Electronic Supplementary Material (ESI) for Dalton Transactions

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 $[Mo^V_2O_2(\mu\text{-}O)(\mu\text{-}S)(aq)]^{2+}$

The aqua ion dimer $[Mo^V_2O_2(\mu\text{-}O)(\mu\text{-}S)(aq)]^{2+}$ was prepared as described in the literature.[1] After a sample of $Na_2[Mo_2O_3S(cys)_2] \cdot 4\ H_2O$ (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 $[Mo_2O_3S(aq)]^{2+}$, 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 $\{(M^{VI})Mo^{VI}_5\}_{12}\{Mo^V_2\}_{30}$-type capsules is delineated by a ring of alternating $\{Mo^V_2\}$ units and $\{M^{VI}\}$ centers including the corresponding O, S atoms. Their size is limited by the positions of the three bridging atoms belonging to the three $\{Mo^V_2\}$ 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, *i.e.* $\{W_3Mo_6O_9\}$, $\{W_3Mo_6O_8S\}$, $\{W_3Mo_6O_7S_2\}$ and $\{W_3Mo_6O_6S_3\}$, 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 = S or 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 *ca.* 3.8 Å and 2.2 Å for the two extreme (hypothetical) $\{W_3Mo_6O_9\}$ and $\{W_3Mo_6O_6S_3\}$ pores in **2a** are in reasonable agreement with the corresponding values of the $\{W^{VI}_{72}Mo^V_{60}\}$-type Keplerates with $\{Mo^V_2O_2(\mu\text{-}O)_2\}$ (*ca.* 3.5 Å[3]) and $\{Mo^V_2O_2(\mu\text{-}S)_2\}$ (*ca.* 2.4 Å[4]) linkers. The openings of the $\{W_3Mo_6O_8S\}$- and $\{W_3Mo_6O_7S_2\}$-type pores should lie in between.

