Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

Molecular recognition of Ca^{2+} cations by internal and external receptors/interfaces in a spherical porous molybdenum-oxide capsule: unusual coordination scenarios

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I) Vibrational Spectroscopy

Of the four normal vibration modes of the free SO_4^{2-} anion, spanning the irreducible representation $A_1 + E + 2F_2$ according to its T_d symmetry, only the two triply degenerate modes $\nu_3(F_2)$ and $\nu_4(F_2)$ are IR active and appear at ca. 1104 cm^{-1} and 613 cm^{-1}, respectively.[1a] Upon coordination, the symmetry of the SO_4^{2-} anion is lowered causing the splitting of the degenerate vibrations and a change in the selection rules. In the case of cluster **1a** the symmetry of the coordinated SO_4^{2-} anion is C_{2v} in accordance with its bridging bidentate coordination and all four vibration modes are expected to appear in the IR spectrum of **1** while the ν_3 mode which appears as a characteristic 1192/1138/1040 cm^{-1} triplet.

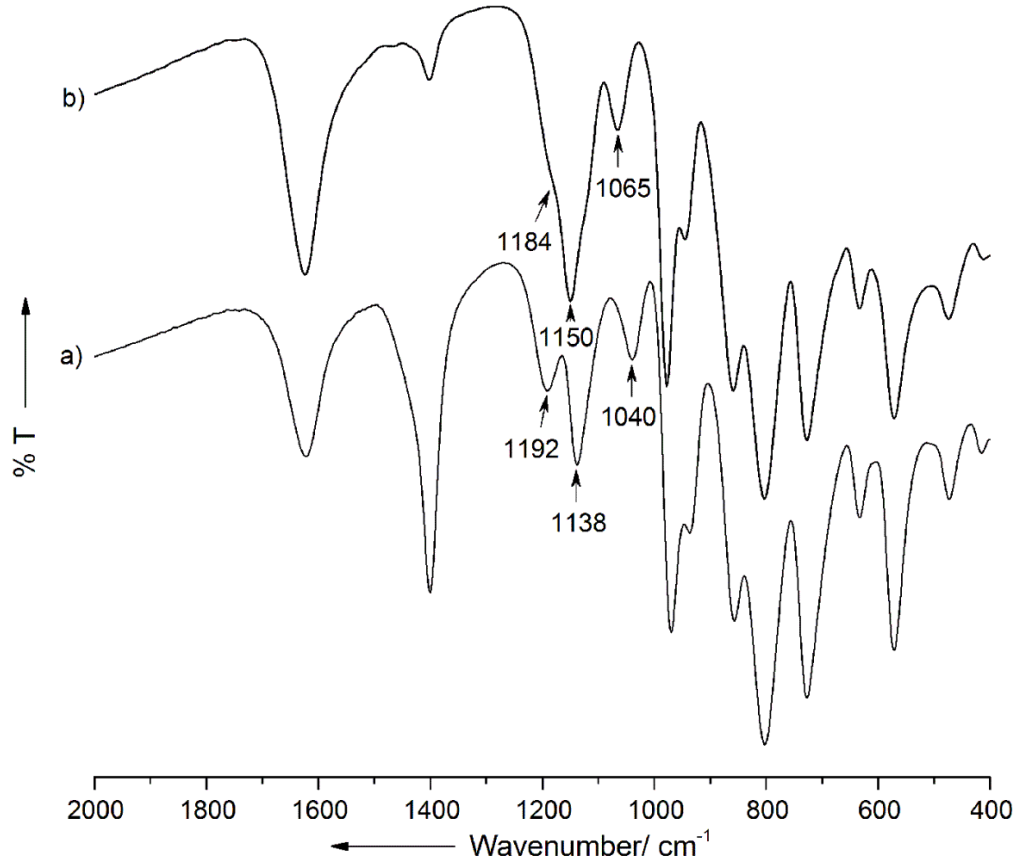

Fig. S1 IR spectra (KBr pellets) of a) **1**, and b) **2** in the 2000–400 cm^{-1} spectral region. The bands assigned to the $\nu_{as}(SO_4)$ mode, in both a) and b), are indicated by arrows.

II) Further Structural Information: Water in the Pores

As the detailed description is very difficult in the present case because of disordered SO_4^{2-} ligands we avoid to refer to it. Anyhow the interesting situation of water guests in the pores is precedented (see, e.g., the interesting butyrate capsule; for details see SI of Ref. 2).

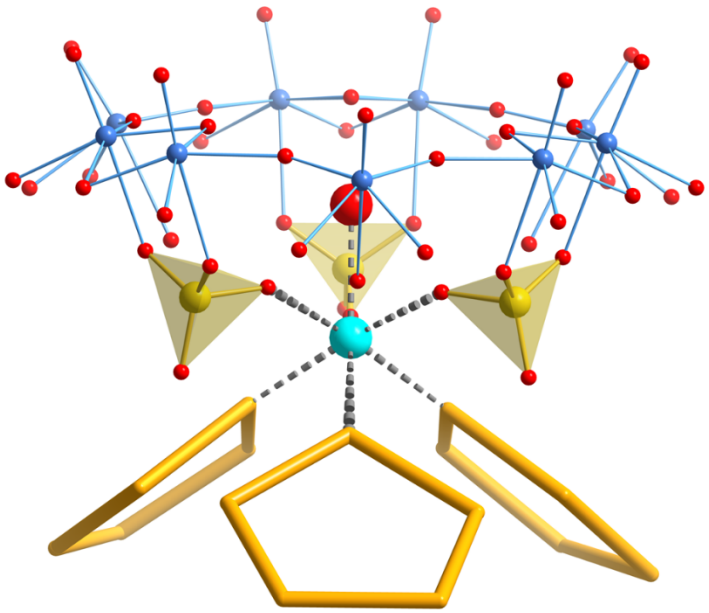

Fig. S2 The side view of the extended pore channel segment showing the coordination environment of the confined Ca^{2+} cation (cyan sphere) spanned by the O-atoms of the sulphate ligands (yellow tetrahedra), pore channel water (enlarged red sphere) and three oxygen atoms belonging to three $(H_2O)_5$ pentagons (yellow) of the $Ca_{20}\{H_2O\}_{60} \equiv Ca_{20}\{(H_2O)_5\}_{12}$ "water assembly". Other colour codes: Mo blue, O red, S yellow.

References

1 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., Wiley, New York, 1986, Part II, pp. 139; Part III, pp. 248–251.

2 C. Schäffer, H. Bögge, A. Merca, I. A. Weinstock, D. Rehder, E. T. K. Haupt and A. Müller, *Angew. Chem., Int. Ed*. 2009, **48**, 8051-8056 (see Supporting Information).