

Exploring the Thermochromism of Sulfite-Embedded Polyoxometalate Capsules

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SUPPORTING INFORMATION

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1. Experimental

Two salts of $[\alpha\text{-Mo}_{18}\text{O}_{54}(\text{SO}_3)_2]^{4-}$ were prepared according to previously published synthesis procedures [1, 2]: $(n\text{Bu}_4\text{N})_6[\alpha\text{-Mo}_{18}\text{O}_{54}(\text{SO}_3)_2][\text{Mo}_6\text{O}_{19}]$ (**1**), used for temperature-dependent single-crystal X-ray crystallography, and $(\text{Pn}_4\text{N})_4[\alpha\text{-Mo}_{18}\text{O}_{54}(\text{SO}_3)_2]\cdot\text{CH}_3\text{CN}$ (**2**) for temperature-dependent IR/Raman and UV/Vis spectroscopy.

[1] D.-L. Long, P. Kögerler, L. J. Farrugia, L. Cronin, *Angew. Chem. Int. Ed.* **2003**, *42*, 4180 – 4183.

[2] C. Baffert, J. F. Boas, A. M. Bond, P. Kögerler, D.-L. Long, J. R. Pilbrow, L. Cronin, *Chem. Eur. J.* **2006**, *12*, 8472 – 8483.

2. Crystallography

Single crystal X-ray crystallography was performed using a crystal of **1** at 100 K and 293 K. Figure S1 shows the structures of **1a** in **1** at 100 K and 293 K with anisotropic displacement ellipsoids of 50 % probability. The two single-crystal crystal structure data sets exhibit virtually identical geometries (Figure S2). Table S1 summarizes average bond distances, which underline the similarity of the two structures. Figure S3 shows the structure of **1a** at emphasizing the O_c (O of corner-sharing MO₆ groups) and O_e (O of edge-sharing MO₆ groups) positions.

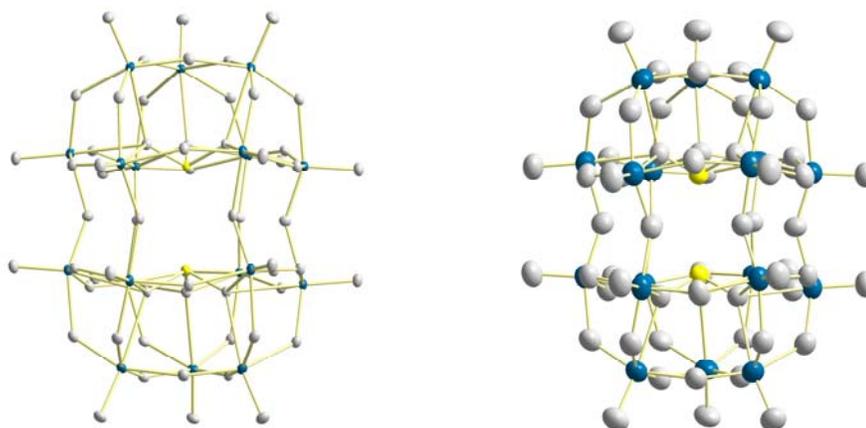
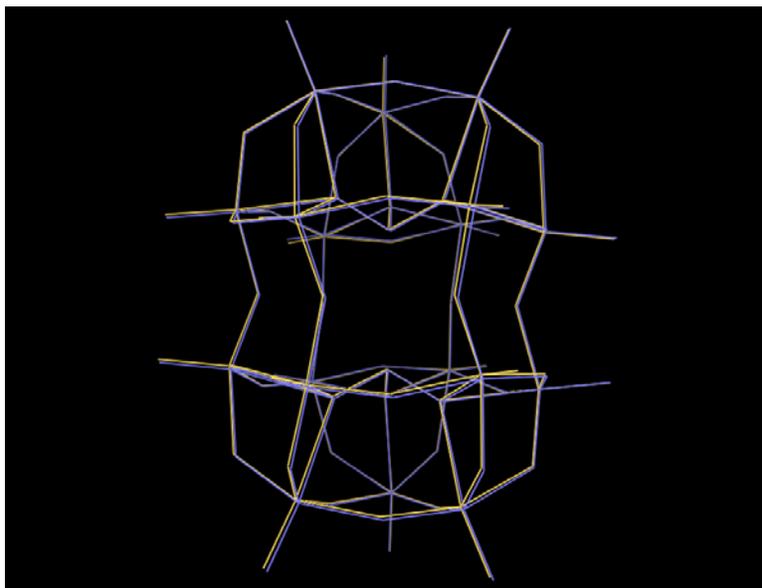


