Flux Crystal Growth, Crystal Structure, and Magnetic Properties of a Ternary Chromium Disulfide Ba₉Cr₄S₁₉ with Unusual Cr₄S₁₅ Tetramer Units

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ABSTRACT: A new ternary chromium disulfide, Ba₉Cr₄S₁₉, has been grown out of BaCl₂ molten salt. Single-crystal structure analysis revealed that it crystallizes in the centrosymmetric space group C2/c with lattice parameters: a = 12.795(3) Å, b = 11.3269(2) Å, c = 23.2057(6) Å, β = 104.041(3)°, and Z = 4. Ba₉Cr₄S₁₉ comprises four face-sharing Cr-centered octahedra with disulfide ions occupying sites on each terminal face. The resulting Cr₄S₁₅ tetramer units are isolated by nonmagnetic Ba-centered polyhedra in the ab plane and barium disulfide (=Ba₂(S₂)₂) layers along the c-axis. Following the structure analysis, the title compound should be expressed as [Ba²⁺]₉[Cr³⁺]₄[(S₂)₂]₁₉, which is also consistent with Cr₂p X-ray photoemission spectra showing trivalent states of the Cr atoms. The unique Cr-based zero-dimensional structure with the formation of these disulfide ions can be achieved for the first time in ternary chromium sulfides, which adopt 1–3 dimensional frameworks of Cr-centered polyhedra.

INTRODUCTION

Polysulfide compounds with S−S bonds or Sₙ²⁻ (2 ≤ n) anions are of great interest because they can be used in a wide range of practical applications, for example, rechargeable alkali ion batteries,¹ vulcanized rubber,² and hydrodesulfurization catalysts.³ The fundamental chemistry underlying such applications is the facile ability of sulfides to form or break covalent S−S bonds in specific reaction environments. However, in contrast to a large number of reports on glasses, frameworks in which the metal centers are anisotropically connected via bridging and/or chelating S⁻ ligands. The S⁻ fragments could be used as building blocks to design new low-dimensional magnetic/electrical materials. However, ternary or multinary polysulfide compounds with nonpaired electrons (i.e., d¹−d⁹ metals) that show magnetism and electrical conductivity have not been sufficiently explored yet,¹⁴,¹⁵ probably because of the high thermodynamic stability of simple binary metal sulfides.

A chromium sulfide system prefers to take oxidation states of chromium between +2 and +4. Although there are two binary chromium disulfides, namely, amorphous and crystalline CrS₃, ternary or multinary Cr-based polysulfides have never been reported. In the chromium sulfide system, ternary chromium sulfides have been the most extensively investigated because of their structural diversity.¹⁶–¹⁹ In particular, the Ba–Cr–S system is the only one that shows a dimensional reduction of a Cr-based structural framework from three-dimensional (3D) (tunnel-like) through two-dimensional (2D) (layers) to one-dimensional (1D) (chains) units when the ratio of Ba/Cr atoms is increased (see Figure 1).¹⁷,²⁰,²¹ It should be noted that only high-pressure methods can access the infinite 1D chains of face-sharing Cr₇S₈ octahedra as observed in Ba₃Cr₂S₆ and Ba₃Cr₂S₆. In contrast, shorter octahedral chains are
crystallizes in the space group C2/c (No. 15) with the following unit cell parameters: \( a = 12.795(3) \, \text{Å} \), \( b = 11.3269(2) \, \text{Å} \), \( c = 23.2057(6) \, \text{Å} \), \( \beta = 104.041(3) \, \text{Å} \), and \( Z = 4 \). The details of the structure refinement are listed in Table 1, atomic coordinates and atomic displacement parameters are given in Table 2, and anisotropic displacement parameters are listed in Table S1. Selected bond distances and angles are summarized in Table S2. Solid-state reactions using a stoichiometric mixture of BaS, CrS\(_3\), and S and were performed in an attempt to synthesize polycrystalline powder samples. Varying the reaction temperature and time did not yield the target phase at all; instead, unidentifiable phases were obtained. This result suggests that BaCl\(_2\) flux is essential to obtain Ba\(_9\)Cr\(_4\)S\(_{19}\).

