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Synthesis, Structure Analysis, and Characterization of a New Thiostannate, $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$

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A new thiostannate, $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$, was synthesized from $SnCl_4$, Na_2S, and dodecylamine (DDA) in the ethanol−water two-solvent system at room temperature. First a suspension was obtained. With increasing crystallization time, single crystals up to several millimeters in size were found at the bottom of the vessel. The compound was characterized by single-crystal X-ray diffraction, solid state ^{119}Sn CPMAS NMR and ^{13}C CPMAS NMR, IR absorption spectroscopy, and thermal analysis. The crystal data are $a = 7.533(2)$ Å, $b = 10.162(2)$ Å, $c = 21.688(4)$ Å, $\alpha = 101.22(3)°$, $\beta = 90.76(3)°$, $\gamma = 101.82(3)°$, triclinic, space group $= P\bar{1}$, and $Z = 1$. The structure consists of one $[Sn_2S_6]^{4-}$ anion, four *n*-dodecylammonium cations, and two water molecules per unit cell. The $[Sn_2S_6]^{4-}$ dimers are formed by two edge-sharing $[SnS_4]$ tetrahedra. The hydrocarbon chains of the cations are straight with the chain direction running parallel to [001]. The chains are in van der Waals contact to each other with the nitrogen atoms pointing in opposite directions for neighboring chains. The positions of all hydrogen atoms were determined; in particular three positions were found which may suggest that the nitrogen atoms are protonated to form cationic groups. The nonorganic constituents of the structure, i.e., anions, water molecules, and ammonium groups, interact to form an infinite layer-like unit parallel to (001).

During the past two decades, the synthesis of new chalcogenide solids such as thiogermanates and thiostannates has received much attention.[1−8] Various synthesis routes have successfully been used to crystallize thiostannates. The starting phases are either molten salts as in the case of $Na_6Sn_2S_7$[1] and $Na_4Sn_3S_8$,[2] aqueous solutions for $Na_4Sn_2S_6\cdot 14H_2O$[3] and $Na_4SnS_4\cdot 14H_2O$,[4] or organic solutions as in the case of $(Et_4N)_2[Sn(S_4)_3]_{0.4}[Sn(S_4)_2(S_6)]_{0.6}$ (Et_4N = tetraethylammonium),[5] for example. Organic cations are now common reactants for the formation of thiostannates; recently the preparation of $(CHAH)_4Sn_2S_6$ (CHAH = cyclohexylammonium), $(DABCOH)_2Sn(S_4)_2(S_6)$ (DABCOH = diazabicyclo[2.2.2]octane), and $(DABCOH)_2Sn(S_4)_3$ was published.[6] The different thiostannates contain a variety of anions like isolated Sn_2S_6 dimers,[3,6] Sn_2S_6 sheets,[1] Sn_3S_7 sheets,[7] and Sn_2S_5 frameworks[8] illustrating the complex crystal chemistry of materials based on tin sulfide.

In 1992, scientists at Mobil successfully synthesized the novel family of mesostructured silica-based materials called M41S. Hexagonal MCM-41, cubic MCM-48, and lamellar MCM-50 were obtained by using cationic surfactants such as cetyltrimethylammonium cations.[9,10] Then, much work was performed on the synthesis of mesostructured materials based on various oxides following pathways involving different interactions between the surfactant (S) and the inorganic part (I).[11−13] For instance, the S^+I^- and $S^+X^-I^+$ interactions were used to prepare mesoporous silica in basic and strongly acidic solutions, respectively.[11] Moreover, the utilization of the covalent interaction (S−I) led to hydrothermally stable mesostructured transition metal oxides with a specific surface area of over 500 m^2/g.[13] Compared with the development of oxide mesostructured materials, little attention has been paid to the preparation of mesostructured materials based on sulfides. A lamellar and a mesoporous tin(IV) sulfide were reported by Huo et al.[11] and Ozin,[14] respectively. Anderson et al.[15] described the synthesis of a mesostructured lamellar molybdenum sulfide. More recently we published an extensive study of two mesostructured tin(IV) sulfides obtained at room temperature in the presence of cetyltrimethylammonium cations.[16,17] Tin was found to be