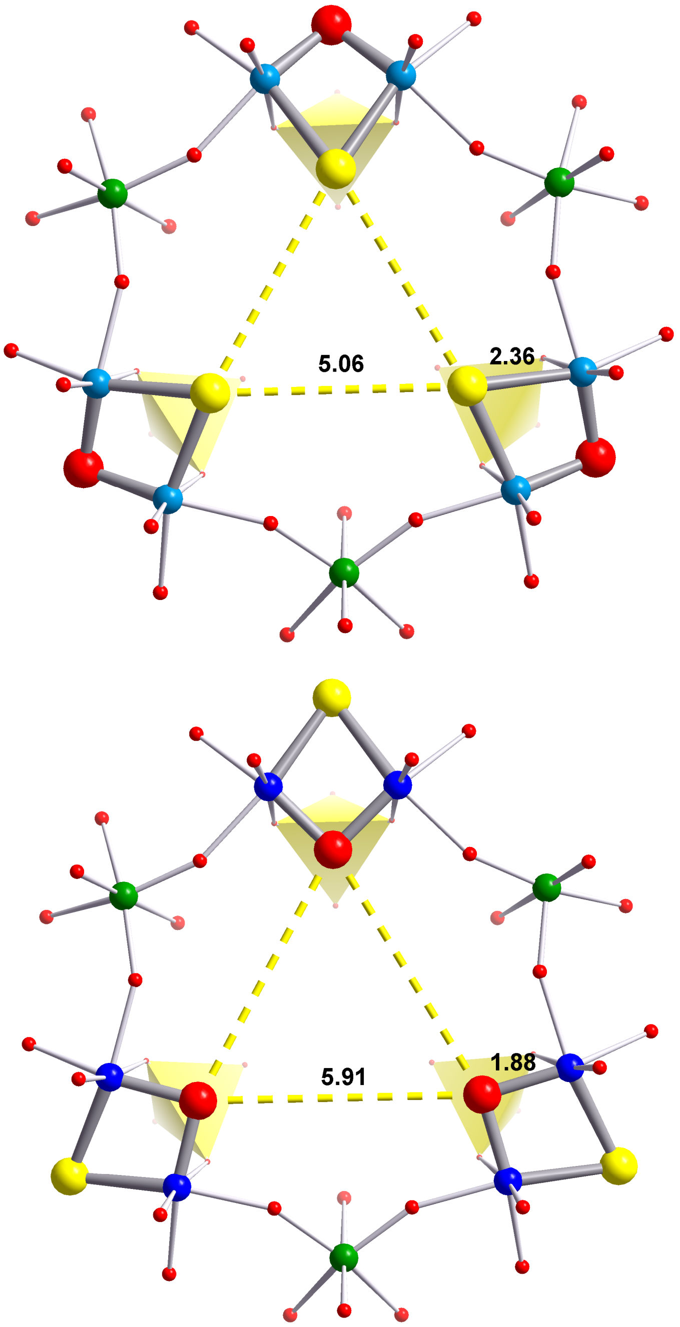

Fig. S1 A rough estimate of possible pore sizes (approximate values in Å): Comparison of the $\{W_3Mo_6O_6S_3\}$ (top) and $\{W_3Mo_6O_9\}$ (bottom) rings/pores (the two possible extremes) in **2a** not considering the consequences of the disorder of the bridging oxo and sulphido ligands (W green, Mo 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 ν_3 stretching mode of SO_4^{2-} (caused by symmetry lowering from T_d to 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 $\{Mo^{V}_2O_2(\mu\text{-}O)_2\}$ 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 *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.

