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New Strontium Polysulfides, SrS_3, and $Sr_2(OH)_2S_4\cdot 10H_2O$, Obtained by the High-pressure Treatment of a Sr–S Mixture

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A new polymorph of SrS_3 was obtained by a reaction of SrS and S with an atomic ratio of Sr:S = 1:5 under a pressure of 5 GPa at 1200 °C. It crystallized in a tetragonal unit cell with $a = 6.708(1)$ Å, $c = 3.942(1)$ Å, and $V = 177.36(6)$ Å^3. It was isotypic with BaS_3, and contained S_3^{2-} polysulfide ions. The product obtained from the high-pressure synthesis contained an amorphous component. It was highly deliquescent and formed a yellowish solution. A new layered polysulfide, $Sr_2(OH)_2S_4\cdot 10H_2O$, crystallized in the solution. The sulfide belonged to a triclinic space group of $P\bar{1}$ (No. 2) with lattice constants of $a = 5.9107(5)$ Å, $b = 7.8682(6)$ Å, $c = 9.4134(6)$ Å, $\alpha = 75.639(6)°$, $\beta = 73.824(3)°$, $\gamma = 71.639(3)°$, $V = 392.83(5)$ Å^3, and $Z = 1$. Each Sr ion was coordinated with one OH ligand and eight H_2O ligands. Six H_2O ligands out of the eight were bridging ligands to form two-dimensional $[Sr_2(OH)_2(H_2O)_{10}{}^{2+}]_\infty$ cationic layers, between which S_4^{2-} tetrapolysulfide ions were situated. The S_4^{2-} anion had a coplanar configuration with a dihedral angle of 180.0°. The stability of S_4^{2-} anions having different conformations was discussed from a viewpoint of ab initio MO calculations on changing the dihedral angles of S_4^{2-}.

Introduction

No element shows as many different structures as sulfur. It shows many types of allotropes, polyanions, and polycations composed of rings or chains of sulfur atoms. Catenation of sulfur atoms is one of the most attractive themes in the chemistry of sulfur. The structural chemistry of polysulfides, therefore, has been extensively studied (see for instance Müller et al.[1] and references therein). Polysulfides of alkali and alkaline earth metals, especially, show a variety of structures composed of S_n^{2-} ions with $n = 2-6$.[1-13] The S_n^{2-} ions are usually monodentate ligands and directly bound to their countercations through their terminal sulfur atoms, but in some cases they can be polydentate ligands.

There are some ways of preparing polysulfides other than the conventional way of solid-state reaction of metals and sulfur in sealed tubes. One is by using solutions of polysulfide ions. Many polysulfides are hygroscopic and show high solubility in water.[1,3] Yellowish solutions containing S_n^{2-} ions are obtained after the deliquescence. The solutions containing S_n^{2-} ions are also obtained by digesting sulfur in aqueous solutions of sulfides. The S_n^{2-} ions (especially S_4^{2-} and S_5^{2-}) are stable in the solutions if acids and oxidants do not coexist. Many polysulfides are prepared from the solutions. Hydrothermal synthesis is commonly used for the preparation of polysulfides. Other methods using CS_2 and H_2S gases or liquid NH_3 are also useful. Most of polysulfides were synthesized by these methods under ambient pressure or under 1∼10 MPa. However, if the reaction conditions can be drastically changed, new polysulfides would be expected to be obtained.

In a previous study, we prepared new sulfides, Ba_3CrS_5 and $Ba_3Cr_2S_6$, under high-pressure and high-temperature reaction conditions.[14] In the high-pressure synthesis, it is easy to keep most excess sulfur in a reaction vessel at higher