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(1) Krebs, B.; Schiwy, W. *Z. Anorg. Allg. Chem.* **1973**, *393*, 63.
(2) Jumas, J. C.; Philippot, E.; Maurin,M. *J. Solid State Chem.* **1975**, *14*, 152.
(3) Krebs, B.; Pohl, S.; Schiwy,W. *Z. Anorg. Allg. Chem.* **1972**, *393*, 241.
(4) Schiwy, W.; Pohl, S.; Krebs, B. *Z. Anorg. Allg. Chem.* **1972**, *402*, 77.
(5) Müller, A.; Schimanski, J.; Römer, M.; Bögge, H.; Baumann, F. W.; Eltzner, W.; Krickemeyer, E.; Billerbeck, U. *Chimica* **1985**, *39*, 25.
(6) Jiang, T.; Ozin, G. A.; Bedard, R. L. *Adv. Mater.* **1994**, *6*, 860.
(7) Jiang, T.; Ozin, G. A.; Bedard, R. L. *Adv. Mater.* **1995**, *7*, 166.
(8) Liao, J. H.; Varotsis, C.; Kanatzidis, M. G. *Inorg. Chem.* **1993**, *32*, 2453.
(9) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1991**, *359*, 710.
(10) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
(11) (a) Huo, Q.; Margolese, D. I.; Ciesla, U.; Demuth, D. G.; Feng, P.; Gier, T. E.; Sieger, P.; Firouzi, A.; Chmelka, B. F.; Schüth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176. (b) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.
(12) Tanev, P. T.; Pinnavaia, T. J. *Science* **1995**, *267*, 865.
(13) (a) Antonelli, D. M.; Ying, J. Y. *Chem. Mater.* **1996**, *8*, 874. (b) Antonelli, D. M.; Nakahira, A.; Ying, J. Y. *Inorg. Chem.* **1996**, *35*, 3126.
(14) Ozin, G. A. *Supramol. Chem.* **1995**, *6*, 125.
(15) Anderson, M. T.; Newcomer, P. *Mater. Res. Soc. Symp. Proc.* **1995**, *371*, 117.
(16) Li, J.; Delmotte, L.; Kessler, H. *Chem. Commun.* **1996**, 1023.
(17) Li, J.; Kessler, H.; Delmotte, L. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 665.

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Table 1. Crystal Data, Data Collection Parameters, and Refinement Data

formula	$(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$
FW	1209.4
a (Å)	7.533(2)
b (Å)	10.162(2)
c (Å)	21.688(4)
α (deg)	101.22(3)
β (deg)	90.76(3)
γ (deg)	101.82(3)
V (Å^3)	1592.3
space group	$P\bar{1}$ (No. 2)
Z	1
temp (°C)	20
λ(Mo Kα) (Å)	0.710 69 (graphite monochromator)
ρ_{calc} (g cm^{-3})	1.263
μ(Mo Kα) (cm^{-1})	19.3
R^a	0.047
$R_w{}^b$	0.046

^{a} $R = \Sigma(|F_{obs} - F_{calc}|)/\Sigma(F_{obs})$. ^{b} $R_w = (\Sigma(|F_{obs} - F_{calc}|w^{1/2})/\Sigma(F_{obs}w^{1/2})$.

Table 2. Recording Conditions for the CPMAS NMR Experiments

	^{119}Sn	^{13}C
pulse width (*μ*s)	3.25	4.1
contact time (ms)	5	1
recycle time (s)	4	5
frequency (MHz)	111 .92	75.47

4-coordinated in the lamellar phase and 6-coordinated in the mesoporous one.

In this paper, the transformation of a supernatant tin sulfide into large crystals was first applied to prepare the new thiostannate $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$. Single-crystal X-ray diffraction structure analysis, solid state ^{119}Sn CPMAS NMR and ^{13}C CPMAS NMR spectroscopy, IR, and thermal analysis were used to characterize this new compound.

Experimental Section

Preparation. The compound was prepared as follows. First, 4.0 g of $SnCl_4\cdot 5H_2O$ (Rhône Poulenc) was dissolved in 34 g of water. Then, an aqueous solution of 6.96 g of $Na_2S\cdot 9H_2O$ (Aldrich) in 50 g of H_2O was added with stirring, leading to a gold-yellow precipitate. Subsequently 20 g of water and after 5 min 12.0 g of dodecylamine (DDA) from Fluka dissolved in 60 g ethanol were added. The resulting mixture was stirred for 4 h and then left for crystallization under static conditions at room temperature. After 45 days, colorless, triclinic single crystals were found in the bottom of the vessel, separated from the reaction mixture, washed with distilled water and ethanol, and dried at room temperature.

