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Structure–Reactivity Relationship for Sulfur–Fluorine Compounds. Gas-Phase Structure of Fluoro Trifluoromethyl Sulfoxide, CF_3SOF, and Trifluoro(trifluoromethyl)sulfurane, CF_3SF_3[1]

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The gas-phase structures of the two S(IV) compounds CF_3SOF and CF_3SF_3 have been determined by electron diffraction. The following geometric parameters (r_a/pm and $\angle_\alpha$/deg, uncertainty values 3σ) have been derived: CF_3SOF, S=O = 142.2 (5), S–F = 159.1 (4), S–C = 188.9 (5), ∠O=S–F = 103.9 (11), ∠O=S–C = 103.6 (35), ∠C–S–F = 93.7 (26), CF_3SF_3, S–F_e = 156.5 (8), S–F_a = 165.5 (5), S–C = 188.7 (7), ∠F_e–S–F_a = 86.1 (10), ∠C–S–F_a = 86.5 (7), ∠F_e–S–C = 98.4 (32). Literature data suggest a quantitative structure–reactivity relationship for sulfur–fluorine compounds. According to this relationship sulfanes and sulfuranes with S–F bonds shorter than 159.5 ± 1.5 pm form adducts with Lewis acids MF_5 (M = As, Sb), whereas compounds with S–F bonds longer than this "critical value" form salts by exchanging fluoride ions with Lewis acids. The above results for CF_3SOF (S–F = 159.1 (4) pm) and CF_3SF_3 (S–F_a = 165.5 (5) pm) confirm this relationship. The former compound, whose S–F bond is very close to the critical value, forms adducts with MF_5, whereas the latter reacts to yield $CF_3SF_2^+MF_6^-$.

Introduction

The chemical properties of a compound such as its stability and chemical reactivity are related to its geometric and electronic structure. In practice, however, very little is known about correlations between geometric structures and chemical reactivities. A quantitative structure–reactivity relationship appears to exist for sulfur–fluorine compounds. The data collected in Table I suggest that sulfur fluorides with S–F bonds longer than ca. 159.5 pm react with strong Lewis acids such as AsF_5 or SbF_5. In most cases the cations formed by F^- abstraction are stabilized by the hexafluorometalates MF_6^- (M = As, Sb). In some cases, however, secondary reactions occur, such as the reaction of CF_3SSF (r(S–F) = 161.1 (3) pm) with SbF_5:

$$2CF_3SSF + 2SbF_5 \xrightarrow{SO_2} 2[CF_3SS^+SbF_6^-]^* \rightarrow [S_4^{2+}(SbF_6^-)_2]\cdot SO_2 + C_2F_6$$

The assumed intermediate, the (trifluoromethyl)sulfonium cation CF_3SS^+ dimerizes to form an S_4^{2+} salt with simultaneous elimination of C_2F_6. Fluorosulfanes or fluorosulfuranes which possess electron lone pairs do not react with AsF_5 or SbF_5, if their S–F bonds are shorter than ca. 159.5 pm, but instead form Lewis acid–base adducts. In persulfuranes, where no electron lone pair is available for adduct formation, this critical value for S–F bond lengths is slightly lowered to ca. 158 pm. Examples, where both, structure and reactivity, are known, are the reactions of CH_3SF_5 with MF_5 (M = As, Sb) and of *trans*-CF_3SF_4Cl with AsF_5. The latter reaction is assumed to proceed in the following way:

$$CF_3SF_4Cl + AsF_5 \rightarrow [CF_3SF_3Cl^+AsF_6^-]^* \rightarrow F_2SCl^+AsF_6^- + CF_4$$

In the context of this structure–reactivity relationship the geometric structure, especially the S–F bond length in CF_3SOF, is of interest. For this compound we have observed the formation of adducts with AsF_5 and SbF_5. If the S–F bond is indeed shorter than 159.5 pm, CF_3SOF would be an additional confirmation of the above structure–reactivity relationship.

From known structural data for SF_4[22,34] and $(CF_3)_2SF_2$[32] it is very likely that the axial S–F bonds in CF_3SF_3 are much longer than 159.5 pm, and this is also reflected in the reactivity of this compound: $CF_3SF_2^+$ cations are readily formed with Lewis acids. An electron diffraction study of CF_3SF_3 has recently been reported by Downs et al.[28] but our results for this compound differ somewhat from those. These differences have no effect on the chemical reactivity discussed above but alter the conclusions concerning bonding properties of sulfuranes compared to those of phosphoranes. The two S(IV) compounds CF_3SOF and CF_3SF_3 are chemically related in so far as CF_3SF_3 reacts very readily with traces of water to form CF_3SOF.