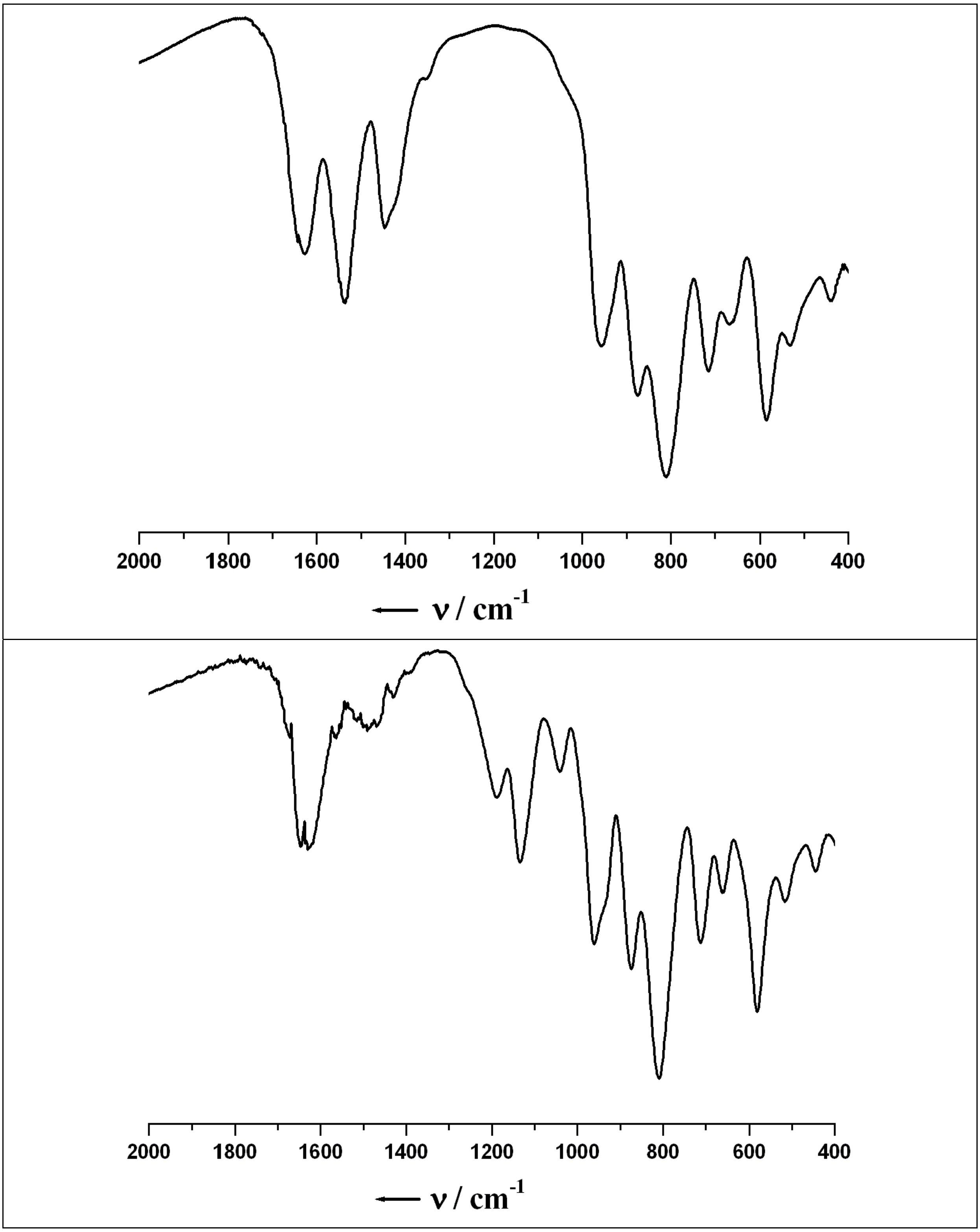

Fig. S2 IR spectra (KBr pellets) of compounds **1** (top) and **2** (bottom).