Crystal Structure Analysis. The single-crystal X-ray diffraction analysis was performed on a Syntex R3 four-circle diffractometer in the *ω* scan mode at 20 °C; 5775 reflections were collected in the 2*θ* range 2−50° (5619 independent reflections), and 5047 reflections having $F > 4\sigma(F)$ were used for refinement with the Siemens XLS package. Scattering factors were used as implemented in the program. Crystal data, data collection parameters, and refinement data are listed in Table 1. Powder X-ray diffraction was performed on a Stoe-STADI-P diffractometer using monochromated Cu Kα_1 radiation; the powder was contained in a capillary.

CPMAS NMR Measurements. The ^{119}Sn CPMAS NMR and ^{13}C CPMAS NMR spectra were recorded on a Bruker MSL300 spectrometer using $Sn(CH_3)_4$ and $Si(CH_3)_4$, respectively, as the chemical shift reference. The conditions are summarized in Table 2. The spinning sideband intensities of ^{119}Sn CPMAS NMR were simulated to give the shielding tensor. The anisotropy $\Delta\sigma$ is defined as $\sigma_{33} - 0.5(\sigma_{11} + \sigma_{22})$ and the asymmetry parameter η by $(\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{iso})$ where $\sigma_{iso} = -\delta_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$.[18,19]

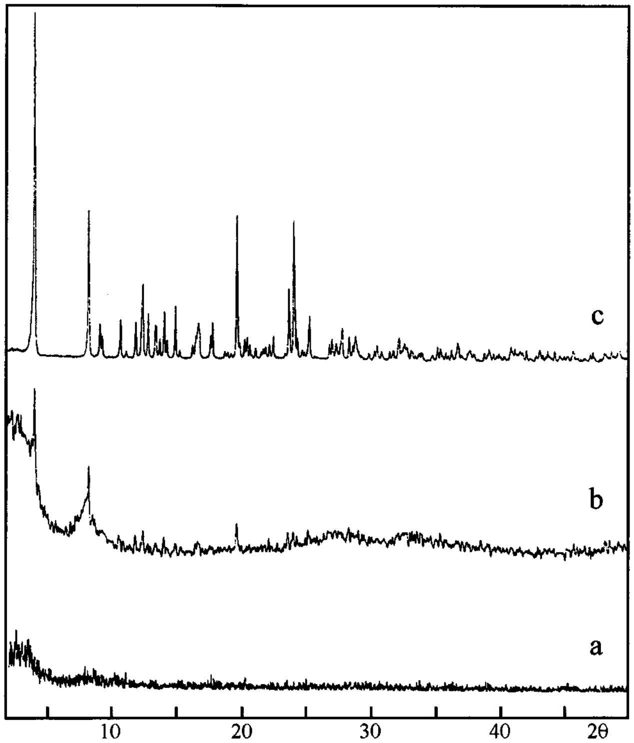

Figure 1. XRD patterns of products obtained in different parts of the vessel: (a) in the upper part after 1 day, (b) in the upper part after 28 days, and (c) at the bottom after 28 days.

IR Spectroscopy. The IR measurements were carried out with a Spectra Tec Research Plan microscope attached to a Nicolet Magna 550 FTIR spectrometer. The analysis was performed by the transmission absorption technique placing the samples on a NaCl disk into the sample stage of the microscope. The spectra were taken by accumulating 200 scans per spectrum with a resolution of 4 cm^{-1}.

Thermal Analysis. Differential thermogravimetric (dtg) and thermogravimetric (TG) analysis was performed on a Setaram TG DSC 111 microanalyzer. The samples were heated under argon with a heating rate of 5 °C min^{-1}.

Elemental Analysis. The elemental analysis was carried out by the French National Center for Scientific Recherch (CNRS). The content of carbon, nitrogen, and sulfur was determined by a home-made Fisons type organic elemental microanalyzer. The samples were heated in an oxygen flow above 850 °C in the case of carbon and nitrogen analysis and 1320 °C for sulfur. The accuracy for these three elements is 0.3%. The tin content was obtained by using a Fisons ARL 3520 emission spectrophotometer; the accuracy is 2%.

