Electronic supplementary information

A further step towards tuning the properties of metal-chalcogenide nanocapsules by replacing skeletal oxide by sulphide ligands

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1. Preparation of the aqua ion dimer \([\text{Mo}^{V} \text{O}_2(\mu-\text{O})(\mu-\text{S})(\text{aq})]^2+\)

The aqua ion dimer \([\text{Mo}^{V} \text{O}_2(\mu-\text{O})(\mu-\text{S})(\text{aq})]^2+\) was prepared as described in the literature.\(^1\)

After a sample of \(\text{Na}_2[\text{Mo}_2\text{O}_3\text{S(cys)}_2] \cdot 4 \text{H}_2\text{O}\) (3.0 g, 4.8 mmol) was dissolved in 1 M hydrochloric acid (30 mL), the solution was stirred for ~30 min, filtered and then passed through a Sephadex G-10 column (diameter 3 cm, length 50 cm), using 1 M hydrochloric acid as eluent. The second brown-yellow fraction (~200 mL), which contained the aqua ion \([\text{Mo}_2\text{O}_3\text{S(aq)}]^2+\), was neutralized partially with aqueous 1 M NaOH solution (150 mL) and then evaporated under reduced pressure until a volume of ~20 mL was obtained. The precipitate of NaCl was removed by filtration and the red filtrate was used for the synthesis of 1 (see text).

2. Pore dimensions

Each of the 20 pores of \({\{(\text{M}^{VI})\text{Mo}^{VI}_3\}\}_2\{\text{Mo}^{V}_2\}_30\)-type capsules is delineated by a ring of alternating \{\text{Mo}^{V}_2\} units and \{\text{M}^{VI}\} centers including the corresponding O, S atoms. Their size is limited by the positions of the three bridging atoms belonging to the three \{\text{Mo}^{V}_2\} units. In case of 2, the bridging oxide and sulphide ligands are found disordered over two positions with half occupancy. Four different types of pores, \textit{i.e.} \{\text{W}_3\text{Mo}_6\text{O}_9\}, \{\text{W}_3\text{Mo}_6\text{O}_8\text{S}\}, \{\text{W}_3\text{Mo}_6\text{O}_7\text{S}_2\} and \{\text{W}_3\text{Mo}_6\text{O}_6\text{S}_3\}, are in principle possible, the two extreme cases being depicted in Fig. S1.

In these two cases the triangle spanned by the three bridging atoms (\(X = \text{S} \text{ or } \text{O}\)) is approximately equilateral and a simple expectable estimation of the openings of possible pore scenarios is obtained as follows: the distances from the centers of X to the those of the triangles is equal to the sum of the van der Waals radii of X (1.50 Å for O and 1.80 Å for S)\(^2\) and the formal pore opening radii. Though the observed disorder affects the found S…S and O…O distances (as well as the Mo-O and Mo-S bond lengths) it is noteworthy that the respective estimated opening diameters of \(\text{ca.} \ 3.8\ \text{Å} \) and \(2.2\ \text{Å}\) for the two extreme (hypothetical) \{\text{W}_3\text{Mo}_6\text{O}_9\} and \{\text{W}_3\text{Mo}_6\text{O}_6\text{S}_3\} pores in 2a are in reasonable agreement with the corresponding values of the \{\text{W}^{VI}_{72}\text{Mo}^{V}_{60}\}\)-type Keplerates with \{\text{Mo}^{V}_2\text{O}_2(\mu-\text{O})_2\} (\text{ca.} \ 3.5\ \text{Å}^3\) and \{\text{Mo}^{V}_2\text{O}_2(\mu-\text{S})_2\} (\text{ca.} \ 2.4\ \text{Å}^4\) linkers. The openings of the \{\text{W}_3\text{Mo}_6\text{O}_6\text{S}\}\- and \{\text{W}_3\text{Mo}_6\text{O}_7\text{S}_2\}\-type pores should lie in between.
**Fig. S1** A rough estimate of possible pore sizes (approximate values in Å): Comparison of the {W$_3$Mo$_6$O$_8$S$_3$} (top) and {W$_3$Mo$_6$O$_9$} (bottom) rings/pores (the two possible extremes) in 2a not considering the consequences of the disorder of the bridging oxo and sulphido ligands (W green, Mo blue, O red, bridging O and S linker-type red and yellow, respectively, SO$_4^{2-}$ yellow tetrahedra).
3. IR spectroscopy