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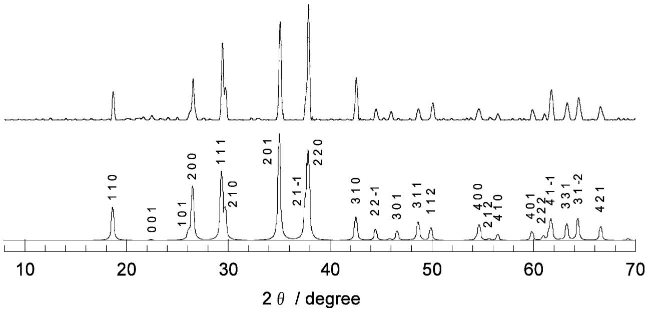

Figure 1. Powder XRD pattern of the as-prepared sample after the reaction of the mixture with SrS:S = 1:4 at 5 GPa and 1200 °C for 30 min. For comparison, the calculated powder pattern of SrS_3 with the tetragonal BaS_3 structure is also presented (bottom). In the calculation of the XRD pattern, a pseudo-Voigt function with constant fwhm of 0.35 was used. The needle-type preferred orientation along the 0 0 1 direction was assumed and simulated by using Toraya function with o1 = 0.9, o2 = 0.05.

temperatures than the boiling point of sulfur. Reaction conditions for this method are quite different from those of the other methods mentioned above. Though the compounds obtained in the previous study were not polysulfides, the study suggests that the high-pressure synthesis opens a new field for preparing new sulfides. In the present study, we have examined reactions of Sr and sulfur under high-pressure conditions to synthesize new strontium polysulfides.

Experimental Section

Synthesis. Strontium sulfide, SrS (Alfa Aesar 99.9%) and sulfur (Rare metallic 200 mesh 99%) were mixed with a molar ratio of Sr:S = 1:5 in an argon-filled glovebox. The mixed powder was put in a BN container with a 5-mm inner diameter and a 5-mm depth. The container was placed in a carbon ring heater, and was packed in a pyrophyllite cube as a pressure medium (20 × 20 × 20 mm^3). The details of the cell assembly are given elsewhere.[15] The cell was pressed at a pressure of 5 GPa by a multianvil assembly, and heated at 600 °C for 30 min. After the reaction, the cell was quenched to room temperature, and the pressure was gradually released. Another sample was prepared at 1200 °C for 30 min at 5 GPa from the same starting mixture.

Characterization. Powder X-ray diffractions (XRD) of the products were measured with a Mac Science M18X-HF diffractometer with Cu Kα radiation. Single-crystal X-ray analysis was performed using a Rigaku R-AXIS imaging plate area detector with graphite monochromated Mo Kα radiation. The structure was solved using the Crystal Structure crystallographic software package.[16] Compositions of the crystals were analyzed with an energy-dispersive X-ray microanalyzer (JED-2110).

Results and Discussion

The New Polymorph of SrS_3. The high-pressure reactions under a pressure of 5 GPa at 600 or 1200 °C gave pale greenish yellow products. The powder XRD pattern of the sample prepared at 1200 °C is shown in Figure 1 (top). It could be indexed with a tetragonal cell with $a = 6.708(1)$ Å, $c = 3.942(1)$ Å, and $V = 177.36(6)$ Å^3, but could not be identified with any reported sulfide. Some single crystals were found in the as-prepared sample. However, their quality was not good enough for the single X-ray structural analysis. We could only perform a preliminary structural analysis, and we confirmed that it was a new strontium tripolysulfide, SrS_3 isotypic with BaS_3,[9] though the reliability factors were rather large ($R = 15.5\%$, $Rw = 11.7\%$). A simulated XRD pattern of SrS_3 is presented in Figure 1 (bottom). It was calculated using the BaS_3 structure with the cell constants and atomic parameters obtained by the preliminary single-crystal analysis. The observed and calculated peak patterns are quite similar to each other. From these observations, it was confirmed that the new tetragonal polymorph of SrS_3 was obtained in the high-pressure and high-temperature reactions.