Results and Discussion

The compound $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$ was prepared in the ethanol−water two-solvent system because the solubility of dodecylamine is higher in ethanol than in water. As a first step a gold yellow precipitate of tin(IV) sulfide was formed by the reaction of $SnCl_4$ and Na_2S in aqueous solution. As the solution of dodecylamine in ethanol was added, the above-mentioned precipitate moved to the surface of the reaction mixture and a clear solution was seen in the lower part of the vessel once the agitation was stopped. Figure 1 shows the XRD patterns of the products formed after different crystallization times and from different sections of the vessel. It can be seen from Figure 1a that the floating product obtained after 1 day shows a short-range periodicity and there was no precipitate seen at the bottom of the vessel. The title compound was slowly formed with increasing crystallization time at ambient temper-

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(18) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021.

(19) Barrie, P. J.; Clark, P. J. H.; Withnall, R. *Inorg. Chem.* **1994**, *33*, 1212.

Table 3. Crystallographic Position Parameters, Occupation Factor *K*, and U_{eq}

atom	*x*	*y*	*z*	*K*	U_{eq} (Å^2)^a
Sn	0.488 04(3)	0.149 48(2)	0.478 70(1)	1.000 00(0)	0.0429(1)
S(1)	0.225 25(1 3)	0.233 70(9)	0.495 03(4)	1.000 00(0)	0.0543(4)
S(2)	0.583 77(14)	0.089 26(9)	0.577 17(4)	1.000 00(0)	0.0530(4)
S(3)	0.271 11(13)	−0.278 12(9)	0.563 97(4)	1.000 00(0)	0.0520(4)
C(24)	0.414 88(80)	0.155 33(59)	1.284 89(19)	1.000 00(0)	0.104(3)
C(23)	0.345 72(67)	0.213 71(45)	1.232 41(16)	1.000 00(0)	0.076(2)
C(22)	0.365 58(59)	0.133 64(42)	1.167 91(16)	1.000 00(0)	0.066(2)
C(21)	0.289 59(58)	0.188 91(40)	1.115 12(15)	1.000 00(0)	0.063(2)
C(20)	0.301 63(57)	0.106 08(40)	1.050 11(15)	1.000 00(0)	0.061(2)
C(19)	0.221 32(57)	0.160 22(40)	0.997 81(15)	1.000 00(0)	0.061(2)
C(18)	0.230 49(58)	0.075 65(40)	0.932 91(15)	1.000 00(0)	0.062(2)
C(17)	0.153 68(57)	0.130 75(40)	0.880 36(15)	1.000 00(0)	0.061(2)
C(16)	0.165 15(59)	0.046 03(40)	0.815 87(15)	1.000 00(0)	0.063(2)
C(15)	0.099 73(58)	0.104 34(40)	0.762 47(15)	1.000 00(0)	0.062(2)
C(14)	0.112 13(58)	0.018 21(39)	0.698 26(15)	1.000 00(0)	0.061(2)
C(13)	0.083 71(59)	0.091 75(40)	0.646 71(15)	1.000 00(0)	0.063(2)
N(2)	0.091 42(42)	0.005 42(30)	0.583 52(12)	1.000 00(0)	0.053(2)
C(12)	1.393 60(74)	0.717 97(55)	1.253 67(19)	1.000 00(0)	0.095(2)
C(11)	1.395 13(67)	0.636 00(47)	1.188 21(19)	1.000 00(0)	0.080(2)
C(10)	1.314 78(61)	0.692 07(43)	1.137 37(18)	1.000 00(0)	0.070(2)
C(9)	1.321 28(61)	0.611 13(43)	1.071 86(18)	1.000 00(0)	0.071(2)
C(8)	1.242 53(61)	0.666 70(43)	1.019 98(18)	1.000 00(0)	0.070(2)
C(7)	1.253 98(61)	0.585 33(42)	0.954 67(18)	1.000 00(0)	0.070(2)
C(6)	1.173 27(61)	0.638 78(43)	0.902 54(18)	1.000 00(0)	0.070(2)
C(5)	1.180 81(58)	0.555 16(42)	0.837 62(17)	1.000 00(0)	0.068(2)
C(4)	1.088 00(59)	0.604 09(41)	0.786 31(17)	1.000 00(0)	0.067(2)
C(3)	1.077 05(57)	0.512 29(40)	0.722 00(17)	1.000 00(0)	0.064(2)
C(2)	0.960 19(55)	0.553 30(37)	0.674 22(16)	1.000 00(0)	0.058(1)
C(1)	0.932 98(51)	0.454 28(37)	0.612 52(16)	1.000 00(0)	0.054(1)
N(1)	0.817 63(47)	0.497 42(31)	0.567 68(13)	1.000 00(0)	0.063(1)
O(H_2O)	0.466 64(42)	0.483 13(30)	0.606 38(13)	1.000 00(0)	0.083(1)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$ (Å^2).

