Inorg. Chem. **1992**, *31*, 2107-2110

conformer observed in the electron diffraction study for $(CF_3)_2PF_3$ has both CF_3 groups in axial positions.[41]

Conclusion

Available data on geometric structures and chemical reactivities of sulfur–fluorine compounds suggest a quantitative structure–reactivity relationship for this class of compounds. So far, however, the number of examples is rather limited. The results of the present structure investigation of CF_3SOF and CF_3SF_3 are in accordance with this relationship. Additional studies on the chemical reactivity of sulfur–fluorine compounds for which gas-phase structures are known or, vice versa, structural studies of compounds whose chemical properties are known are required to confirm or modify the above relationship. In this context the investigation of the chemical reactivity of $(CF_3)_2SOF_2$ ($S-F_a$ = 164.1 (4) pm[43]) is planned in the near future.

Acknowledgment. R.M. and W.M. acknowledge support by the Minister für Wissenschaft und Forschung, Nordrhein-Westfalen and the Fonde der Chemischen Industrie. H.O. and I.W. are grateful for financial support by the Deutsche Forschungsgemeischaft.

Supplementary Material Available: Tables listing numerical values for the total intensities of CF_3SOF and CF_3SF_3 and full correlation matrices for both compounds (6 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Properties of $Ba_6Co_{25}S_{27}$: A Perovskite-like Superstructure of Co_8S_6 and Ba_6S Clusters

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Received August 15, 1991

We have prepared single crystals of a new ternary barium cobalt sulfide, $Ba_6Co_{25}S_{27}$, by cooling a melt containing BaS, CoS, and Co from 975 °C. The structure, determined by single-crystal X-ray diffraction, is cubic ($Pm3m$) with a = 10.033 (3) Å, Z = 1, and R = 2.6%, R_w = 2.4%. The structure contains an octahedrally coordinated cobalt atom, nearly cubic clusters of eight cobalt atoms, and an unusual arrangement of barium atoms. The electric resistivity and magnetic susceptibility measurements show that $Ba_6Co_{25}S_{27}$ is a poor metal with a resistance minimum at 8 K and is Pauli paramagnetic with a small Curie contribution indicating that either the Co_8 cluster or the octahedrally coordinated cobalt atom has a magnetic moment.

Introduction

In a previous report,[1] we have suggested that the unusual features of the high-temperature copper oxide superconductors could be duplicated in solid-state compounds with anions other than oxygen, in particular nitrogen and sulfur. In order to test this hypothesis, we are investigating the synthesis, structure, and properties of new ternary nitrides and sulfides. Herein, we report our first new ternary sulfide, $Ba_6Co_{25}S_{27}$. We also mention the synthesis of the isostructural compound $Ba_6Ni_{25}S_{27}$.

A first-row transition metal to the left of copper may have 3d orbitals with energies similar to those of the sulfur 3p orbitals, which would result in extensive mixing of the states at the Fermi level. Large electropositive cations, such as the heavier alkaline earth metals, may help "enforce" the perovskite-related structure of the copper oxide superconductors, as well as increase the oxidizing power of the oxygen.[1] We have chosen to explore the barium cobalt sulfide phase diagram, since these three elements satisfy the above criteria. Since many new barium iron sulfides have been discovered in the last 20 years,[2] there promise to be several new barium cobalt sulfides as well.

Only two barium cobalt sulfides have been reported in the literature. Ba_2CoS_3 is isostructural[3] with Ba_2FeS_3, while $BaCoS_2$ has been reported[4] to be isostructural with $BaNiS_2$, the only reported barium nickel sulfide. The former compounds along with all other known barium iron sulfides contain FeS_4 tetrahedra sharing edges and/or corners. With the exception of a high-pressure polymorph[5] of Ba_2FeS_3, and $BaNiS_2$, in which nickel is pentacoordinated to sulfur in a nearly square pyramidal environment, the transition metal is always tetrahedrally coordinated to sulfur atoms. Furthermore, these compounds do not contain any metal–metal bonding, except for a few barium iron sulfides which contain isolated iron pairs.