Experimental Section

CF_3SF_3 was synthesized by "low pressure–cold surface" fluorination according to Braun et al.[35] A 7.0-mmol (1.414-g) sample of CF_3SSCF_3

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Table I. S–F Bond Lengths of Sulfur–Fluorine Compounds and Their Reactivity with Lewis Acids

compd	r(S–F)/pm		ref	products	ref
O_2SF_2	153.1 (2)		3	$O_2SF_2 \cdot AsF_5$	4
NSF_3	155.2 (3)		5	$NSF_3 \cdot MF_5$ (M = As, Sb)	6
OSF_2	158.3 (3)		7	$OSF_2 \cdot MF_5$ (M = As, Sb)	4
$CH_2{=}SF_4$	157.5 (12)[a]	159.5 (12)[b]	8	$CH_2{=}SF_4 \cdot AsF_5$	9
$FN{=}SF_4$	156.7 (5)[a]	157.7 (12)[c]	10	$FN{=}SF_4 \cdot MF_5$ (M = As, Sb)	10
CF_3SOF	?			$CF_3SOF \cdot MF_5$ (M = As, Sb)	11
CF_3SF_4Cl	158.3 (2)		12	$F_2SCl^+AsF_6^-$	13
CH_3SF_5	159.3 (4)[a]	157.7 (13)[b]	14	$CH_3SF_4^+MF_6^-$ (M = AS, Sb)	15
OSF_4	154.0 (3)[a]	159.7 (3)[b]	16	$OSF_3^+MF_6^-$ (M = As, Sb)	17
CF_3SSF	161.1 (3)		18	$S_4^{2+}(SbF_6)^- \cdot SO_2$	19
FSSF	163.5 (2)		20	$S_2F^+AsF_6^-$, $S_2F^+BF_4^-$	21
SF_4	154.2 (5)[a]	164.3 (5)[b]	22	$SF_3^+MF_6^-$ (M = P, As, Sb) $SF_3^+BF_4^-$	23 23
NSF	164.3 (2)		24	$NS^+MF_6^-$ (M = As, Sb)	25
$(CH_3)_2NSF_3$	156.3 (9)[a]	167.0 (7)[b]	26	$(CH_3)_2NSF_2^+MF_6^-$ (M = As, Sb) $(CH_3)_2NSF_2^+BF_4^-$	27 27
CF_3SF_3	159.6 (11)[a]	167.9 (4)[b]	28	$CF_3SF_2^+MF_6^-$ (M = P, As, Sb) $CF_3SF_2^+BF_4^-$	29, 30 30
CH_3SF_3	157.5 (5)[a]	168.9 (1)[b]	28	$CH_3SF_2^+AsF_6^-$, $CH_3SF_2^+BF_4^-$	31
$(CF_3)_2SF_2$		168.1 (3)[b]	32	$(CF_3)_2SF^+MF_6^-$ (M = As, Sb)	33

[a] $(S–F)_{eq}$. [b] $(S–F)_{ax}$. [c] Mean $(S–F)_{ax}$.

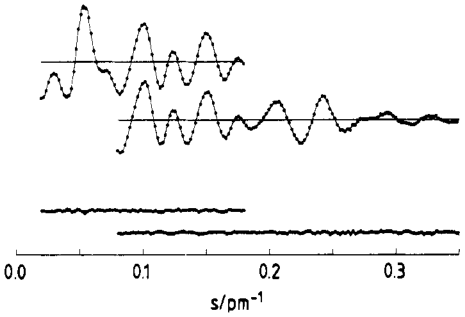

Figure 1. CF_3SOF: Experimental (dots) and calculated (full line) molecular intensities and differences.

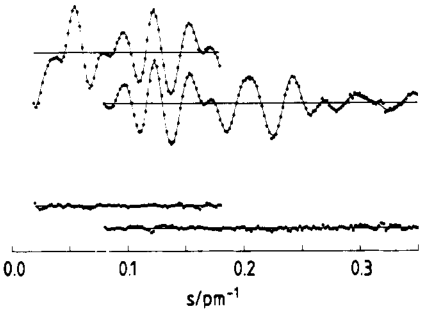

Figure 2. CF_3SF_3: Experimental (dots) and calculated (full line) molecular intensities and differences.