ature, and single crystals were found at the bottom of the vessel. As shown in Figure 1b, the product in the upper part of the vessel is of low crystallinity when the crystallization time is 28 days. It can be considered to be a mixture of the short-range order material and the crystalline title solid. Figure 1c corresponds to the ground triclinic colorless single crystals of $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$ up to 6 mm in size found at the bottom of the vessel. When the crystallization time reached 45 days, a clear solution was obtained with colorless single crystals. Throughout the crystallization a clear solution was observed in the middle section of the vessel. Considering these observations, it may be assumed that, with the addition of dodecylamine into the reaction mixture, the amorphous tin(IV) sulfide initially formed interacts strongly with the surfactant to lead to a hybrid mesophase, which might be indicated by the broad diffraction peak at 2−5° (2θ). Then, a slow process of "charge density matching"[11] occurring between the inorganic part and the organic part may lead gradually to the compound $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$. Experiments were performed with other amines with different chain lengths. No crystallization was observed when octylamine was used. However, with hexadecylamine a polycrystalline material isostructural with the title material was obtained. The d_{100} values are 21.3 and 26.9 Å for the dodecylamine- and hexadecylamine-containing compounds, respectively.

The bulk elemental analysis gave a molar composition of 2:5.97:48.70:4.5 Sn:S:C:N, which is in good agreement with the unit cell content $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$ as determined by the structure analysis.

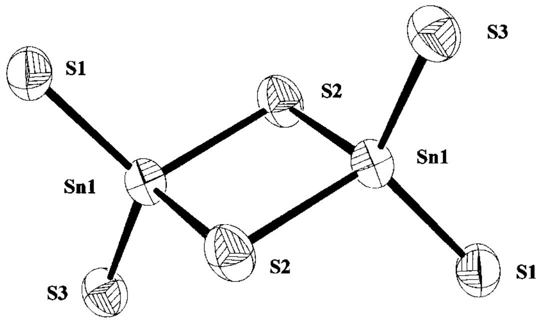

Figure 2. The $[Sn_2S_6]^{4-}$ dimer.

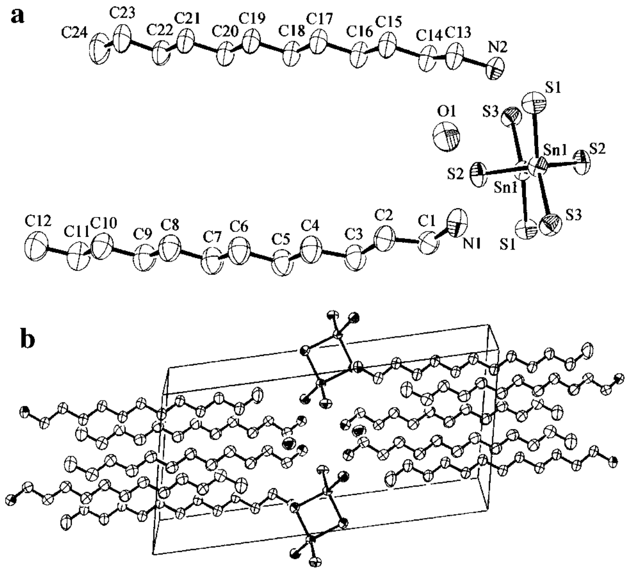

Figure 3. Perspective view of the structure of $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$: (a) a close-up view and (b) an overview.