The title compound, $Ba_6Co_{25}S_{27}$, is isostructural with the mineral djerfisherite,[6] which is similar to Co_9S_8, the mineral pentlandite,[7] both of the latter containing cubic metal clusters and an octahedrally coordinated cobalt atom.

Experimental Section

Sample Preparation. $Ba_6Co_{25}S_{27}$ was first discovered by X-ray powder diffraction of the products produced in high-temperature reactions (900 °C) of barium sulfide, cobalt sulfide, and cobalt powder in graphite containers which were sealed in evacuated quartz tubes. Semiquantitative electron microprobe analysis of the crystalline product indicated the presence of a new phase with a Ba:Co:S molar ratio of approximately 1:4:5. The new phase, in fact, does not form from reactants heated at this molar ratio; however, it readily forms in mixtures containing less than 50 atom % sulfur. The crystal used for the structure determination was crystallized from the melt (heated to 975 °C and then cooled to 850 °C at 2 °C/h in a graphite boat and sealed in an evacuated quartz tube to prevent reaction with atmospheric oxygen) containing a Ba:Co:S molar ratio of 1:4:4. Singe-phase polycrystalline $Ba_6Co_{25}S_{27}$ can be made by reacting a pressed pellet (40000 psi) containing a BaS:CoS:Co molar ratio of reactants of 6:21:4. The reaction was carried out in an alumina crucible sealed in an evacuated (10 mTorr) quartz tube and heated to 850 °C for 2 days. BaS was purchased from Aesar (99.9%), and CoS was synthesized from the elements (99.8+% Co, S: 99.999% S). $Ba_6Co_{25}S_{27}$ forms gold metallic crystals which melt congruently at 950 °C, contain no ferromagnetic impurity, and are largely insensitive to the atmosphere.

$Ba_6Ni_{25}S_{27}$ has been detected by powder X-ray diffraction in multiphase samples. Reactions containing stoichiometric amounts of BaS,

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Table I. Single-Crystal X-ray Diffraction Data for $Ba_6Co_{25}S_{27}$

crystal system	cubic
space group	*Pm*3*m* (No. 221)
Z	1
a, Å	10.033 (3)
V, $Å^3$	1010 (1)
d(calcd), g/cm^3	5.201
mol wt	3162.9
approx crystal size, mm^3	0.3 × 0.1 × 0.1
$2\theta_{max}$, deg; scan type	55; $\omega-2\theta$
octants measd	(hkl); $(\bar{h}\bar{k}\bar{l})$
X-ray radiation	Mo Kα (λ = 0.71073 Å)
monochromator	graphite
temp, K	298
no. of reflns collected	2768
no. of independent reflns	283 (R_{int} = 3.04%)
no. of obsd independent reflns	281 ($F > 3.0\sigma(F)$)
abs coeff (μ), mm^{-1}	17.050
R, R_w, %[a]	2.6, 2.4
F(000)	1443

[a] $R = \sum|F_o - F_c|/\sum|F_o|$; $R_w = [\sum w(|F_o - F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F)$.

Table II. Positional and Isotropic Thermal Parameters for $Ba_6Co_{25}S_{27}$

atom	site	*x*	*y*	*z*	U_{eq},[a] $Å^2$
Ba(1)	(6f)	0.5	0.5	0.19603 (6)	0.0151 (2)
Co(1)	(24m)	0.13220 (5)	0.36218 (7)	0.13220	0.0156 (2)
Co(2)	(1a)	0.0	0.0	0.0	0.0124 (4)
S(1)	(1b)	0.5	0.5	0.5	0.0146 (7)
S(2)	(6e)	0.0	0.2361 (2)	0.0	0.0136 (4)
S(3)	(8g)	0.2767 (1)	0.2767	0.2767	0.0161 (2)
S(4)	(12h)	0.0	0.5	0.2462 (2)	0.0139 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

NiS, and S show a large impurity of $BaNiS_2$. $Ba_6Ni_{25}S_{27}$, as well as BaS and Ni_3S_2, is seen in reactions with a slight deficiency of sulfur and with a slight excess of barium. $Ba_6Ni_{25}S_{27}$ has an X-ray powder diffraction pattern similar to that of $Ba_6Co_{25}S_{27}$, with the same lattice parameters.