Figure S1. Structure of **1a** at 100 K (left) and 293 K (right) with anisotropic displacement ellipsoids set to 50 % probability (Mo: blue, O: grey, S: yellow).

Table S1 Summary of average value of thermal parameters ($1/3\text{Tr}(U_{ij})$) at 100 K and 293 K.

Temperatures	Mo / Å ²	O / Å ²	S / Å ²
100 K	0.00973	0.01296	0.00865
293 K	0.05348	0.05850	0.04367

a)



b)

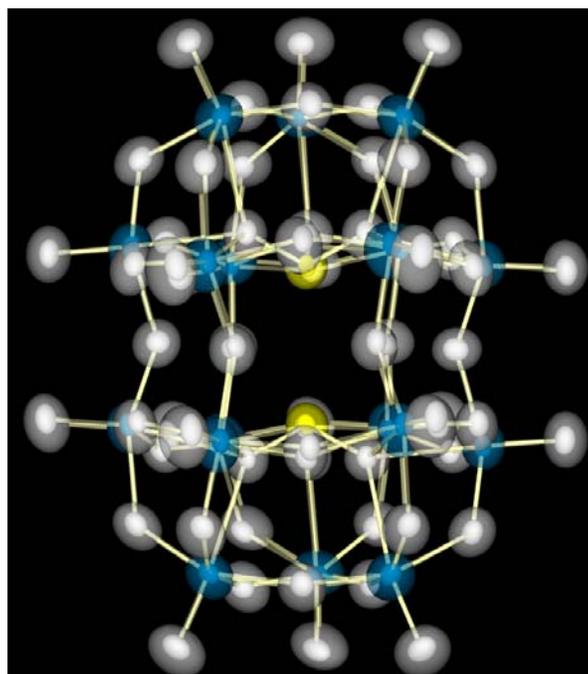


Figure S2. Top: Composite plots of the geometries of cluster **1a** at 100 K (yellow) and 293 K (blue). Bottom: Overlay plot with thermal displacement ellipsoids (80 % probability) at 100 and 293 K (Mo: blue, O: grey, S: yellow).

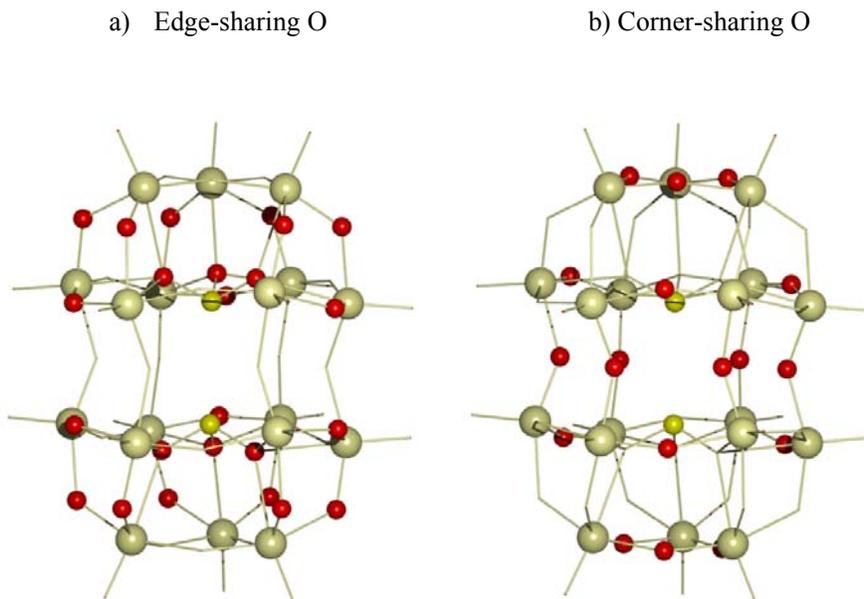


Figure S3. Plots of cluster **1a** emphasizing edge-sharing O_c (left) and corner-sharing O_c (right) positions (red spheres).