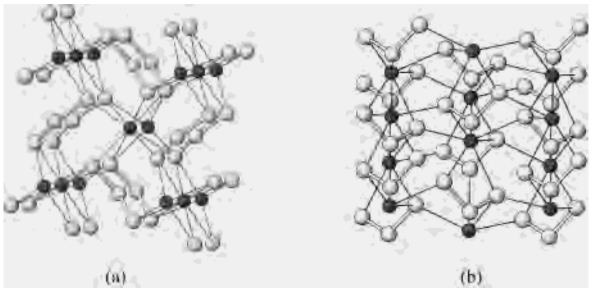

Figure 2. Comparison of the crystal structure with two polymorphs of SrS_3. (a) Tetragonal SrS_3 prepared by high-pressure synthesis. (b) Orthorhombic SrS_3. Open and filled circles represent S and Sr atoms, respectively. The S−S bonds in the S_3^{2-} anions are shown as thick sticks while the Sr−S bonds are shown as thin lines.

Lutz and co-workers[8,12] reported the existence of two polymorphs of strontium tripolysulfide, SrS_3(A) and SrS_3(B). The crystal system and the structure of SrS_3(A) are still unknown. The XRD pattern of the newly prepared SrS_3 in this study is different from that of SrS_3(A). The structure of SrS_3(B) was determined by Schnering et al.[9] SrS_3(B) belongs to an orthorhombic system, and its calculated density is 3.07 g cm^{-1}, which is quite smaller than the calculated density of 3.44 g cm^{-1} of the tetragonal SrS_3. The larger density of the tetragonal phase suggests that the tetragonal SrS_3 is a high-pressure form.

The structure of tetragonal SrS_3 is presented in Figure 2 (a). It is composed of Sr^{2+} ions and S_3^{2-} polyanions. Thick and thin bonds in the figure show the S−S bonds of S_3^{2-} tripolyanions and Sr−S bonds, respectively. For comparison, the orthorhombic form of SrS_3 is shown in Figure 2 (b). In the orthorhombic form, Sr atoms are coordinated by seven sulfur atoms with Sr−S distances of 3.01 to 3.30 Å. The bond angle of the S_3^{2-} ion is 106.6°. On the other hand, the Sr atoms in the tetragonal (high-pressure) form are coordinated by eight sulfur atoms with Sr−S distances of 2.97 to 3.29 Å. The bond angle of S_3^{2-} ions is 107.9°. Note that the coordination number increases from 7 to 8 in the orthorhombic and tetragonal forms, respectively, though the bond lengths and angles of S_3^{2-} are not significantly different.

Characterization and the Crystal Structure of $Sr_2(OH)_2S_4 \cdot 10H_2O$. The as-prepared samples prepared by high-pressure and high-temperature conditions contained tetragonal SrS_3 and an amorphous component. The amorphous

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Table 1. Crystallographic Data of $Sr_2(OH)_2S_4{\cdot}10H_2O$

formula weight	517.64
space group	$P\bar{1}$ (No. 2)
a (Å)	5.9107(5)
b (Å)	7.8682(6)
c (Å)	9.4134(6)
α (deg)	75.639(6)
β (deg)	73.824(3)
γ (deg)	71.639(3)
V (Å^3)	392.83(5)
Z	1
D_{calc} (g·cm^{-3})	2.19
D_{obs} (g·cm^{-3})	2.22
R, R_w[a]	0.032, 0.043

[a] $R(F_o) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $Rw(F_o) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ ($w = 1/\sigma(F_o)^2$).

Table 2. Atomic Parameters and Thermal Vibrational Parameters of $Sr_2(OH)_2S_4{\cdot}10H_2O$

atom	x	y	z	B_{eq} (Å^2)[a]
Sr(1)	0.15641(8)	0.20685(6)	0.04368(5)	1.158(9)
S(1)	0.4016(3)	0.2039(2)	0.5343(2)	2.32(3)
S(2)	0.3250(3)	0.4820(2)	0.5107(2)	2.48(3)
O(1)	−0.2328(6)	0.4733(5)	0.1293(4)	1.52(7)
O(2)	−0.2049(6)	0.0449(5)	0.1301(4)	1.66(7)
O(3)	0.5908(7)	0.1290(5)	−0.1485(4)	1.62(7)
O(4)	0.4033(7)	0.3261(5)	0.1596(4)	1.69(7)
O(5)	−0.1122(7)	0.3429(5)	−0.1651(4)	1.78(7)
O(6)	0.0091(8)	0.1333(6)	0.3464(5)	2.67(9)

