes of all cell ingredients excluding those of the crystal water molecules. The given calculated values for C, N, H are related to a formula with 50 crystal water molecules less than given (note: **2** and **3** as

all similar compounds show slow weathering, *i.e.* loss of crystal water). The (small number of) disordered/encapsulated oxalic acid molecules in **2a** cannot be determined.

Additional information about the Hofmeister Series

- 1) The series describes, according to the original discovery, the order of effectiveness of different ions in stabilising a protein and their ability to salt the protein out.
- 2) Strongly hydrated ions considerably increase the difference between the hydrogen bond donating and accepting capacity of the linked water molecules resulting in the breakdown of the water network. Now it is evident that the understanding of the effects of cationic and anionic solutes on protein behaviour in solution which was originally considered by Hofmeister only phenomenologically, requires a deeper understanding of the interaction of water molecules with the specific solutes' architectures; see ref. 8 and M. Chaplin, Water Structure: <http://www.lsbu.ac.uk/water/>
- 3) The cation "behaviour" in the present type of nanocontainers^{5a} can be correlated with the (not fully understood) Hofmeister series while anions hydrate more strongly than cations as in case of the same ionic radius the hydrogen atoms can approach closer in anions (see: T. E. Creighton, *Proteins: Structures and Molecular Properties*, Freeman, New York, 2nd edn, 1997, pp. 156, 263–264, 295–296; A. A. Zavitsas, *J. Chem. Phys. B*, 2001, **105**, 7805).

Model calculations

A central (H₂O)₂NH₄⁺ triangular H-bond pattern with an average H-bond energy of -16 kJ mol⁻¹ is found embedded in a larger and much stiffer six-membered ring with an average H-bond energy of -81 kJ mol⁻¹.