Table S1. Average Mo-O bond distances in **1a**.

Bond		Mo- O_c -Mo	Mo- O_c	
			Mo- O_c -Mo	Mo- O_c (S)-Mo
Mo-O distance / Å	100 K	1.91	1.93	2.48
	293 K	1.91	1.92	2.48

4. UV-vis spectra

UV-vis spectra of **2** were recorded at various temperatures. Diffuse reflection and transmission spectra were measured using pure **2** powder and cast film on quartz substrate, respectively.

Figure S4 shows UV-vis spectra characterized as a diffuse reflection (350 nm - 600 nm at liquid nitrogen temperature and room temperature) and transmission spectra (200 nm – 900 nm from 50 K to 300 K). The widening band by ~8 nm is observed in diffuse reflection spectra measured at room temperature compared to low temperature. On the other hand, transmission spectra show growth of shoulder around 340 nm with increasing in temperature.

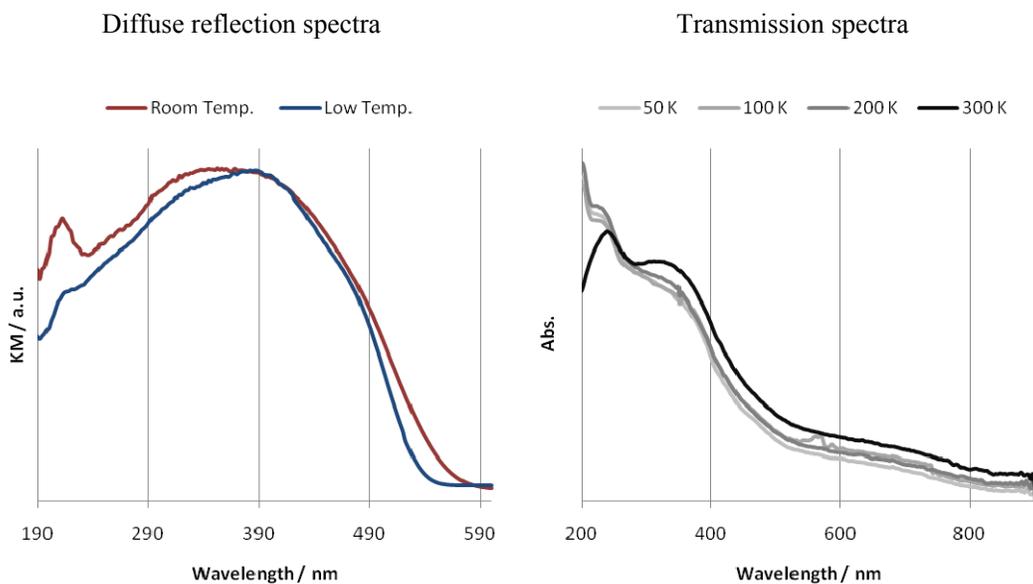


Figure S4. Uv-vis spectra of **2**.