[a] $B_{eq} = 8/3\,\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$.

part showed a hygroscopic property, and formed a yellow solution when it was kept in air. A few days later many orange transparent single crystals were found in the yellow solution. To confirm the reproduction of crystals, we did the same experiments several times, and obtained single crystals in every trial. The sample prepared at 600 °C was more hygroscopic than the sample prepared at 1200 °C, and produced many large crystals. The crystals were stable in the solution, but once they were taken out of the solution, they were slowly decomposed.

A single crystal with 0.4 × 0.2 × 0.1 mm^3 was selected for single-crystal X-ray analysis. The crystal was mounted on the top of a glass capillary, and coated with a thin epoxy bond to avoid decomposition. Structural analysis revealed that the crystal was a new layer-structured strontium polysulfide, $Sr_2(OH)_2S_4{\cdot}10H_2O$, having S_4^{2-} polysulfide ions. The crystallographic data and atomic parameters are listed in Tables1 and 2, respectively. In the refinement, the positions of hydrogen atoms were not determined. EDX analysis on several crystals showed that the atomic ratio of Sr to S was 1 to 1.9−2.0. The ratio showed a good agreement with the composition determined from the X-ray analysis. The density of $Sr_2(OH)_2S_4{\cdot}10H_2O$ was measured on several crystals by picnometer method using benzene-diiodemethane solutions. The observed density of 2.22 g cm^{-3} showed good agreement with the value of 2.19 g cm^{-3} calculated from the composition of $Sr_2(OH)_2S_4{\cdot}10H_2O$.

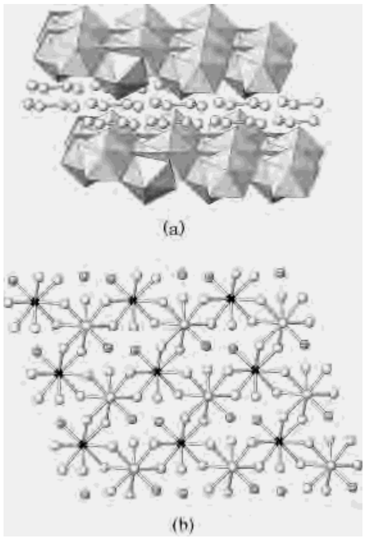

Figure 3. (a) Crystal structure of $Sr_2(OH)_2S_4{\cdot}10H_2O$. The Sr layers are shown using a polyhedral model. The coordination polyhedra are connected with each other through their edges to form the cationic $[Sr_2(OH)_2{\cdot}10H_2O^{2+}]_\infty$ layers, between which the S_4^{2-} anions are situated. (b) Structure of the $[Sr_2(OH)_2{\cdot}10H_2O^{2+}]_\infty$ layer. The Sr atoms are represented with black circles. The oxygen atoms in the H_2O ligands are shown as open circles. The hatched circles are OH ligands.

The structure of $Sr_2(OH)_2S_4{\cdot}10H_2O$ is shown in Figure 3 and the selected bond distances and angles are listed in Table 3. The $Sr_2(OH)_2S_4{\cdot}10H_2O$ has a layered structure composed of two-dimensional $[Sr_2(OH)_2{\cdot}10H_2O^{2+}]_\infty$ cationic layers and S_4^{2-} tetrapolysulfide anions. Figure 3(a) shows the Sr layers using a polyhedral model. Each Sr ion in the layer is coordinated with nine oxygen atoms, and forms a SrO_9 coordination polyhedron with 14 triangular faces. The polyhedra are connected with each other through their edges to form the cationic layers, between which the S_4^{2-} anions are situated. Among the nine oxygen atoms around the Sr ion, three are terminal and the others are bridging ligands. The structure of the layer projected on the $a-b$ plane is presented in Figure 3(b). The bond distance between a terminal oxygen atom (O4) and strontium was 2.541 Å. The distance was much smaller than the other Sr−O distances ranging from 2.660 to 2.707 Å. Since the distance of Sr−O4 is comparable to the average Sr−OH bond distance of 2.569 Å in a strontium hydroxide, $Sr(OH)_2$,[17] the O4 atom should be assigned as an OH ligand. The other oxygen atoms were assigned to H_2O ligands. The oxygen atoms in H_2O and the OH^- ions are shown by open and hatched circles in Figure 3(b), respectively. Among the eight H_2O molecules, six are bridging, and two are terminal ligands. The OH ligands are terminal, and are situated in open spaces in the layer.