Table 4. Selected Bond Distances and Angles

Distances (Å)			
Sn(1)−S(1)	2.318(1)	Sn(1)−Sn(1A)	3.382(1)
Sn(1)−S(2)	2.471(1)	C(13)−N(2)	1.486(4)
Sn(1)−S(2A)	2.440(1)	C(1)−N(1)	1.480(5)
Sn(1)−S(3A)	2.324(1)		
Angles (deg)			
S(1)−Sn(1)−S(3)	118.3(0)	S(2A)−Sn(1)−S(3)	111.7(0)
S(2)−Sn(1)−S(3)	111.8(0)	S(1)−Sn(1)−S(2)	108.7(0)
Sn(1)−S(3)−Sn(1A)	122.5(0)	Sn(1)−S(2)−Sn(1A)	87.1(0)

The atomic coordinates together with the displacement parameters are summarized in Table 3. Selected bond distances and angles are listed in Table 4. The structure of $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$ consists of $[Sn_2S_6]^{4-}$ anions and *n*-dodecylammonium cations (DDAH) as the main constituents and is completed by two water molecules per unit cell which occupy interstices between anions and cations. The $[Sn_2S_6]^{4-}$ dimers are formed by two edge-sharing $[SnS_4]$ tetrahedra (Figure 2). Isolated $[Sn_2S_6]^{4-}$ dimers are located at the center of the (010) plane of each unit cell.

The hydrocarbon chains of the cations are straight with the chain direction running parallel to [001] (Figure 3). The chains are in van der Waals contact to each other with the nitrogen atoms pointing in opposite directions for neighboring chains. The quality of the X-ray data allowed the positions of all hydrogen atoms to be determined. In addition to the protons connected to the carbon atoms of the chains, three hydrogen positions were detected around the nitrogen atom at a distance of *ca.* 1 Å. In contrast, no protons were observed next to the sulfur atoms.

According to a bond valence calculation[20] with respect to the anion, each of the four terminal sulfur atoms of the $[Sn_2S_6]^{4-}$

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(20) Brown, I. D. In *Structure and Bonding in Crystals*; O'Keeffe, M., Navrotsky, A., Eds.; Academic Press: New York, 1981; Vol. 2, Chapter 14.

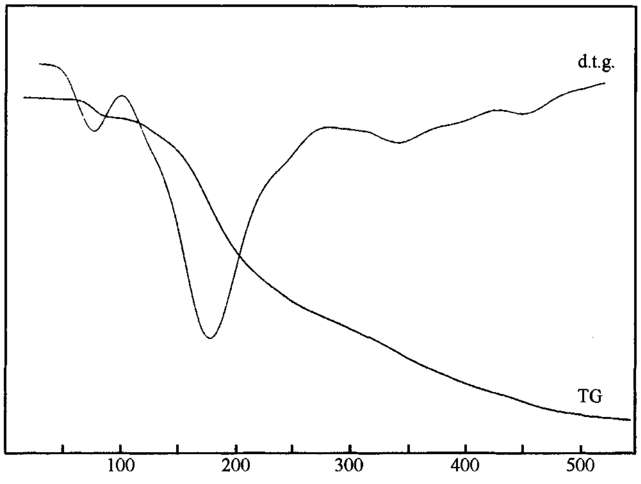

Figure 4. TG–dtg curves of $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$.

anion has a remaining bond valence of 0.8 for further interactions. Although the structure analysis is not able to prove whether all hydrogen positions around the nitrogen atoms are fully occupied, we may assume that the amine is protonated. Thus, the charge of the $[Sn_2S_6]^{4-}$ anions is compensated by the ammonium groups of the chain molecules. The shortest distances between the terminal sulfur atoms and the nitrogen atoms are 3.22–3.38 Å. These values correspond to the sum of the ionic radii: $r_{NH_4^+} = 1.48$ Å, $r_{S^{2-}} = 1.84$ Å.[21]

In addition to the ionic interactions, two types of hydrogen bonds exist in the structure. The water molecules interact both with the ammonium groups by O···H–N bonds with an O–N distance of 2.77 Å and with the terminal sulfur atoms by O–H···S bonds ($d_{O-S} = 3.34$ Å). Thus, the nonorganic constituents of the structure, i.e., anions, water molecules, and ammonium groups, interact to form an infinite layer-like unit parallel to (001).

