Electronic Supplementary Material (ESI) for Dalton Transactions

Synthesis, structure and host-guest properties of $(Et_4N)_2[Sn^{IV}Ca^{II}(chloranilate)_4]$, a new type of robust microporous coordination polymer with a 2D square grid structure

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Supplementary Information

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S1 Further crystallographic details

Modelling of CS_2 within $1{\cdot}2CS_2$

Two significant peaks of electron in the asymmetric unit were assigned as sulfur atoms with partial occupancies. The crystal symmetry results in a total of eight positions for the sulfur atoms within each square hole; separations betweens various pairs of sulfur atoms are consistent with the inclusion of CS_2. The carbon atoms of the CS_2 molecules could not be unambiguously identified. The assigned positions of the sulfur atoms in a cavity is represented in Figure S1. The use of the "SQUEEZE" routine with PLATON supported the inclusion of a single CS_2 molecule in each square cavity with the program indicating a total of 34.5 electrons per square cavity; one CS_2 per cavity would correspond to 38 electrons.

Modelling of CH_3CN and H_2O within $1{\cdot}2CH_3CN{\cdot}0.5H_2O$

Peaks of residual electron density were consistent with the presence of acetonitrile within the crystal channels. Three significant peaks of electron density within the asymmetric unit were assigned as the carbon and nitrogen atoms of a disordered acetonitrile molecule within each of the square cavities. Site occupation factors were applied to the atoms consistent with each acetonitrile molecule occupying one of four symmetry-related sites. Constraints were placed on the CC and CN bonds in keeping the expected bond distances for acetonitrile. Following assignment of the acetonitrile, the highest peak of residual electron density was located in the centre of the channels but situated halfway between the planes of anionic networks, level with the nitrogen atom of the tetramethylammonium cations. This peak was assigned as the oxygen atom of a water molecule and was refined with a site occupancy of 25%. No hydrogen atoms were assigned in either the acetonitrile

or the water molecules. A representation of the solvent molecules in the structure is presented in Figure S2.

a)

b)