In most alkali and alkaline-earth polysulfides, the polysulfide anions are directly connected with their countercations, such as in the tetragonal and orthorhombic SrS_3 mentioned above. For example, in cesium pentasulfide hydrate, $Cs_2S_5{\cdot}H_2O$, Cs atoms are bonded with both sulfur and oxygen atoms.[18] The S_4^{2-} anions in $Sr_2(OH)_2S_4{\cdot}10H_2O$, however, are situated in interlayer regions of cationic Sr layers, and have no direct bonds with Sr^{2+} cations. The dihedral angle of the S_4^{2-} anion is 180.0(1)°. This is the first example of the polysulfide having coplanar S_4^{2-} anions.

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Table 3. Selected Bond Distances (Å) and Angles (deg) of $Sr_2(OH)_2S_4{\cdot}10H_2O^a$

Sr−O1	2.666(4) × 2	−O4 (in OH)	2.541(4)	S1−S2 (terminal)	2.058(2)
−O2	2.660(4) × 2	−O5	2.675(4)	S2−S2 (center)	2.123(3)
−O3	2.685(4) × 2	−O6	2.707(4)		
S1−S2−S2	101.69(11)	dihedral angle of S_4^{2-}	180.0(1)		
α-Na_2S_4		$BaS_4{\cdot}H_2O$			
S−S (terminal)	2.074	S−S (terminal)	2.069, 2.079		
S−S (center)	2.061	S−S (center)	2.063, 2.062		
dihedral angle of S_4^{2-}	97.81	dihedral angles of S_4^{2-}	76.2, 76.5		

[a] For comparison, S−S bond distances (Å) and dihedral angles (deg) of α-Na_2S_4 and $BaS_4{\cdot}H_2O$ are listed.

The S−S bond distances of 2.058 and 2.123 Å were observed for the terminal and central bonds of the S_4^{2-} anion, respectively. Some tetrapolysulfides, such as Na_2S_4[3] and $BaS_4{\cdot}H_2O$,[19,20] were analyzed by single-crystal X-ray structure studies. In these compounds, the S−S bond distances are 2.069−2.079 Å for the terminal bond and 2.061−2.063 Å for the central bond. While the distance of the terminal S−S bond in $Sr_2(OH)_2S_4{\cdot}10H_2O$ is similar to those of the Na and Ba sulfides, the central S−S bond in $Sr_2(OH)_2S_4{\cdot}10H_2O$ is 0.06 Å longer than those of the Na and Ba compounds. A detailed discussion about the S−S bond distances is given below.

Configuration of the S_4^{2-} Anion in $Sr_2(OH)_2S_4{\cdot}10H_2O$. Hordvik[21] reported the relationship between the bond length and the dihedral angle of S−S bonds in polysulfides. He made a curve for predicting the central S−S bond distance from the dihedral angle. The observed value of 2.13 Å for $Sr_2(OH)_2S_4{\cdot}10H_2O$ showed a good agreement with the predicted value of 2.10 Å from his curve. More recently, Jaroudi et al.[22] discussed the relation between the bond distance and torsion angle of S_4^{2-} anions in $BaS_4{\cdot}H_2O$ and α-Na_2S_4. The bond distances and angles of these compounds are also listed in Table 3. The dihedral angles of S_4^{2-} ions in these compounds were much smaller than those in $Sr_2(OH)_2S_4{\cdot}10H_2O$ as shown in the table.

