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$(CN_3H_6)_4[Zn_3(SeO_3)_5]$: The First Organically Templated Selenite**

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An astonishing variety of inorganic networks templated by organic species have been reported over the last 10 years.[1] A great deal of attention has been paid to the structure-directing role of the organic species,[2] and the structural effect of variously coordinated cations, for example distorted octahedral vanadium[3] and pyramidal tin(II).[4] Less exploratory work has been carried out on the "anionic" part of the inorganic network, and most groups reported so far (phosphate,[5] germanate,[6] etc.) invariably adopt tetrahedral coordination. The possibilities of incorporating the pyramidal $[HPO_3]^{2-}$ hydrogen phosphite group into extended structures templated by *inorganic*, alkaline earth cations was explored a few years ago.[7] Herein we report the synthesis, crystal structure, and some properties of $(CN_3H_6)_4[Zn_3(SeO_3)_5]$, the first organically templated phase to contain the pyramidal selenite $[SeO_3]^{2-}$ ion.

$(CN_3H_6)_4[Zn_3(SeO_3)_5]$, which is built up from 13 framework atoms, consists of layers of distorted ZnO_4 tetrahedra and SeO_3 groups, sharing vertices. The two distinct zinc atoms both form four Zn-O-Se bonds to selenium atom neighbors resulting in average Zn1–O and Zn2–O bond lengths of 1.950(4) and 1.972(4) Å, respectively. Zn2 has twofold rotational symmetry. The three crystallographically distinct selenium(IV) atoms adopt their characteristic pyramidal coordination, with the lone pair of electrons presumably directed towards the fourth tetrahedral vertex. Average Se–O bond lengths of 1.679(4), 1.682(4), and 1.691(4) Å result for Se1, Se2, and Se3, respectively, in good agreement with previous studies.[8] The terminal Se1–O7 and Se3–O8 bonds are short ($d = 1.648(4)$ and 1.648(5) Å, respectively), indicating that the oxygen atoms are not protonated.[8] Se3 occupies a crystallographic mirror plane. The average Zn-O-Se bond angle of the six bridging O atoms is 124.9° (spread of values: 119.3(2) – 127.7(2)°).

The connectivity of the ZnO_4 and SeO_3 units in $(CN_3H_6)_4[Zn_3(SeO_3)_5]$ results in infinite, anionic layers of stoichiometry $[Zn_3(SeO_3)_5]^{4-}$ which propagate normal to [010]. A novel grouping of three adjacent ZnO_4 tetrahedra

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doubly capped by a pair of Se2 atoms (as selenite groups) is present (Figure 1). This results in an exceedingly large O5-Zn2-O5 bond angle of 130.4(2)°, where O5 forms the Zn2-O-Se2 bridge. The layers are completed by nominal (Se1 – O7)

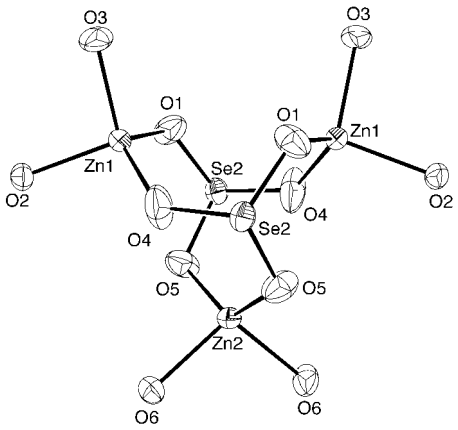

Figure 1. Structure of the $[Zn_3Se_2O_{12}]^{10-}$ fragment in $(CN_3H_6)_4[Zn_3(SeO_3)_5]$, showing the top-and-bottom capping of three adjacent ZnO_4 groups by Se2 (50% thermal ellipsoids).

groups which link the $Zn_3Se_2O_{12}$ moieties in the [100] direction, and nominal (Se3 – O8) pairs which fuse these groupings in the [001] direction (Figure 2). This connectivity results in bifurcated 12-ring windows (i.e., windows built up from 12 polyhedral building blocks, six ZnO_4 and six SeO_3 groups) in the (101) plane. The maximum dimensions of this slightly squashed 12-ring, measured from O atom to O atom, are approximately 8.4×8.9 Å. The Se3 lone pairs point into this 12-ring.