X-ray Structural Determination. Diffraction data were collected from an irregularly shaped crystal mounted on a glass fiber, using a Syntex $P2_1$ diffractometer and Mo Kα radiation. Experimental details are listed in Table I. The diffraction peaks were consistent with a primitive cubic unit cell with a lattice constant of 10.033 Å. The Laue class was found to be *m*3*m*, and no systematic absences were observed. The possible cubic space groups that give no extinctions are *P*23, *Pm*3, *P*432, *P*43*m*, and *Pm*3*m*. The structure was solved by direct methods and refined using an empirical absorption correction (ψ scan) in the highest symmetry space group, *Pm*3*m*, with atomic parameters listed in Table II. Refinement in the other groups did not significantly improve the fit. Structure solution and refinement were carried out using SHELXTL PLUS Rel. 4.11 software (Siemens). The analytical forms of the scattering factor tables for the neutral atoms[8] were used, and all scattering factors were corrected for both real and imaginary components of anomalous dispersion.[9] Selected bond distances and angles for the refined structure are given in Table III.

Structure Description. $Ba_6Co_{25}S_{27}$ can be approximately described as cubic close-packed layers of barium and sulfur atoms, S(2), S(3), and S(4), with three barium atoms for every thirteen sulfur atoms in each layer. Three-eighths of the tetrahedral holes are filled with cobalt atoms, Co(1), as are $^1/_{16}$th of the octahedral holes between alternating layers, Co(2). For both types of cobalt atoms the nearest neighbor close-packed atoms are sulfur atoms only. Between layers in which there are no cobalt atoms in octahedral sites, $^1/_{16}$th of the octahedral holes contain sulfur atoms, S(1), coordinated only to six barium atoms.

The Co(1) atoms form a nearly cubic cluster with two relatively short Co–Co distances of 2.653 (1) Å and another Co(1)–Co(1) distance of 2.766 (2) Å. The metal cluster is capped on all faces by sulfur atoms with an average Co–S distance of 2.24 Å. Each cube is then bridged to other cubes via eight octahedrally coordinated sulfur atoms connected to the vertices of the cube. As shown in Figure 1, this leads to tetrahedral coordination for the eight cobalt, Co(1), atoms in the cube. The Co(2) atoms are coordinated with perfect octahedral symmetry to six sulfur S(2) atoms (at a distance of 2.369 (2) Å), each of which caps a face of a Co(1) cube. Only two opposite faces of the Co(1) cube are capped by S(2) atoms; the other four faces are capped by S(4) atoms which are not coordinated to octahedral cobalt atoms. The Co(1) cube is elongated along the Co(2)–Co(2) axis by 0.11 Å, so that the cube is in fact slightly rectangular.

Table III. Selected Atomic Distances (Å) and Angles (deg) for $Ba_6Co_{25}S_{27}$

Co(1)–S(2)	2.262 (2)	S(2)–Co(1)–S(3)	123.3 (1)
Co(1)–S(3)	2.223 (1)	S(2)–Co(1)–S(4)	107.4 (0)
Co(1)–S(4)	2 × 2.232 (1)	S(3)–Co(1)–S(4)	107.0 (1)
		S(4)–Co(1)–S(4)	103.0 (1)
Co(2)–S(2)	6 × 2.369 (2)		
Co(1)–Co(1)	2 × 2.653 (1), 2.766 (2)	Co(1)–S(2)–Co(1)	54.1 (0), 124.0 (1)
Ba(1)–S(1)	3.050 (1)		
Ba(1)–S(3)	4 × 3.270 (2)		
Ba(1)–S(4)	4 × 3.217 (2)		
Ba(1)–Ba(1)	4 × 4.313 (2), 3.934 (2)		

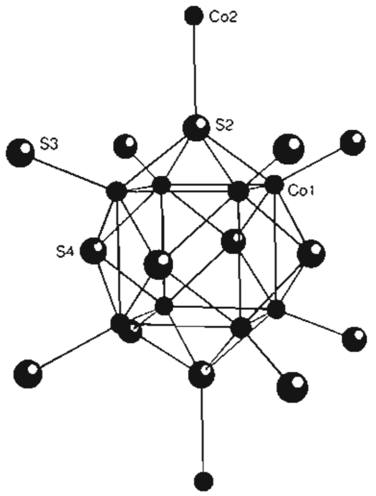

Figure 1. Structure and coordination of the cobalt cube cluster. The small black spheres are cobalt atoms, and the larger shaded spheres are sulfur atoms.