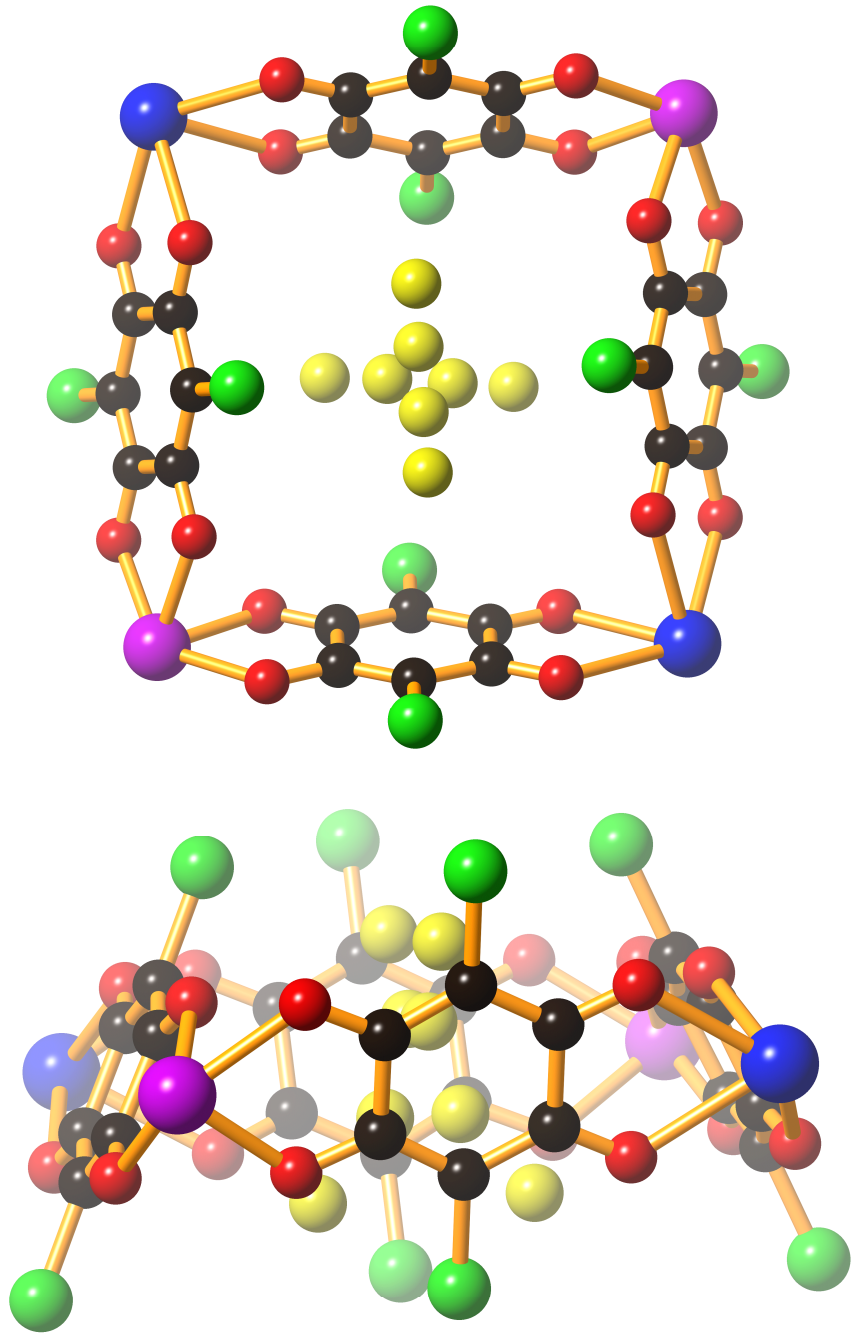


Figure S1. A representation of the positions of the sulfur atoms from CS_2 within the square cavity of the anionic coordination network in the structure of $1 \cdot 2CS_2$; a) a view from normal to the anionic network; b) a view from almost parallel to the plane of the anionic network.