Figure 3 shows the schematic view of the Ba\(_9\)Cr\(_4\)S\(_{19}\) crystal structure along the [100] direction. The present compound possesses a Cr\(_4\)S\(_{15}\) tetramer unit, half of which is an asymmetric unit because the middle point between two Cr1 atoms is positioned on a 2-fold axis (see Figure 4a). The four Cr-centered octahedra in the tetramer are linked by sharing the common S\(_6\) faces along the [301] direction. Two sulfur atoms, S6 and S7, bound to the Cr2 atom on each terminal face in the tetramer unit are coupled to each other at a bond distance of \( d_{S6−S7} = 2.0998(19) \, \text{Å} \), in contrast to significantly longer distances between any other adjacent S−S bonds (~3.5 Å) in the Cr1/Cr2 octahedra. This short bond distance strongly suggests a dimerization of S6 and S7 atoms into a disulfide ion (S\(_6\)\(^2\))\(^−\). In fact, the intramolecular distance is consistent with those typically observed in disulfide compounds.\(^{22,23}\) Therefore, the terminal Cr2(S\(_2\))\(_4\) octahedron is more distorted than the Cr1S\(_6\) octahedron, which is also rationalized by a comparison of their distortion indices: \( D_{\text{Cr1}} = 0.01242 \) for Cr1S\(_6\) and \( D_{\text{Cr2}} = 0.01648 \) for Cr2(S\(_2\))\(_4\). Figure S1 shows the local coordination environment around Ba sites. These Ba atoms have 9- or 10-fold coordination for S atoms. In particular, Ba2, Ba3, and Ba5 are bound to disulfide ions (S9–S10, S9–S11, and S10–S11), which are described in detail below.

Each Cr\(_4\)S\(_{15}\) tetramer unit is separated via nonmagnetic Ba atoms in the ab plane so as to form a two-dimensional slab with four CrS\(_6\) octahedral thickness, alternately stacked with a Ba\(_4\)S\(_4\) (=Ba\(_2\)(S\(_2\))\(_2\)) layer along the c-axis. As shown in Figure 4b, the four sulfur atoms (S9 × 2, S10, and S11) in the Ba4S\(_4\) layers form two types of disulfide ions (S9–S10 and S9–S11) along the [110] direction. The intramolecular bond distance between S9 and S11 (=1.892(4) Å) is shorter than that between S10 and S11 (=2.058(3) Å) atoms. The nearest interdimeric S−S distance corresponding to \( d_{S9−S9} = 4.433(3) \, \text{Å} \) is significantly long, indicating a very weak interaction between the ions.

Considering the structure formed by disulfide ions, the chemical formula can be expressed as Ba\(_9\)Cr\(_4\)(S\(_6\))\(_{11}\). Based on the charge balance, all chromium cations in Ba\(_9\)Cr\(_4\)(S\(_6\))\(_{11}\) should be trivalent. The results of the bond valence sum (BVS) calculation are summarized in Table 3. The BVS values of Cr1 and Cr2 atoms are 2.83 and 2.946, respectively, which agree well with the expected ones. The BVS values of the S6, S7, S9, S10, and S11 atoms comprising disulfide ions are also

### Table 1. Results of the Structure Refinement of Ba\(_9\)Cr\(_4\)S\(_{19}\) using Single-Crystal X-ray Diffraction Data

| Parameter                  | Value          |
|----------------------------|----------------|
| formula                    | Ba\(_9\)Cr\(_4\)S\(_{19}\) |
| formula weight             | 2053.11        |
| radiation                  | Mo Kα (\(λ = 0.71073 \, \text{Å}\)) |
| \(T\) (K)                  | 297            |
| crystal system             | monoclinic     |
| space group                | C2/c (No. 15)  |
| \(a\) (Å)                  | 12.7695(3)     |
| \(b\) (Å)                  | 11.3269(2)     |
| \(c\) (Å)                  | 23.2057(6)     |
| \(β\) (°)                  | 104.041(3)     |
| \(V\) (Å\(^3\))           | 3256.16(13)    |
| \(Z\)                      | 4              |
| \(D_{\text{cal}}\) (g/cm\(^3\)) | 4.188        |
| \(F_{100}\)                | 3616           |
| no. of measured reflections| 11692          |
| no. of unique reflections  | 3326           |
| no. of observed reflections| 2837           |
| \(R_{\text{int}}\) (%)    | 2.89           |
| final \(R_f/\sigma R\) (%) | 2.57/4.31      |
| GoF                        | 1.035          |
| maximum/minimum residual peak (e/Å\(^3\)) | 1.284/−1.093 |

This study reports the first ternary chromium disulfide Ba\(_9\)Cr\(_4\)S\(_{19}\), which could be obtained by a flux crystal growth method using BaCl\(_2\) molten salt. This new compound shows a unique zero-dimensional structure composed of Cr\(_4\)S\(_{15}\) tetramer units thanks to the incorporation of disulfide ions.