Six equivalent barium atoms form a perfect octahedron around a central sulfur, with a Ba–S distance of 3.050 (1) Å. The Ba–Ba intraoctahedral distances are 4.313 (2) Å, while the Ba–Ba interoctahedral distance is 3.934 (2) Å. The sulfur atoms in the close-packing layers face- and edge-cap the barium octahedron with Ba–S distances of 3.217 (2) and 3.270 (2) Å. Each barium has fourteen near neighbors: four barium atoms and eight sulfur atoms from the close packing, one sulfur in the center of the barium octahedron, and one barium in the next cluster (the short Ba–Ba distance is achieved through a vacant octahedral hole).

The cobalt and barium clusters as individual units form a perovskite-like ($SrTiO_3$) structure. The octahedral cobalt atoms, Co(2), are at the corners of the perovskite cell, the cobalt clusters are centered at the midpoint of the cell edges, and the barium octahedron is in the center of the cell. A stereoscopic view of the perovskite base and central barium cluster is shown in Figure 2.

Magnetic Susceptibility Measurement. The Faraday technique was used to measure the magnetic susceptibility of a 58.9-mg powder sample as a function of temperature, in a previously calibrated system.[10] Small amounts of ferromagnetic impurities were removed manually using a strong magnet. The susceptibility was measured as a function of the applied field and found to be field dependent, indicating a small remaining contamination of ferromagnetic impurity. The ferromagnetic contribution was subtracted from the data by the method of Owen and Honda.[11] The measured magnetic susceptibility for both cooling and heating, shown in Figure 3, is paramagnetic with a small temperature

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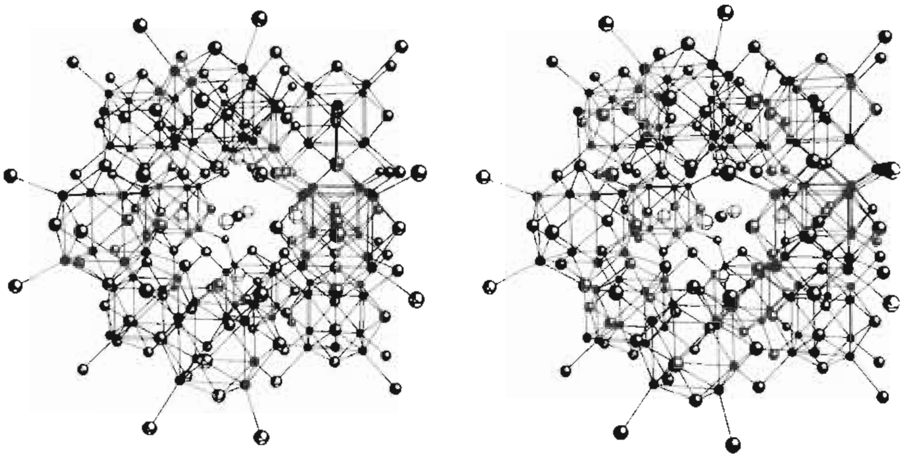

Figure 2. Stereoscopic view of a barium octahedron and its coordination to 12 cobalt clusters. The large white spheres are barium atoms, the grey spheres are sulfur atoms, and the small black spheres are cobalt atoms.