4. IR and Raman spectra

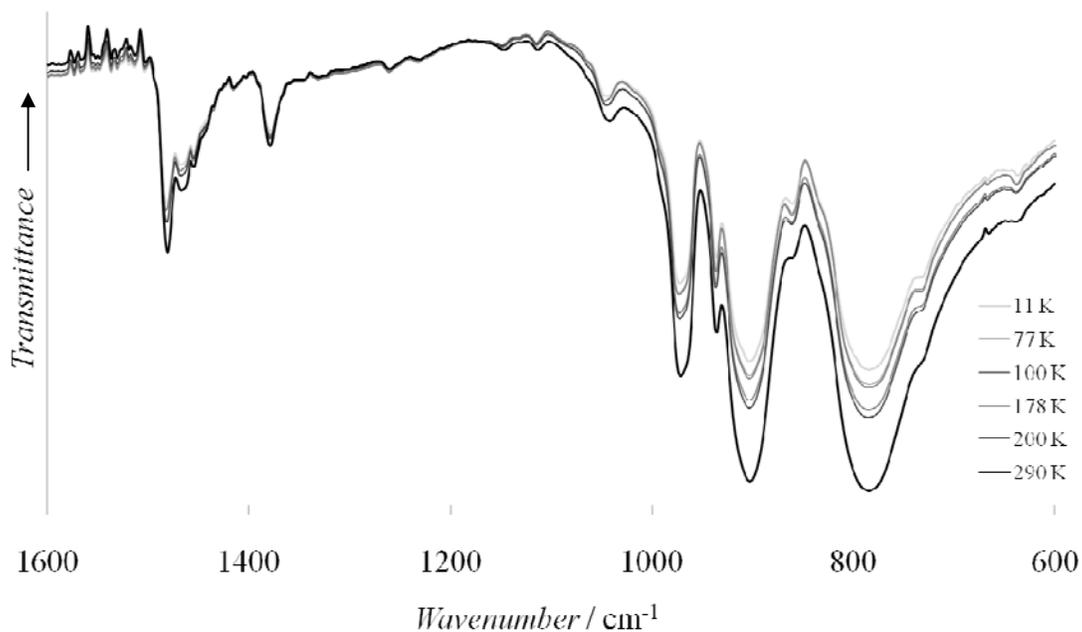


Figure S5. IR spectra of **2** (KBr pellets) for temperatures ranging from 11 K to 290 K.

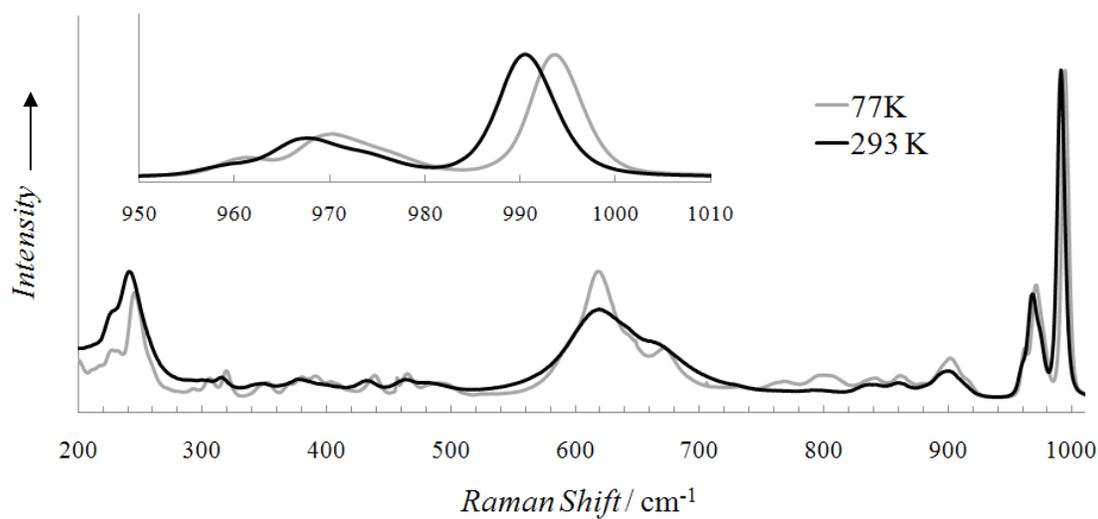


Figure S6. Raman spectra of **2** at 77 K and 293 K. Inset: magnified 950 cm^{-1} to 1010 cm^{-1} range.