### RESULTS AND DISCUSSION

A photograph of single crystals of Ba\(_9\)Cr\(_4\)S\(_{19}\) is shown in Figure 2. The single-crystal structure analysis revealed that Ba\(_9\)Cr\(_4\)S\(_{19}\) typically linked by other Cr-centered polyhedra to form a 3D framework.

Figure 1. Relationship between the low-dimensional framework of Cr-centered polyhedra and the molar ratio of Ba/Cr.
consistent with the results of structural characterization. X-ray photoemission spectroscopy (XPS) measurements were performed to further investigate the oxidation states of these Cr ions. Figure 5 shows the Cr 2p XPS spectrum collected from single crystals of Ba₉Cr₄(S₂)₄S₁₁. The Cr 2p⁰⁷² spectrum is decomposed into two components with binding energies of 575.37 and 577.43 eV, which could be assigned to Cr³⁺ species. The component at the lower binding energy should be assigned to the Cr₂ atom bonded to a disulfide ion with an overall charge of −2.²⁴ The Cr₁/Cr₂ atomic ratio estimated from their spectral areas is 0.64:0.36, which roughly agrees with that obtained by structure analysis.

Both Cr₁ and Cr₂ atoms in a six-fold coordination form nonequivalent bonds with the surrounding sulfur ligands at
distances ranging from 2.35 to 2.50 Å. These Cr–S bond distances are consistent with those in related ternary chromium sulfides with trivalent Cr ions, such as Ba$_5$Cr$_3$S$_6$ and CsCr$_3$S$_6$. The Cr1–Cr1 and Cr1–Cr2 bond distances in the tetramer unit are 2.9854(14) and 2.8579(10) Å, respectively. Based on Pauling’s third rule, a face-sharing octahedron is less stable than the corner- and edge-sharing ones because of the larger Coulomb repulsion between the neighboring cations in the former. The cation–cation distance between the ideal face-sharing octahedra can be described as $1.16 \times d_{Cr-S}$. Because the Cr-centered octahedra are distorted, the average bond distances of Cr1–(S1/S2/S2) and Cr1–(S3/S4/S5) were considered to roughly estimate the Cr–Cr bond distances expected from ideal face-sharing (Cr1)$_2$S$_9$ and (Cr1)(Cr2)$_2$S$_9$ octahedra, respectively. As a result, the bond distances of 2.843 Å for Cr1–Cr1 and 2.771 Å for Cr1–Cr2 were obtained. The corresponding experimental values are 5.0 and 1.3% larger than the calculated values. This bond elongation possibly results from the reduction in Coulomb repulsion between the Cr atoms. However, its degree is not very large compared with those observed with 1D sulfides Ba$_5$Cr$_3$S$_6$ and Ba$_3$Cr$_2$S$_6$ with infinite 1D chains of face-sharing octahedra, in which the Cr–Cr bond distances are more than 10% longer than those expected from the ideal octahedra.

Dimensional reduction is widely observed in other multinary chalcogenides. For example, RE-Ga-S systems (RE: rare-earth metal) systematically decrease the dimensional framework composed of Ga-centered polyhedra from 2D to 0D with increasing the molar ratio of RE/Ga. In contrast, the zero dimensionality of Ba$_5$Cr$_3$S$_6$ is not in line with the relationship between the low-dimensional framework and the molar ratio of Ba/Cr in the Ba–Cr–S system. The molar ratio of Ba/Cr for Ba$_5$Cr$_3$S$_6$ is 2.25, which is within the regime for the 1D framework (Figure 1). It is likely that two types of the arrangement of disulfide ions play an important role in the crossover from 1D to 0D. In the first, two disulfide pairs are arranged in a 2D manner between the 2D slabs composed of Cr-based tetramer units. Such a low-dimensional arrangement of polysulfide ions interrupts direct linkage between the metal-centered polyhedra. Similar dimensional reduction induced by polysulfide ions is observed in di- or multinary (oxy-) polysulfide compounds (e.g., VS$_2$ and Ba$_{15}$S(VO)$_6$S$_4$). In the second type, disulfide ions occur on the terminal Cr-centered octahedra in the tetramer units, which would cause the breaking of 1D chains into smaller fragments. However, a disulfide ion does not always function as a ligand that reduces the dimensionality. For example, the amorphous chromium sulfide Cr$_5$S$_3$ (=Cr(S$_2$)$_1$S) comprises 1D chains of trivalent Cr atoms surrounded by six sulfur atoms, all of which form disulfide ions. The three sulfur atoms are shared between each neighboring Cr atom in a chain and one of them is coupled with a sulfur atom from another chain, resulting in a complex 3D framework. Therefore, the existence of non-magnetic Ba atoms, which break the linkages of Cr-centered octahedra, is essential for dimensional reduction.