Figure 4 shows the TG–dtg curves of the compound. It can be assumed that the first stage of weight loss below 100 °C is mainly due to desorption of water. The corresponding weight loss is 3.6%. The stages between 100 and 540 °C may correspond to an incomplete decomposition of the dodecylammonium cation and the loss of sulfur-containing species (weight loss: 54.8%). The observed total weight loss is 58.4%, and the residue consists of cassiterite SnO_2 and herzenbergite SnS. The main source of oxygen to form cassiterite SnO_2 probably results from slight leaking in the system. The reduction of Sn^{IV} to Sn^{II} is presumably accompanied by the oxidation of S^{-II} to S^{-I} resulting from the formation of an organic disulfide.[7] In addition, the residue of the TG experiment under air only consists of cassiterite SnO_2 and the observed weight loss (74.1%) is close to the calculated one (75.1%). It is likely that some organic species are left in the residue when the experiment is carried out under an argon flow since the weight loss in that case is lower than the calculated one corresponding to the formation of SnO_2 and SnS.

Figure 5 shows the solid state ^{119}Sn CPMAS NMR spectrum of the sample. The narrow line at 59.4 ppm is assigned to the isotropic resonance of tetrahedrally coordinated Sn^{IV}, and all other signals are spinning sidebands; this was confirmed by using different spinning rates. Although high spinning speeds were used, an extensive array of spinning sidebands is observed, which shows that there is a chemical shift anisotropy. The ^{119}Sn shielding tensor of the title compound is axially symmetric ($\eta = 0$). The other principal elements of the ^{119}Sn tensor are given as follows: $\sigma_{11} = -299.70$ ppm; $\sigma_{22} = -299.70$ ppm; $\sigma_{33} = 420.93$ ppm; $\Delta\sigma = 720.63$ ppm.

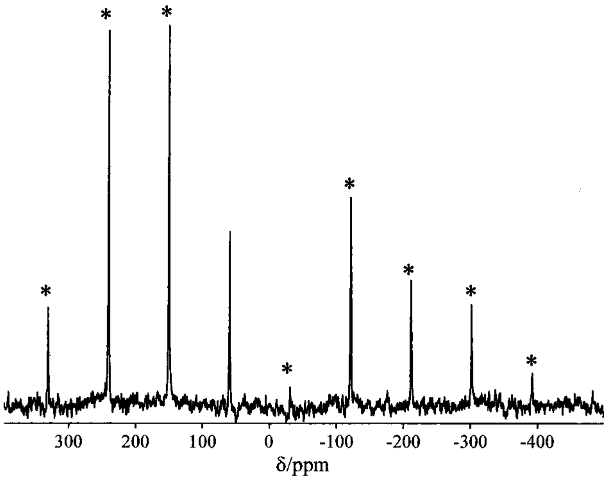

Figure 5. ^{119}Sn CPMAS NMR spectrum of $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$. The asterisks (*) designate spinning sidebands.

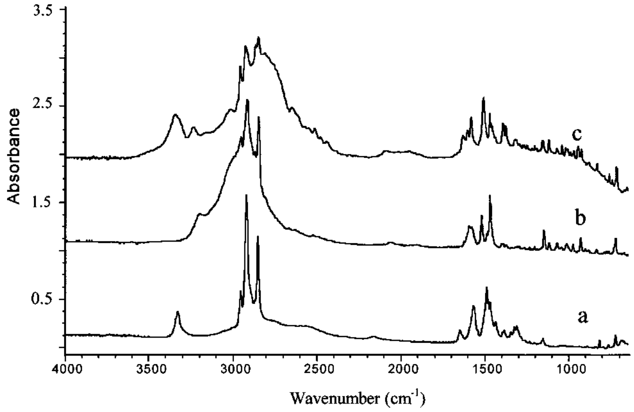

Figure 6. IR spectra: (a) dodecylamine, (b) dodecylamine hydrochloride, and (c) $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$.