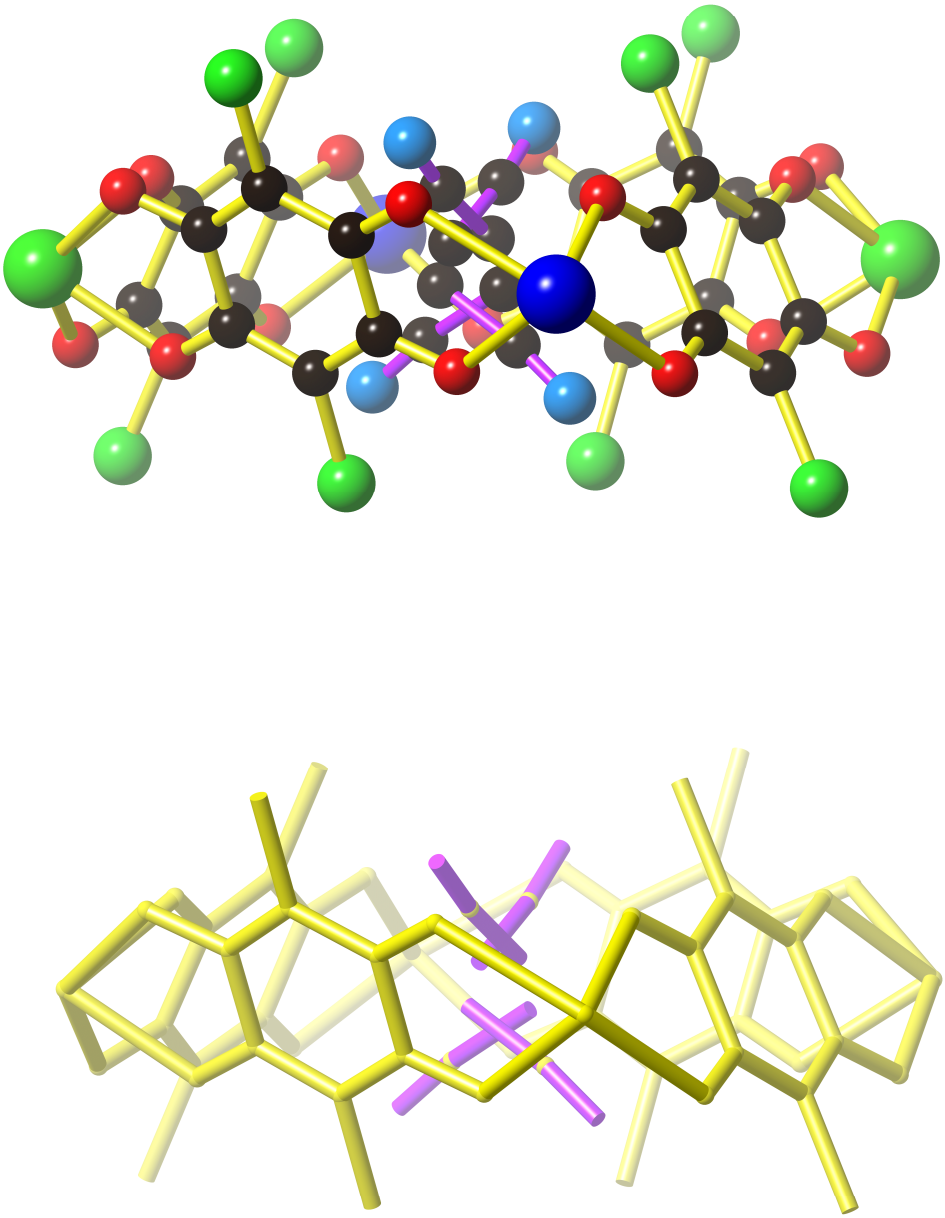


Figure S2. Representations of the disordered acetonitrile molecules in the square cavities of **1**·2CH_3CN·0.5H_2O; a) ball and stick representation; b) stick representation.

S2 Mossbauer measurements

Mossbauer spectroscopy clearly indicates the absence of Sn(II) in the compound. All tin is present as Sn(IV). At T = 93.6 K, IS = 0.0441(2), QS = 1.049(2), line width = 0.784(5) all in mm / sec.

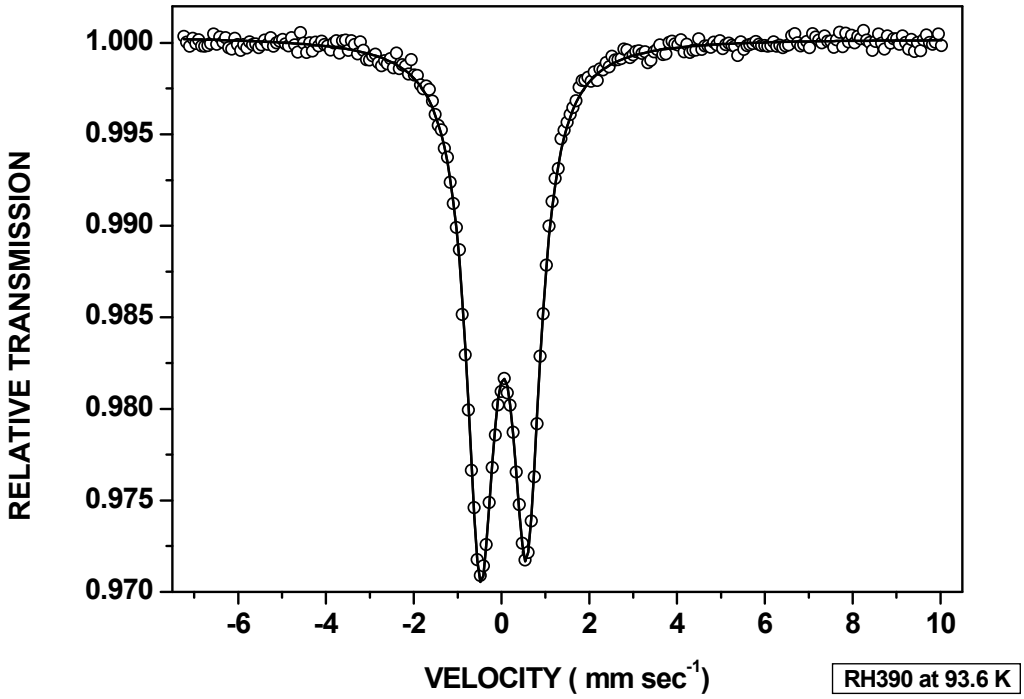
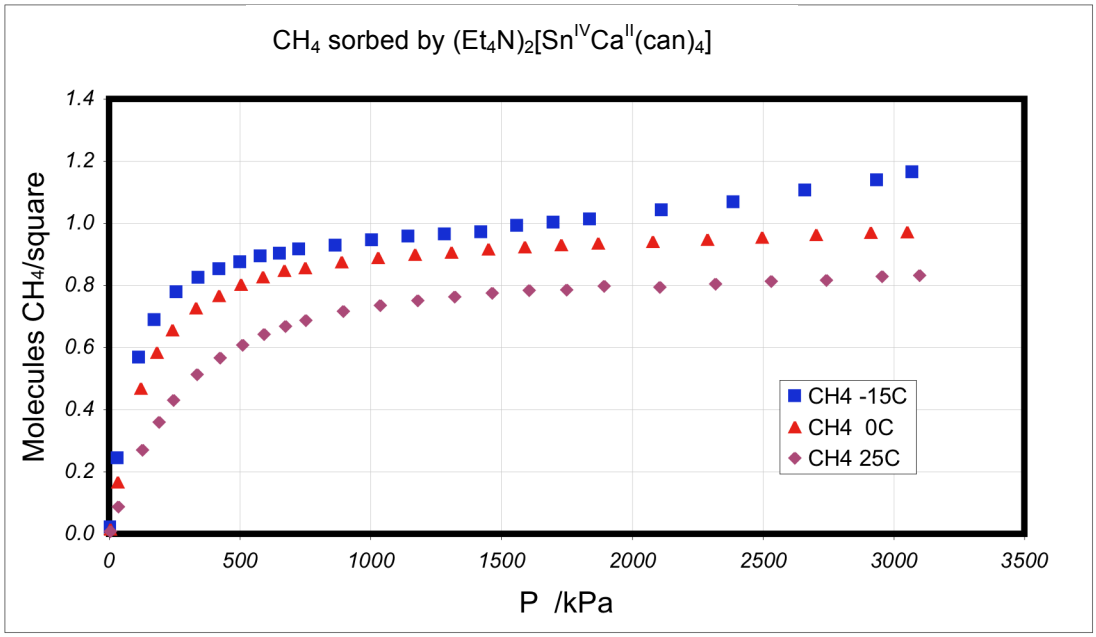