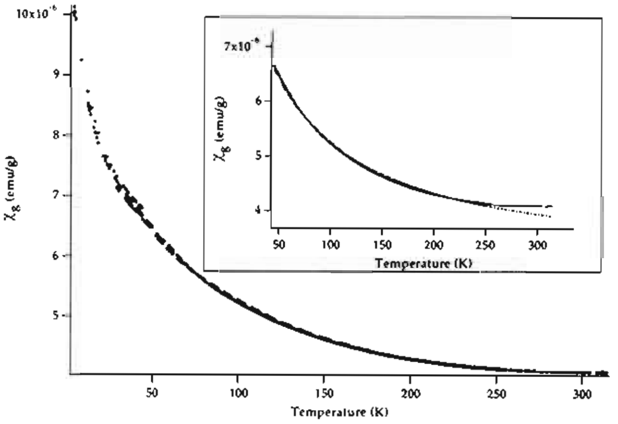

Figure 3. Magnetic susceptibility as a function of temperature for $Ba_6Co_{25}S_{27}$. Inset: comparison of the Curie law fit (dash-dot line) with data.

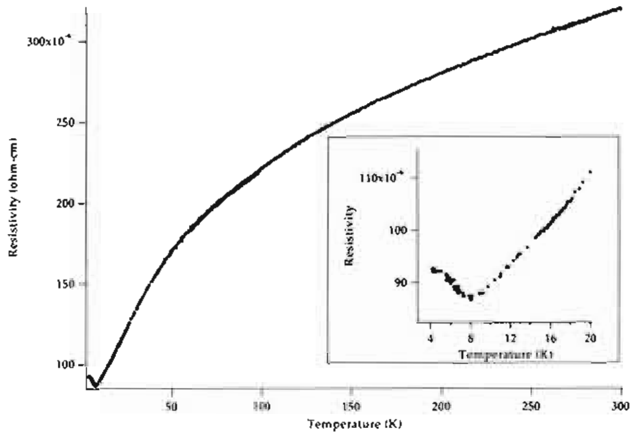

Figure 4. Electric resistivity as a function of temperature for $Ba_6Co_{25}S_{27}$. Inset: expansion of data showing the resistivity minimum at 8 K.

dependence. A peak at 50 K due to a small dioxygen impurity from the apparatus' atmosphere was omitted from the data in which it appeared.

Electrical Resistivity Measurement. Four-probe resistivity measurements were performed at 13 Hz by lock-in detection. The contacts were shown to be ohmic by the linearity of the I–V characteristic. Resistivities were calculated using the method of van der Pauw[12] for flat samples.

Cooling and heating curves of the resistivity versus temperature from room temperature to 4.2 K, shown in Figure 4, were determined for polycrystalline pellet (8.0 mm in diameter, 1.3 mm thick) sintered at 850 °C for 100 h. Indium electrical contacts were made at four points on the edge of the pellet. Contact resistances were measured to be less than 5 Ω. The room-temperature resistivity of the pellet was 3.2×10^{-4} Ω cm. The resistivity dropped sharply at low temperatures and reached a resistivity minimum at 8 K (see inset).

To confirm the room-temperature value, resistivity measurements were also made on a $0.3 \times 0.2 \times 0.2$ mm^3 single crystal of $Ba_6Co_{25}S_{27}$. Using four contacts, two with indium metal and two with silver paint, the resistivity of the single crystal was 2.3×10^{-4} Ω cm at room temperature, indicating that the pellet used for resistivity measurements was well sintered. The resistivity of the single crystal had a temperature dependence similar to that of the polycrystalline pellet down to 220 K, at which point the silver paint contacts failed.

Results and Discussion

Structure. Metal atom clusters such as the one found in $Ba_6Co_{25}S_{27}$ are of interest to molecular chemists, but in a recent review[13] only a few nonmolecular solids with discrete octanuclear clusters were mentioned. Co_9S_8 and the mineral pentlandite, $(Fe, Co, Ni)_9S_8$, both contain a perfect cube of metal atoms capped by six sulfur atoms and bridged to four other cubes by eight apical sulfur atoms. The clusters are also bridged by a metal atom octahedrally coordinated to six cube-face-capping sulfur atoms. Using the notation of Schafer and von Schnering,[14] this gives a connectivity pattern $[Co_8S^i_6]S^{a-a}_{6/6}$. In this notation, sulfur S^i (inner) atoms bridge metal atoms in the core of a cluster, while sulfur S^a (apical) atoms have only one nearest neighbor metal atom in each cluster and often bridge between clusters (e.g. S^{a-a}).