At present, the low-dimensional magnetism of the Ba–Cr–S system has not been sufficiently investigated because it is difficult to obtain sufficient samples to measure physical properties. Based on the structure analysis, the Cr$_4$S$_9$ tetramer unit can be regarded as a spin tetramer with two types of nearest-neighbor interactions: $J_1$ for Cr1–Cr2 and $J_2$ for Cr1–Cr1. Figure 6 shows the temperature dependence of the magnetic susceptibility ($\chi = M/H$) of Ba$_6$Cr$_4$S$_{19}$ in a magnetic field of 10 kOe. The data were collected from several tiny single crystals, which were identified as the present phase by single-crystal X-ray diffraction (XRD). No significant difference was observed between the zero-field-cooled (ZFC) and field-cooled (FC) data. The $\chi(T)$ does not obey the Curie–Weiss law in the measured temperature range; instead, it monotonically decreases with the decrease of the temperature. The upturn observed below 40 K is probably due to impurity phases or defects in the lattice. A close inspection, however, detected a small kink at approximately 320 K, implying an antiferromagnetic ordering. Given the similar values of the Cr1–(Cr1/Cr2) bond angles (Table S3), both $J_1$ and $J_2$ are expected to be antiferromagnetic. In principle, the ideal spin tetramer model does not exhibit a long-range magnetic order regardless of the sign/magnitude of the intratetramer interactions. If Ba$_6$Cr$_4$S$_{19}$ is magnetically ordered, additional terms such as interchain interactions and magnetic anisotropies should be taken into account to describe the magnetic behaviors. Higher-temperature data of $\chi(T)$, theoretical calculations, and neutron diffraction experiments would be needed in future research.

**CONCLUSIONS**

In conclusion, we have demonstrated the successful crystal growth of a new member of the Ba–Cr–S system, Ba$_6$Cr$_4$S$_{19}$, from BaCl$_2$ molten salt. The polysulfide ligands, which had never been formed in extended chromium sulfides, allowed access to the 0D framework of Cr-centered octahedra. The high-temperature flux method with non-sulfide molten salt shown in the present study opens up possibilities for obtaining novel low-D polysulfide magnets.

**EXPERIMENTAL SECTION**

**Synthesis.** Ba$_6$Cr$_4$S$_{19}$ single crystals were obtained by a flux crystal growth method using BaCl$_2$ molten salt. First, 0.875 mmol of BaS (High Purity Chemicals, 3N), 0.25 mmol of Cr$_3$S$_3$ (High Purity Chemicals, 3N), and 0.25 mmol of BaCl$_2$ (Rare Metallics, 3N) were thoroughly mixed, pelletized, and then loaded into an alumina crucible and sealed in a silica tube under vacuum. These starting materials were then heated in a muffle furnace to 1050 °C for 6 h, held for 24 h, cooled to 750 °C for 60 h, and then cooled to room temperature by turning the furnace off. To remove the flux and green powdery byproduct, the product was repeatedly washed with distilled water by sonication. Black block single crystals were collected
Characterization. Structure determination of the single crystals was performed by a Rigaku XtaLab mini II diffractometer (Mo Kα radiation). The structure was solved by a dual-space algorithm method (SHELXT)\textsuperscript{32} and refined by a full-matrix least-squares method with SHELXL\textsuperscript{33} using an Olex²\textsuperscript{34} graphical user interface. X-ray photoemission spectroscopy (XPS) measurements were performed using a Mg Kα X-ray source (JEOL, JPS-9010MC). The Fermi level was calibrated using the C 1s signal. The magnetic susceptibility measurements were conducted in a magnetic field (H) of 1 kOe under zero-field-cooled (ZFC) and field-cooled (FC) conditions.

■ ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c06017.

Local coordination environment around Ba atoms; anisotropic displacement parameters; selected bond distances and bond angles; and crystallographic information (CIF)

Crystal structure; anisotropic displacement parameters; and bond distances and bond angles (PDF)

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Notes

The authors declare no competing financial interest.

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