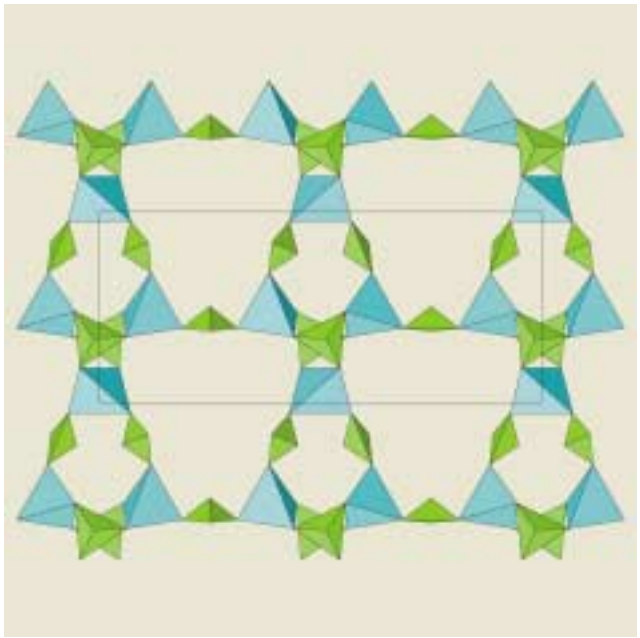

Figure 2. Polyhedral view down [010] of the sheet topology of $(CN_3H_6)_4[Zn_3(SeO_3)_5]$. The ZnO_4 groups are light blue, and the SeO_3 lone pair of electrons is represented by the fourth vertex of the flattened, light green, pseudo-tetrahedron.

The C–N distances for the propeller-shaped $[CN_3H_6]^+$ ions are typical.[9] The C2-centered guanidinium cation displays a striking templating effect in occupying the 12-ring window of the Zn/Se/O layer and bonding to it by way of N–H···O hydrogen bonds (Figure 3). The C1- and C3-centered guanidinium cations serve to bridge the inorganic layers in the [010] direction (Figure 4). Eleven of the twelve symmetry-independent guanidinium hydrogen atoms are involved in

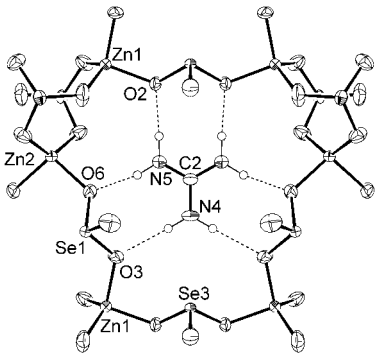

Figure 3. View approximately down [010] of a 12-ring window in $(CN_3H_6)_4[Zn_3(SeO_3)_5]$ showing the templating effect of the guanidinium cation, with the proposed N–H···O hydrogen bonds indicated by dotted lines. Note the Se3 lone pair of electrons projecting into the 12-ring window.

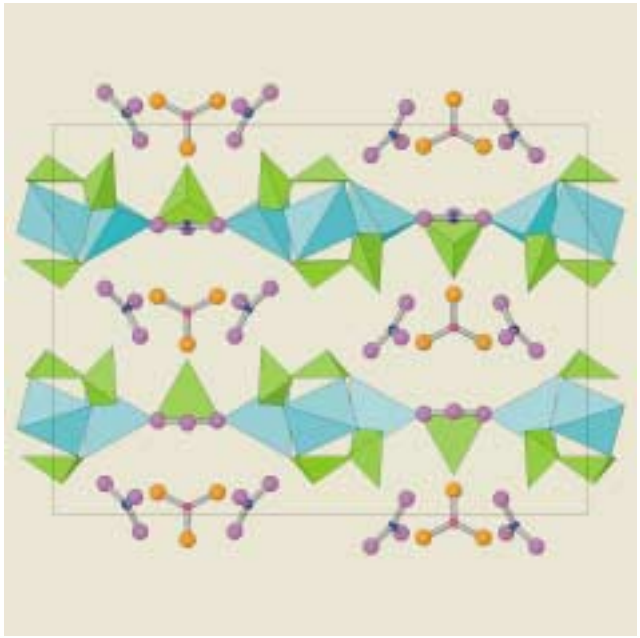

Figure 4. View down [100] of the $(CN_3H_6)_4[Zn_3(SeO_3)_5]$ structure showing the sandwich-motif of alternating inorganic and organic layers (inorganic color scheme as for Figure 2). For clarity, the C1-centered guanidinium cation is colored (C: blue; N: purple) as is the C3-centered species (C: red; N: orange).

N–H···O hydrogen bonds, assuming a maximum H···O bond length of 2.3 Å. Based on geometrical positioning of the H atoms [d(N–H) = 1.00 Å], these H···O contacts vary in length from 1.91 to 2.29 Å. Seven of the acceptor oxygen atoms form parts of Zn-O-Se bridges and the two terminal Se–O groups accept two hydrogen bonds each.