$Ba_6Co_{25}S_{27}$ contains similar $[Co_8S^i_6]$ clusters, but one cobalt cluster in four is replaced by a sulfur-centered octahedron of barium atoms, $[SBa_6]$. The connectivity is essentially the same except that only one-fourth of the octahedral cobalt sites are filled. This gives a connectivity formula of $[SBa_6]S^{i-a}_{8/4}Co^{a-a}_{0/6} + 3([Co_8S^i_6]S^{a-a}_{8/4}Co^{a-a}_{2/6})$. The only other synthetic compound[15] of this type is $K_6LiFe_{24}S_{26}Cl$, where the barium atoms are replaced by potassium, the octahedral cobalt is replaced by a lithium, the tetrahedral cobalt atoms are replaced by iron, and the octahedral sulfur is replaced by chlorine. The mineral djerfisherite,[6] which has been found in meteorites with an approximate chemical formula of $K_6Na(Fe,Cu,Ni)_{24}S_{26}Cl$, also has the $Ba_6Co_{25}S_{27}$ structure. Djerfisherite is found with varying amounts of alkali and transition metals. Iron is the primary transition element in djerfisherite, with 8%–14% by weight copper and less than 1.5% by weight nickel.

The thermal and atmospheric stability of compounds with this structure type and the already known variety of elements that can occupy the different crystallographic sites in this structure lead us to believe that there may be many other compounds of this type with the general formula $A_6M^oM^t_{24}S_{26}X$. A = Ba or K are of appropriate size to replace sulfur atoms in the close-packed layers. M^t is a tetrahedrally coordinate metal such as Co, Ni, Fe, or Cu.

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M^o is an octahedrally coordinate metal which may be the same as M^t. M^o in Co_9S_8 can be replaced by Ru, Rh, or Pd,[16] and octahedral Ag is found in natural[17] $(Fe,Ni)_8AgS_8$. Although a variety of metals can occupy the M^o site, it is believed that the octahedrally coordinated metals are extremely important to the stability of the metal clusters.[18] X may be S or Cl, which is assumed to substitute in the (1b) site. Preliminary investigations into compounds related to $Ba_6Co_{25}S_{27}$ indicate that the related phase $Ba_6Ni_{25}S_{27}$ also exists. This would be the first case of cube clusters containing only nickel atoms. We have been unable to synthesize the related selenides if they exist.

The tetrahedral cobalt (Co(1)) to sulfur distance in $Ba_6Co_{25}S_{27}$ is slightly larger, averaging 2.24 Å (see Table II), than those in Co_9S_8 (2.20 Å) and in the thiospinel Co_3S_4 (2.18 Å).[7] The octahedral cobalt (Co(2)) to sulfur distance, 2.369 (2) Å, is again slightly longer than the corresponding distances, 2.36 and 2.34 Å, in Co_9S_8 and CoS, respectively. These longer distances are expected from the lower average oxidation state of cobalt in $Ba_6Co_{25}S_{27}$ relative to the above binary compounds. Ba–S distances are only somewhat larger (3.217 (2) Å, 3.270 (2) Å) than that in BaS (3.19 Å), except for the case of the sulfur at the center of the barium octahedron, for which the distance is shortened to 3.050 (1) Å. The closest S–S distance is 3.35 Å, which is too long to have S–S bonding such as that seen in CoS_2, where the S–S distance is 2.12 Å.[19]

Physical Properties. To explain the temperature-dependent paramagnetism of $Ba_6Co_{25}S_{27}$, the magnetic susceptibility was fit to the Curie–Weiss law, $\chi = \chi_0 + C/(T + \Theta)$, at temperatures from 50 to 300 K, giving $\chi_0 = 3.0 \times 10^{-6}$ emu/g, $C = 3.2 \times 10^{-4}$ emu K/g, and $\Theta = 42$ K. The positive χ_0 is consistent with the observed metallic behavior. The fit is poor at high temperatures, with the calculated susceptibility falling off more quickly than that observed as temperature is increased (see inset). This suggests that the Pauli paramagnetic contribution to χ_0 is in fact temperature dependent and indicates that the value of the Weiss constant may not be well determined. Such temperature dependence is expected if there is a high density of states at the Fermi level or significant electron–electron interactions. The unusually high Pauli paramagnetic susceptibility, 3.8×10^{-4} emu/mol of cobalt, also indicates that $Ba_6Co_{25}S_{27}$ has a high density of states at the Fermi level and/or significant electron–electron interactions. In comparison, Pd metal has the largest susceptibility of the nonmagnetic elements, 5.5×10^{-4} emu/mol. The susceptibility of palladium metal is known to be greatly enhanced by electron–electron interactions,[20] so that it is almost ferromagnetic.