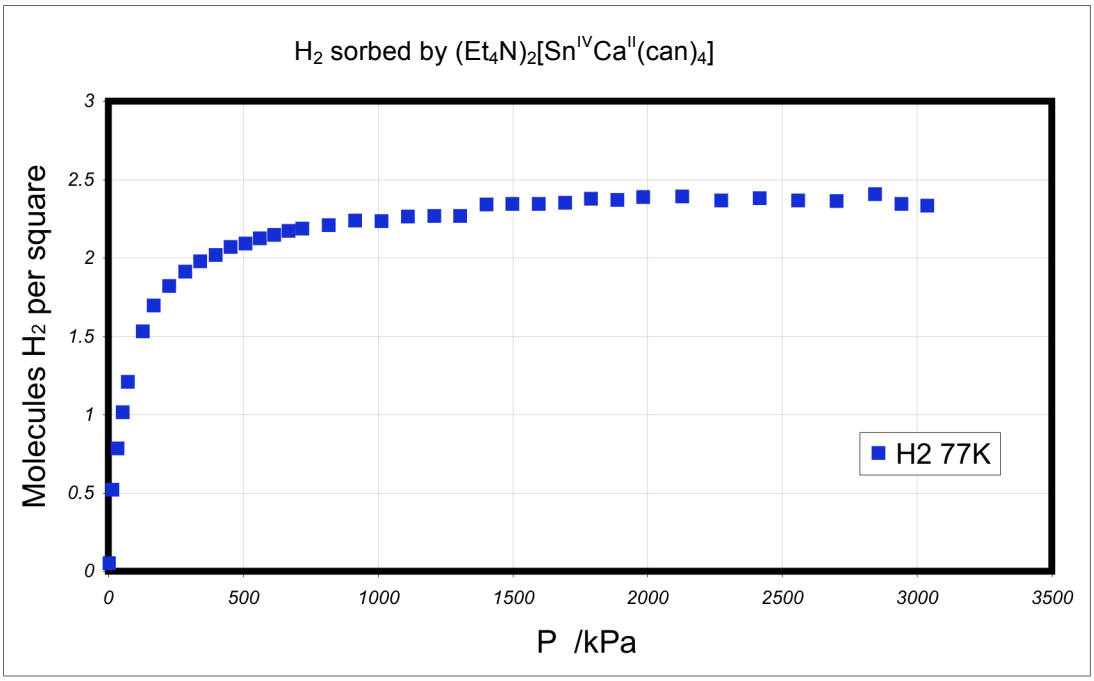
Figure S3. Mossbauer spectrum of $(Et_4N)_2[Sn^{IV}Ca^{II}(can)_4]$ at 93.6 K