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The $(CN_3H_6)_4[Zn_3(SeO_3)_5]$ structure is completely different to those of previously characterized "inorganic" zinc selenites, all of which contain a dense network of ZnO_6 octahedra and $(H)SeO_3$ pyramids.[10] The 12-ring templating effect of the C2-centered guanidinium cation may be likened to its effect in templating polyhedral 12-rings (six ZnO_4 and six PO_4 tetrahedra) in zincophosphate (ZnPO) frameworks,[11] although the overall structures of the ZnPO materials are completely different to that of the title compound. $(CN_3H_6)_4[Zn_3(SeO_3)_5]$ is the first member of a family of organically templated selenites which we will describe in more detail in the near future.

Experimental Section

Synthesis: Guanidinium carbonate (1.80 g, 10 mmol), ZnO (0.81 g, 10 mmol), SeO_2 (2.22 g, (20 mmol), and H_2O (20 mL) were added to a PTFE bottle, shaken well, and placed in a 95 °C oven. The bottle was vented and recapped after 1 h. An essentially quantitative yield of intergrown transparent slabs (longest dimension up to 1 mm) of $(CN_3H_6)_4[Zn_3(SeO_3)_5]$ was recovered by vacuum filtration after 7 days.

Properties: A simulation based on the $(CN_3H_6)_4[Zn_3(SeO_3)_5]$ single-crystal structure was in excellent agreement with X-ray powder data, indicating phase purity and high crystallinity. Thermogravimetric analysis/differential thermal analysis (TGA/DTA) (ramp at 10 °K min^{-1} to 900 °C in air) for $(CN_3H_6)_4[Zn_3(SeO_3)_5]$ revealed the onset of a multistage 72 % weight loss at ~200 °C, which was complete by ~580 °C. Strong endothermic transitions at ~205, ~270, and ~570 °C were apparent. The weight loss of ~23 % occurring between ~200 °C and ~280 °C probably corresponds to loss of the guanidine template molecules (calcd 22.0 %). The overall weight loss is in fair agreement with a scheme involving the loss of all the organic species and selenium (as SeO_2) to result in a residue of $3 \times ZnO$ (calcd 77 %). The FTIR spectrum for $(CN_3H_6)_4[Zn_3(SeO_3)_5]$ revealed strong peaks at 3344 and 1671 cm^{-1}, corresponding to guanidinium N–H stretches and C–N/C=N stretches, respectively. Elemental analysis was satisfactory (%): calcd: C 4.48, H 2.26, N 15.69; found: C 4.11, H 2.23, N 14.59.

Structure determination: A crystal of $(CN_3H_6)_4[Zn_3(SeO_3)_5]$ (broken fragment, dimensions $\sim 0.27 \times 0.12 \times 0.11$ mm) was selected for data collection on a Bruker SMART 1000 CCD diffractometer (graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 300$ K): orthorhombic cell parameters from 4753 reflections ($4.6° < 2\theta < 50°$), 16466 reflections scanned ($2° < 2\theta < 50°$). After merging ($R_{Int} = 0.055$), 1830 of the 2429 unique reflections were considered observed [$I > \sigma(I)$]. An absorption correction was applied with SADABS[12] (min., max. equivalent transmission factors = 0.496, 0.862). The structure was solved by direct methods using SHELXS,[13] refined by full-matrix least squares using CRYSTALS,[14] and illustrated using ORTEP[15] and ATOMS.[16] Hydrogen atoms associated with the guanidinium cations were placed geometrically and refined by riding. Final residuals: $R(F) = 0.026$, $R_w(F) = 0.028$.

Crystal data: $(CN_3H_6)_4[Zn_3(SeO_3)_5]$, $M_r = 1071.25$, orthorhombic, space group *Pbcm* (no. 57), $a = 8.9007(4)$, $b = 15.0771(7)$, $c = 20.5096(9)$ Å, $V = 2752.3(4)$ Å^3, $Z = 4$, $\mu = 92.9$ cm^{-1}, $\rho_{calcd} = 2.586$ g cm^{-3}, $F(000) = 2048$. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411298.

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Correlation of the Topology of the Electron Density of Pyrite-Type Transition Metal Sulfides with Their Catalytic Activity in Hydrodesulfurization**

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Transition metal sulfides (TMSs) are an important class of catalysts that are stable under the severe conditions of sulfo-reductive hydroprocessing of petroleum-based feedstocks.[1, 2] Systematic experimental[2, 3] and theoretical[2–5] studies on the hydrodesulfurization (HDS) activity towards dibenzothiophene (DBT) of various metal sulfide catalysts have shown that the strength of the metal–sulfur bonding plays an important role in the HDS process. Two different models for assessing the M–S bond strength have been developed.[2, 5] In the model developed by Topsøe et al.,[2] the M–S bond energy is obtained from the bulk modulus of the metal and the degree of filling of the TMS d band (calculated by ab initio methods). This model predicts that HDS activity is inversely correlated with M–S bond strength. Hence, the highest activity is

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