4. Raman spectroscopy

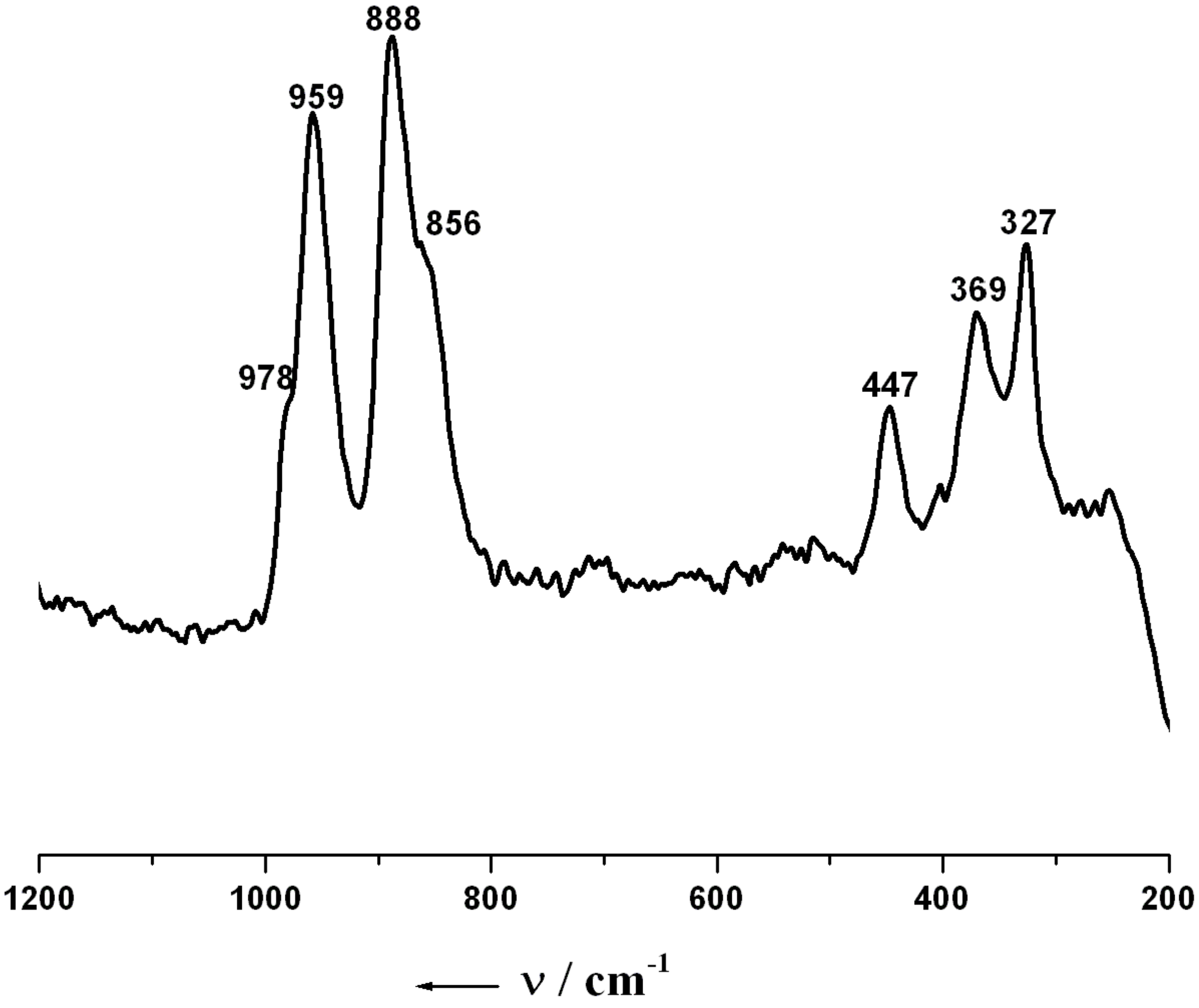

Fig. S3 Raman spectrum of an aqueous solution of **2** (λ_{exc} = 785 nm; see text for an explanation).

5. UV-Vis absorption spectroscopy

The electronic absorption spectra of all Keplerates of the type $\{M^{VI}_{72}Mo^{V}_{60}\}$ (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 mol^{-1} L cm^{-1}) as well as the shift to higher energy upon substitution of W (λ_{max} = 375 nm)[3] for Mo (λ_{max} = 450 nm)[6,12] are consistent with an assignment to a charge transfer transition from the (bonding) 4*d* electrons of the $\{Mo^{V}_2\}$ linkers to the pentagonal units. Hypsochromic shifts observed upon substitution of the $\{Mo^{V}_2O_2(\mu\text{-}O)(\mu\text{-}S)\}$ (Fig. S4) and $\{Mo^{V}_2O_2(\mu\text{-}S)_2\}$ [4] linkers by the $\{Mo^{V}_2O_2(\mu\text{-}O)_2\}$ ones may reflect the weak contribution of bridging sulphide ligands to the Mo–Mo bonding.[13]

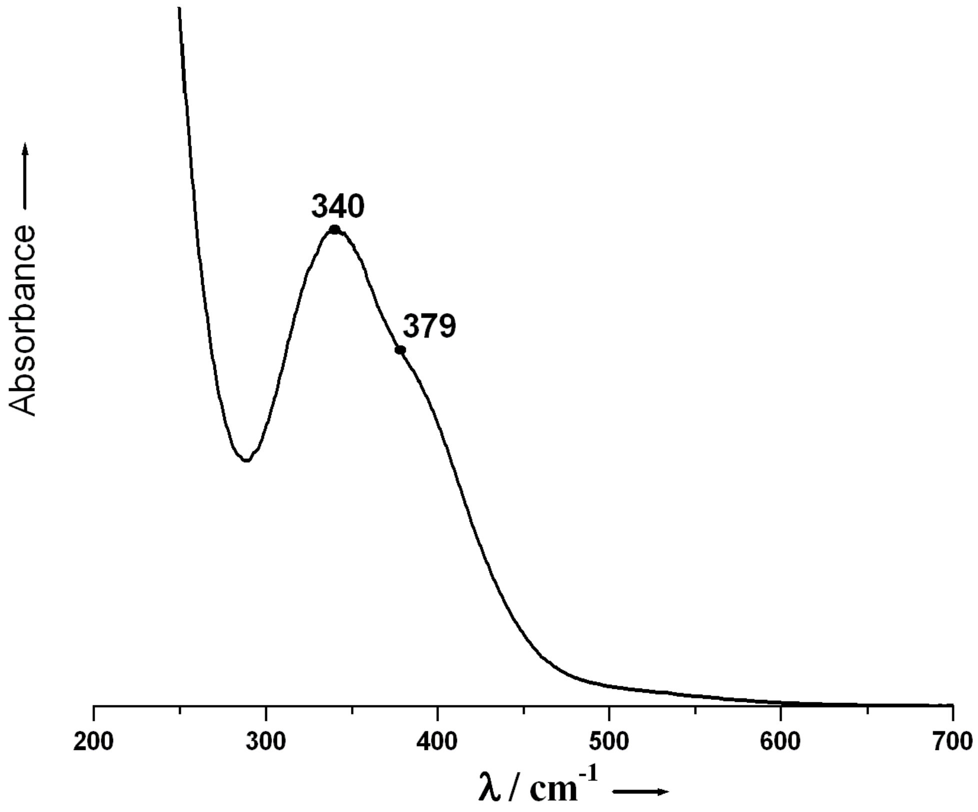

Fig. S4 Aqueous solution UV/Vis electronic absorption spectrum of **2**.

5. References

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