SAND2000-1275J

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JUN 07 2000
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Synthesis, Structure and Properties of $(CN_3H_6)_4 \cdot Zn_3(SeO_3)_5$, the First Organically-Templated Selenite**

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[**] This work is supported by the US Department of Energy under contract DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US DOE.

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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] In this paper we report the synthesis, crystal structure, and some properties of $(CN_3H_6)_4{\cdot}Zn_3(SeO_3)_5$, the first organically-templated phase to contain the pyramidal selenite $[SeO_3]^{2-}$ anion.

$(CN_3H_6)_4{\cdot}Zn_3(SeO_3)_5$, 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 make four Zn–O–Se bonds to selenium atom neighbours resulting in average Zn1–O and Zn2–O bond distances of 1.950 (4) and 1.972 (4) Å, respectively. Zn2 has 2-fold 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 distances 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 (Table 1), indicating that they 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°.

The connectivity of the ZnO_4 and SeO_3 units in $(CN_3H_6)_4{\cdot}Zn_3(SeO_3)_5$ 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 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] 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.

The C–N distances for the propeller-shaped $[CN_3H_6]^+$ cations 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 12 guanidinium hydrogen atoms are involved in 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 H bonds each.

The $(CN_3H_6)_4{\cdot}Zn_3(SeO_3)_5$ 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. $(CN_3H_6)_4{\cdot}Zn_3(SeO_3)_5$ is the first member of a family of organically templated selenites which we will describe in more detail in the near future.

Keywords: organic templating · hydrothermal synthesis · zinc selenite · crystal structure

Experimental Procedure

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

Properties: A simulation based on the $(CN_3H_6)_4{\cdot}Zn_3(SeO_3)_5$ single crystal structure was in excellent agreement with X-ray powder data, indicating complete phase purity and high crystallinity. TGA/DTA (ramp at 10 °C/min to 900 °C in air) for $(CN_3H_6)_4{\cdot}Zn_3(SeO_3)_5$ revealed the onset of a multi-stage 72% weight loss at ~200 °C, which was complete by ~580 °C. Strong endothermic transitions at ~205 °C, ~270 °C, and ~570 °C were apparent. 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 × ZnO (calc. 77%). The FTIR spectrum for $(CN_3H_6)_4{\cdot}Zn_3(SeO_3)_5$ revealed a strong peak at 3344 cm^{-1}, corresponding to N–H stretches, and a strong peak at 1671 cm^{-1}, corresponding to C=N stretches. Elemental analysis (Galbraith Laboratories) xxxxxx.

Structure Determination: A crystal of $(CN_3H_6)_4{\cdot}Zn_3(SeO_3)_5$ (broken fragment, dimensions ~0.27 × 0.12 × 0.11 mm) was selected for data collection on a Bruker SMART 1000 CCD diffractometer (graphite-monochromated Mo $K\alpha$ radiation, λ = 0.71073 Å, T = 300 K): orthorhombic cell parameters from 4753 reflections (4.6° < 2θ < 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: $(CN_3H_6)_4 \cdot Zn_3(SeO_3)_5$, $M_r = 1071.25$, orthorhombic, space group *Pbcm* (No. 57), $a = 8.9007$ (4) Å, $b = 15.0771$ (7) Å, $c = 20.5096$ (9) Å, $V = 2752.3$ (4) Å^3, $Z = 4$, $\mu = 92.9$ cm^{-1}, $\rho_{calc} = 2.586$ g cm^{-3}, $F(000) = 2048$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-_____.

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Figure Captions

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

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

Figure 3: View approximately down [010] of a 12-ring window in $(CN_3H_6)_4{\cdot}Zn_3(SeO_3)_5$ 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 projecting into the 12-ring window.

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

Table 1: Selected Bond Distances(Å) and Angles(deg) for $(CN_3H_6)_4 \cdot Zn_3(SeO_3)_5$

Zn1-O1	1.943(4)	Zn1-O2	1.979(3)
Zn1-O3	1.959(4)	Zn1-O4	1.918(4)
Zn2-O5 × 2	1.958(4)	Zn2-O6 × 2	1.986(4)
Se1-O3	1.699(4)	Se1-O6	1.691(4)
Se1-O7	1.648(4)	Se2-O1	1.696(4)
Se2-O4	1.666(4)	Se2-O5	1.685(4)
Se3-O2 × 2	1.713(3)	Se3-O8	1.648(5)
C1-N1	1.303(7)	C1-N2	1.320(7)
C1-N3	1.326(7)	C2-N4	1.35(1)
C2-N5 × 2	1.316(6)	C3-N6	1.34(1)
C3-N7 × 2	1.323(6)		

Zn1-O1-Se2	124.7(2)	Zn1-O2-Se3	119.29(19)
Zn1-O3-Se1	122.4(2)	Zn1-O4-Se2	135.4(3)
Zn2-O5-Se2	120.1(2)	Zn2-O6-Se1	127.7(2)

Justification for Publication in *Angew. Chem. Int. Ed.*

Organically-templated inorganic networks are currently of great interest as evidenced by the recent review by Cheetham *et al.* (ref. 1 above) in *Angew. Chem. Int. Ed.* The title compound is of interest for several reasons:

- It is the first organically-templated phase to contain the pyramidal selenite group as part of the inorganic network. The resulting $(CN_3H_6)_4 \cdot Zn_3(SeO_3)_5$ structure is completely different to those of any known "pure inorganic" selenites.

- The doubly-capped $[Zn_3Se_2O_{12}]^{10-}$ group is unique and displays extreme distortion of the nominal tetrahedral O–Zn–O bond angles.

- One of the templating guanidinium cations shows a particularly nice "fit" in a framework 12-ring window, which compares with its somewhat similar behavior in templating zincophosphate networks.

Short text for table of contents:

The organically-templated $(CN_3H_6)_4{\cdot}Zn_3(SeO_3)_5$ structure is completely different to that of any "inorganic" selenite. One of the guanidinium cations displays a particularly clear template effect in occupying a 12-ring window and bonding to the inorganic network by way of N–H···O hydrogen bonds.