The IR spectra of 1 and 2 (Fig. S2) show the characteristic band pattern for the metal-oxide skeleton of the \{M^{VI}_{72}Mo^{V}_{60}\}-type Keplerates between 1000 and 400 cm\(^{-1}\), thus confirming the presence of the 12 pentagonal \{(W^{VI})W^{VI}_{5}\} units in an (approximate) icosahedral arrangement (for details see refs. 5 and 6). Additionally they show the characteristic features of (symmetrically) bridging acetate and sulphate ligands, respectively.\(^7\) The asymmetric and symmetric COO stretching modes are observed at 1537 and 1447 cm\(^{-1}\) in the spectrum in 1 while the characteristic band triplet based on the splitting of the triply-degenerate \(v_3\) stretching mode of \(SO_4^{2-}\) (caused by symmetry lowering from \(T_d\) to \(C_{2v}\)) is observed at 1189, 1134 and 1044 cm\(^{-1}\) in the spectrum of 2 (see ref. 8 for a related example). (Weak features between 1400 and 1550 cm\(^{-1}\) in the spectrum of 2 are assigned to vibrational bending modes of methylammonium cation.)

Regarding the characteristic absorption bands of the linkers in 1 and 2, it is worth noting that those caused by the asymmetric and symmetric Mo–O–Mo stretching modes are commonly observed at 735-765 and 430-480 cm\(^{-1}\) in dinuclear complexes with the \{Mo^{V}_{2}O_2(\mu-O)_2\} core; the corresponding linker stretching Mo–S–Mo modes are expected at ~460 and ~360 cm\(^{-1}\).\(^9\)–\(^11\) Correspondingly the spectra of both 1 and 2 show a fairly intense band at \textit{ca.} 715 cm\(^{-1}\) (see e.g. refs. 3, 4 and 12) which is consequently assigned to a Mo\(^{V}\)–O–Mo\(^{V}\) stretching mode; but no definite conclusion could be reached regarding the bands of the Mo\(^{V}\)–S–Mo\(^{V}\) stretching modes.
Fig. S2 IR spectra (KBr pellets) of compounds 1 (top) and 2 (bottom).
4. Raman spectroscopy

Fig. S3 Raman spectrum of an aqueous solution of 2 ($\lambda_{exc} = 785$ nm; see text for an explanation).
5. UV-Vis absorption spectroscopy

The electronic absorption spectra of all Keplerates of the type \( \{ \text{M}^{\text{VI}}_{72} \text{Mo}^{\text{V}}_{60} \} \) (M = Mo, W) in aqueous solution show an intense absorption band in the visible or near-UV region. The high intensity of these bands (> \( 10^5 \text{ mol}^{-1} \text{ L cm}^{-1} \)) as well as the shift to higher energy upon substitution of W (\( \lambda_{\text{max}} = 375 \text{ nm} \))3 for Mo (\( \lambda_{\text{max}} = 450 \text{ nm} \))6,12 are consistent with an assignment to a charge transfer transition from the (bonding) 4d electrons of the \( \{ \text{Mo}^{\text{V}}_{2} \} \) linkers to the pentagonal units. Hypsochromic shifts observed upon substitution of the \( \{ \text{Mo}^{\text{V}}_{2} \text{O}_2(\mu-\text{O})(\mu-\text{S}) \} \) (Fig. S4) and \( \{ \text{Mo}^{\text{V}}_{2} \text{O}_2(\mu-\text{S})_2 \} \)4 linkers by the \( \{ \text{Mo}^{\text{V}}_{2} \text{O}_2(\mu-\text{O})_2 \} \) ones may reflect the weak contribution of bridging sulphide ligands to the Mo–Mo bonding.13

![Aqueous solution UV/Vis electronic absorption spectrum of 2.](image)

**Fig. S4** Aqueous solution UV/Vis electronic absorption spectrum of 2.
5. References