Jaroudi et al.[23] also pointed out that the central bonds were shorter than the terminal ones in $BaS_4{\cdot}H_2O$ and α-Na_2S_4. This is not true in the case of $Sr_2(OH)_2S_4{\cdot}10H_2O$. Molecular orbital calculations of S_4^{2-} anions with different dihedral angles, θ, would be helpful in explaining the different structural features of these sulfides. Kao[23] reported ab initio studies of S_4^{2-} having the special geometries of syn-, gouche-, and antistructures using Gaussian 70 with the 44-31G basis set, and concluded that the anti-type conformation ($\theta = 180°$) was most stable among them. However, most S_4^{2-} anions in reported crystal structures have gouchetype conformations with dihedral angles around 90°. The antitype conformation with $\theta = 180°$ was first observed in $Sr_2(OH)_2S_4{\cdot}10H_2O$ as mentioned above. For detailed studies of the effect of θ on the bond distance and total energy E_{total} of the S_4^{2-} anion, we performed the MO calculation of the S_4^{2-} anion by changing θ stepwise from 70 to 180°. All calculations were carried out using the Gaussian 03 program package[24] at the MP3/6-31G level. The distances $r1$ and $r2$, and the angle α of the S_4^{2-} anion, shown in Figure 4 (a), were optimized on each step of θ.

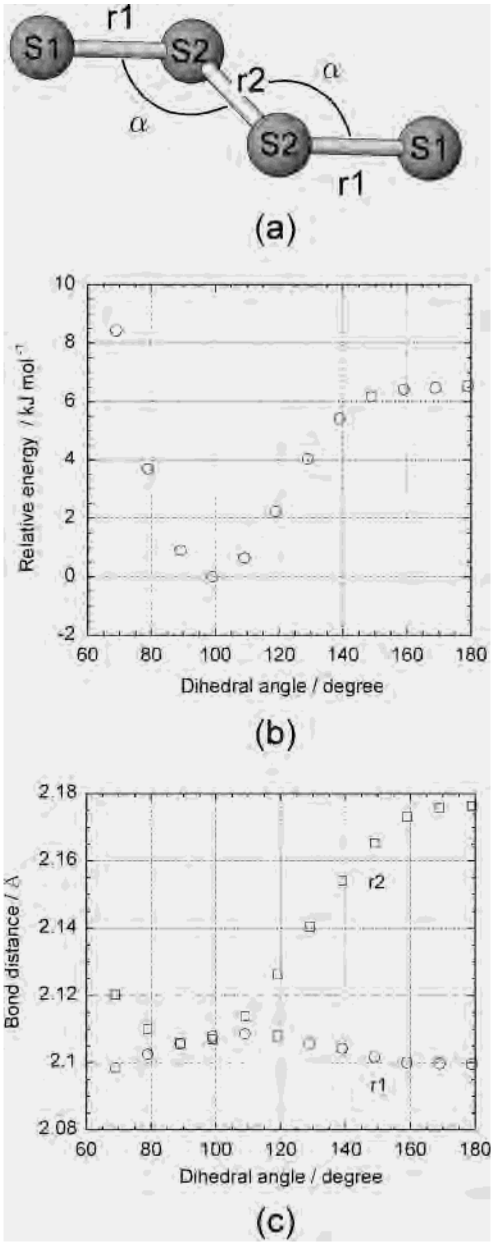

Figure 4. (a) Structure and geometrical parameters of the S_4^{2-} dianion. Dependence of the total energy (b) and optimized bond distance (c) on the dihedral angle θ.