The Curie constant, C, gives an effective magnetic moment per cobalt atom of 0.57 μ_B for $Ba_6Co_{25}S_{27}$. If the paramagnetism were due to a magnetic iron impurity (at $S = 2$, $g = 2$ and $\mu = 4.9$ μ_B, for example), this would require a 1% iron impurity in the cobalt powder, which is 99.8% pure. This suggests that the slight Curie paramagnetism is intrinsic to the material. If we assign the entire paramagnetism to the single octahedral cobalt, we calculate a moment of 2.8 μ_B per Co(2), consistent with an oxidation state of +1 (Co^I, $S = 1$, $\mu = 2.8$ μ_B; low-spin Co^{II}, $S = {}^1/_2$, $\mu = 1.7$ μ_B). Another possibility is to assign the paramagnetism to the metal cluster—doing so yields a moment of 1.63 μ_B per Co_8 cluster, which is close to that expected for one unpaired electron per cluster ($S = {}^1/_2$, $\mu = 1.7$ μ_B); this could be the case if the octahedral cobalt atoms (Co(2)) are Co^{III} (low spin, $S = 0$), which would make each Co_8 cluster a 59-electron unit. Only microscopic measurements, such as electron spin resonance, can determine the origin of this moment unambiguously.

$Ba_6Co_{25}S_{27}$ is a poor metal with a resistivity that is about 100 times higher than that of copper at room temperature. The resistivity decreases by a factor of 3.5 at low temperatures. Simple metals have resistivity vs temperature curves that are linear (with a positive slope) or concave upward at low temperatures. Since $Ba_6Co_{25}S_{27}$ has a resistivity vs temperature curve that is concave downward, a scattering mechanism which decreases sharply at low temperatures is suggested.

This mechanism may involve either magnetic moments in the sample or Umklapp scattering of phonons. If there is a strong correlation between magnetic moments in the bulk sample, then once the magnetic moments become correlated at low temperatures, electrons are no longer able to undergo spin-flip scattering. Such correlation may by the source of the large Θ obtained in the magnetic susceptibility measurements. This phenomenon is seen in metallic compounds that show magnetic order[21] and in correlated systems such as heavy fermion metals.[22] If the resistivity is dominated by Umklapp scattering at high temperatures, we would expect to see an exponential drop in the resistivity at low temperatures.[23] This is probable since the large unit cell makes the Bruillouin zone small so that phonons which undergo Umklapp scattering at the zone boundary are likely to be low in energy. A second-order phase transition could also cause this effect, but we would then expect to see an anomaly in the magnetic susceptibility in the same temperature range.

The resistance minimum at 8 K may be due to scattering with isolated impurity spins as explained by Kondo[24] for magnetic alloys.

Conclusions

$Ba_6Co_{25}S_{27}$ is the first ternary compound with the djerfisherite structure. Due to the stability and variability of this structure type, $Ba_6Co_{25}S_{27}$ may be the first of a series of new compounds, many of which would be metallic conductors with unusual electric and magnetic properties as seen in $Ba_6Co_{25}S_{27}$.

Acknowledgment. We thank Abby Wizansky and Andrew A. Guzzelian for their preliminary work on this project. G.J.S. is grateful for the partial support by the REU program sponsored by the Materials Science Center at Cornell, through Grant NSF-DMR88-8516616. Support of this work by the Office of Naval Research is greatly appreciated.

Supplementary Material Available: Tables giving the structure solution and refinement summary for $Ba_6Co_{25}S_{27}$, complete bond lengths and angles, and complete anisotropic thermal parameters (6 pages); a listing of observed and calculated structure factors (1 page). Ordering information is given on any current masthead page.

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