Figure 6 illustrates the comparison of the IR spectrum of the title compound (Figure 6c) with those of solid dodecylamine (Figure 6a) and dodecylammonium hydrochloride (Figure 6b). The unprotonated form of dodecylamine has a sharp absorption band at 3330 cm^{-1} and very narrow bands corresponding to the C–H stretching modes. By protonation of dodecylamine the sharp absorption band occurring at 3330 cm^{-1} (N–H stretching vibrations) is shifted to a lower wavenumber at 3200 cm^{-1} together with a broadening of the C–H stretching region. The IR spectrum of the title compound exhibits a band at 3235 cm^{-1} and a similar broad feature, and it may be concluded that dodecylamine is present in the protonated form within this new material. The additional band occurring at 3350 cm^{-1} may be attributed to O–H stretching vibrations of hydrogen-bonded water molecules.

It may also be assumed that dodecylamine is protonated in the title compound from the ^{13}C CPMAS NMR spectrum (Figure 7). The presence of a protonated or an unprotonated nitrogen atom has an effect on the ^{13}C CPMAS NMR spectra of dodecylamine (Figure 7). The signals of the ^{13}C CPMAS NMR spectrum of pure dodecylamine (Figure 7a) were assigned to the corresponding carbon atoms based on the closely related spectrum of decylamine.[22]

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(21) Pauling, L. In *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960.

(22) Eggert, H.; Djerassi, C. *J. Am. Chem. Soc.* **1973**, *95*, 3710.

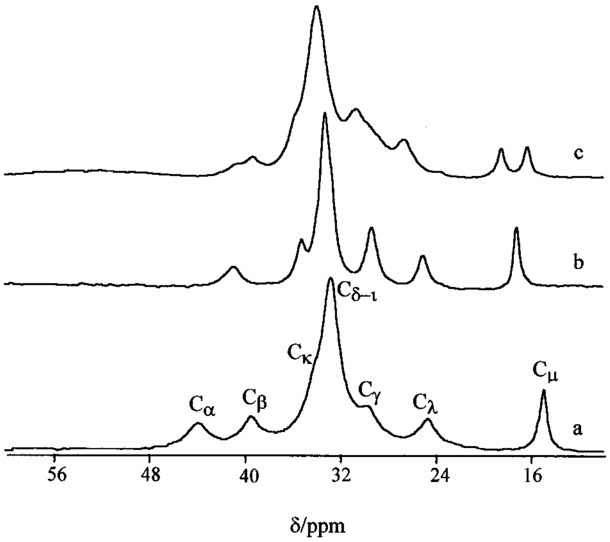

Figure 7. ^{13}C CPMAS NMR spectra: (a) dodecylamine, (b) dodecylamine hydrochloride, and (c) $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$.

The ^{13}C CPMAS NMR spectrum of dodecylamine hydrochloride (Figure 7b) is different from that of dodecylamine (Figure 7a). Due to the protonation of the nitrogen atom, the signal representing the carbon atom C_α (connected to the nitrogen atom) is shifted to a higher field. By contrast, the signals of $C_{\gamma-\mu}$ move to a lower field. Such a phenomenon is also observed in the case of $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$ (Figure 7c) compared with dodecylamine. On the basis of the similarity between the ^{13}C CPMAS NMR spectra of the title compound and dodecylamine hydrochloride, we may conclude that dodecylamine has been protonated during the formation of $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$. At the same time, a splitting of the signal of the methyl groups occurs. Such a phenomenon has been observed due to environmental,[23] crystallographic,[24] or conformational[25] effects. In the present case, it is caused by the different positions of the methyl groups. Indeed, the methyl groups in the compound occupy two crystallographically independent positions which seemingly possess quite different environments.

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Supporting Information Available: Tables of the experimental conditions, structure determination and refinement, bond lengths and angles, H atom coordinates with esd's and U_{iso}, and anisotropic thermal parameters (10 pages). Ordering information is given on any current masthead page. Structure factor tables may be obtained directly from the authors.

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(23) Boxhoorn, G.; van Santen, R. A.; van Erp, W. A.; Hays, G. R.; Huis, R.; Clague, D. *J. Chem. Soc., Chem. Commun.* **1982**, 264.

(24) Ballmann, E. G.; Groombridge, C. J.; Harris, R. K.; Packer, K. J.; Say, B. J.; Tanner, S. F. *Philos. Trans. R. Soc. London, Ser. A* **1981**, *299*, 643.

(25) Schaefer, J.; Stejskal, E. O. In *Topics in Carbon-13 NMR Spectroscopy*; Levy, G. C., Ed.; Wiley-Interscience: New York, 1979; Vol. 3, p 283.