S3 Gas sorption Isotherms

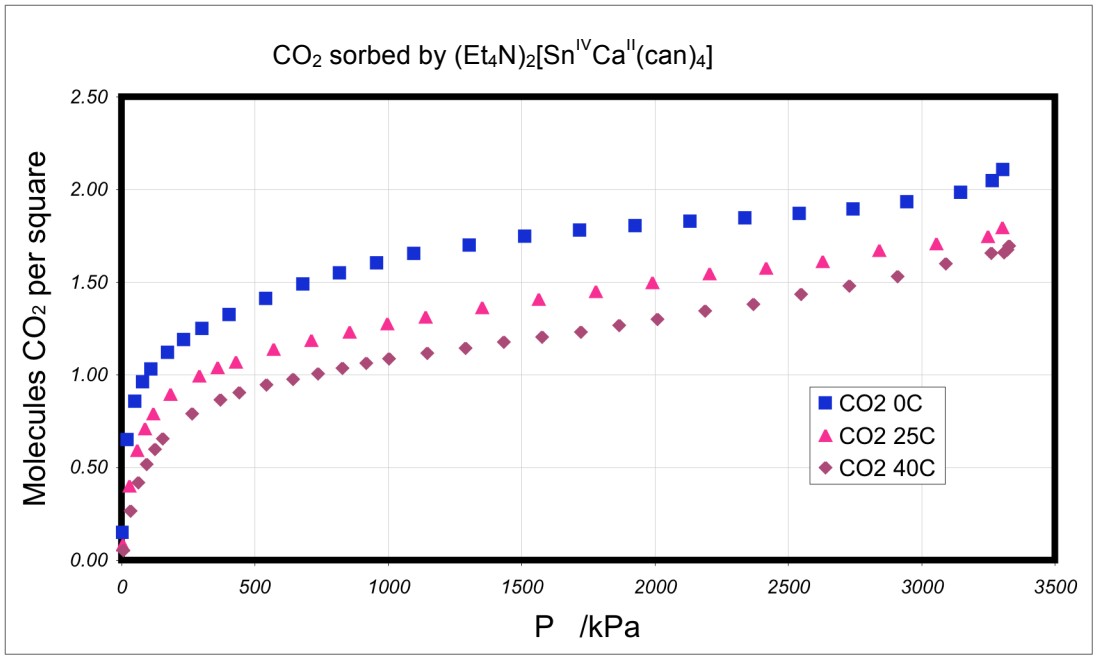
a)



b)



c)



d)

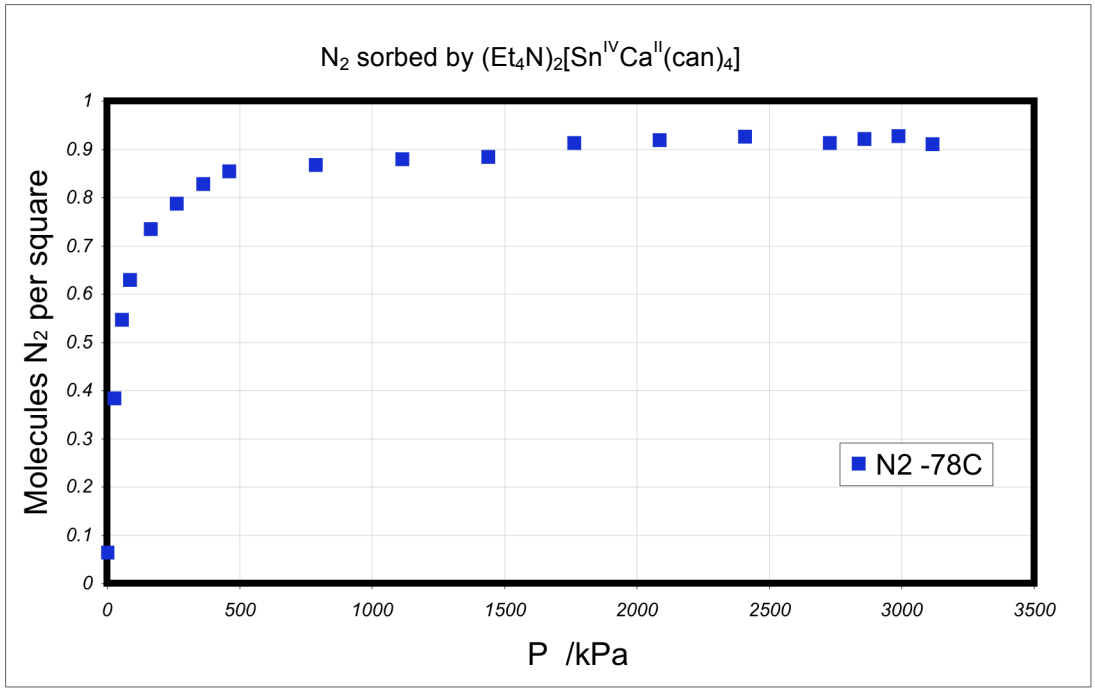


Figure S4. Isotherms for the sorption of a) methane b) hydrogen c) carbon dioxide and d) nitrogen. The vertical axis in each graph represents the number of molecules of gas sorbed per $[NEt_4][Ca_{0.5}Sn_{0.5}(can)_2]$ formula unit, which corresponds to a single "square" within the anionic network.

S4 Thermogravimetric trace for 1.