The changes of E_{total} and the optimized bond distances as a function of θ are shown in Figures 4 (b) and (c). The total energy E_{total} showed the minimum value at $\theta = 100°$, which was set to zero in Figure 4(b). This angle was close to the

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observed dihedral angle of 97.81° in α-Na_2S_4. As θ increased from 100 to 180°, the E_{total} increased and showed almost a constant value above 150°. This calculation shows that the S_4^{2-} with $\theta = 180°$ is 6.2 kJ/mol higher (or more unstable) in total energy than that with $\theta = 100°$. However, the difference of the E_{total} between these two configurations is not so large. The dihedral angles of the S_4^{2-} anions in $BaS_4 \cdot H_2O$ are 76.2 and 76.5°, which are much smaller than 100°. The calculated E_{total}'s of the S_4^{2-} in $BaS_4 \cdot H_2O$ are 4 kJ/mol higher (more unstable) than the minimum E_{total}, and are only 2 kJ/mol lower than that of S_4^{2-} in $Sr_2(OH)_2S_4 \cdot 10H_2O$.

The optimized bond distances ($r1$ and $r2$) vs θ are shown in Figure 4 (c). Although the optimized values are about 0.04 Å longer than the observed ones in α-Na_2S_4, $BaS_4 \cdot H_2O$, and $Sr_2(OH)_2S_4 \cdot 10H_2O$, the curves in Figure 4(c) well explain the difference between $r1$ and $r2$ values in these polysulfides. The optimized terminal bond distances ($r1$) are slightly shorter than central bond distances ($r2$) in the region of $\theta < 100°$. These results correspond with the observation of the terminal and central bond distances in α-Na_2S_4 ($\theta = 97.8°$) and $BaS_4 \cdot H_2O$ ($\theta = 76.2$ and 76.5°). On the other hand, when the θ value reaches around 180°, $r2$ becomes much larger than $r1$. This explains the larger $r2$ value in $Sr_2(OH)_2S_4 \cdot 10H_2O$. The difference between the optimized $r1$ and $r2$ is 0.08 Å at $\theta = 180°$. It shows a good agreement with the observed difference of 0.07 Å in the strontium compound.

The elongation of $r2$ is explained by the electron distribution among the four sulfur atoms. Kao[23] pointed out that the two electron charges were not localized on either the terminal or the central atoms. We also obtained the same result. The charge densities of the two extra electrons of S_4^{2-} indicated that the electrons were distributed on all atoms in all configurations. For the S_4^{2-} anions with θ around 100°, higher electron densities were observed on the terminal sulfur atoms than on the center atoms. This is the case for α-Na_2S_4 and $BaS_4 \cdot H_2O$. On the other hand, for the S_4^{2-} anion with $\theta = 180°$, higher electron densities were observed on the center sulfur atoms. The high electron densities on the central sulfur atoms induces a strong repulsion between them, which would be responsible for the quite long distance of the central S−S bond in $Sr_2(OH)_2S_4 \cdot 10H_2O$.

Conclusion

Two new polysulfides, SrS_3 and $Sr_2(OH)_2S_4 \cdot 10H_2O$, have been obtained by the high-pressure and high-temperature treatment of Sr and S mixtures. SrS_3 crystallized in a tetragonal form composed of Sr^{2+} and S_3^{2-} polysulfide ions. This phase is the third and high-pressure polymorph of strontium trisulfides. The products obtained by the high-pressure synthesis contained a highly deliquescent amorphous phase; $Sr_2(OH)_2S_4 \cdot 10H_2O$ was obtained from the deliquescent solution. The $Sr_2(OH)_2S_4 \cdot 10H_2O$ contained coplanar tetrapolysulfide ions, S_4^{2-}, which were packed in the interlayer regions of cationic $[Sr_2(OH)_2 \cdot 10H_2O^{2+}]_\infty$ sheets. Each Sr atom in the sheet is coordinated with one OH ion, six bridging H_2O ligands, and two terminal H_2O ligands. The MO calculation of the S_4^{2-} anion explained the longer central S−S bond distance rather than the terminal bond distance in $Sr_2(OH)_2S_4 \cdot 10H_2O$. This is the first example of the compound containing the S_4^{2-} anion with coplanar and anti geometry.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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