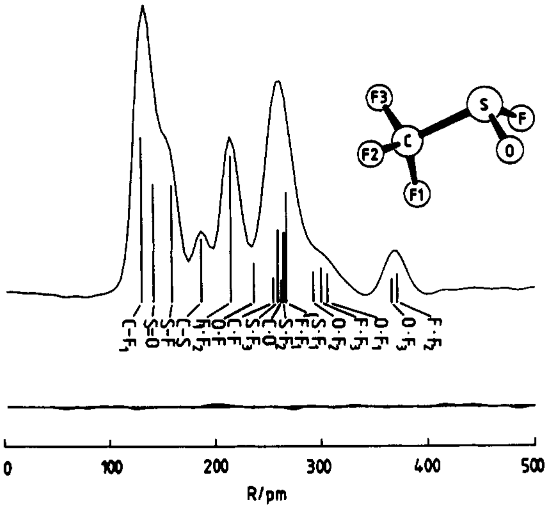

Figure 3. CF_3SOF: Experimental radial distribution function and difference curve. An artificial damping factor of $\exp(-20s^2)$ was used.

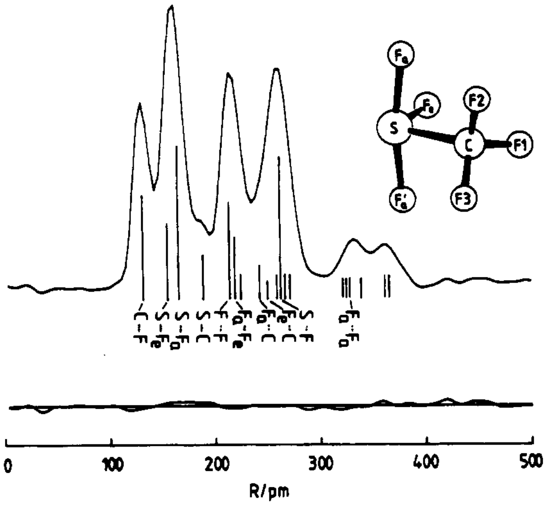

Figure 4. CF_3SF_3: Experimental radial distribution function and difference curve. An artificial damping factor of $\exp(-20s^2)$ was used. Nonbonded distances between CF_3 fluorines and SF_3 fluorines are not labeled.

was condensed at 77 K into a 100-mL stainless steel reactor. The fluorination was performed at 153 K for 6 h, and excess fluorine was pumped off at 77 K. The yield was 95%. The purity was checked by ^{19}F-NMR spectroscopy.

CF_3SOF was prepared by mild hydrolysis of CF_3SF_3 according to Ratcliffe and Shreeve.[36] A 15-mmol (2.37-g) amount of CF_3SF_3 was condensed into a 2-L glass flask and 200 mbar of air was added. After 14 days at room temperature, the air was pumped off at 77 K. The sample was purified by fractional condensation at 183–188 K in order to remove the formed SiF_4. The yield of spectroscopically pure CF_3SOF was ca. 50%.

The samples were transported from Dortmund to Tübingen at liquid-nitrogen temperature. The electron diffraction intensities were recorded with a Balzers Gas Diffractograph[37] at two camera distances (25 and 50 cm) and with an acceleration voltage of ca. 60 kV. The electron wavelength was determined from ZnO diffraction patterns, which in turn were calibrated by CO_2 gas diffraction. The sample reservoirs were kept

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Table II. Results of the Electron Diffraction Analysis for CF_3SOF^a

Geometric Parameters

S=O	142.2 (5) (p_1)	∠C–S–F	93.7 (26) (p_7)
S–F	159.1 (4) (p_2)	∠F–C–F	109.9 (3) (p_8)
S–C	188.9 (5) (p_3)	tilt(CF_3)	3.9 (26) (p_9)
C–F	132.2 (3) (p_4)	δ(F1CSF)	40 (7) (p_{10})
∠O=S–F	103.9 (11) (p_5)	δ(F1CSO)^b	−60 (7)
∠O=S–C	103.6 (35) (p_6)		

Interatomic Distances and Vibrational Amplitudes

	dist	amplitude		dist	amplitude
C–F	132	4.8 (4) (l_1)	S·F3	258	9 (3) (l_7)
S=O	142	4.3 (6) (l_2)	S·F2	264	
S–F	159	4.7 (3) (l_3)	S·F1	268	
C–S	189	5.4 (4) (l_4)	O·F2	292	17 (3) (l_8)
F1·F2	216	6.0 (2) (l_5)	F·F3	300	
O·F	237	10 (3) (l_6)	O·F1	306	
C·F	254		O·F3	369	9 (1) (l_9)
C·O	261		F·F2	370	
F·F1	268	17^c			

^{a} r_a distances in pm and $\angle_\alpha$ angles in deg. Numbers in parentheses are 3σ values and refer to the last digit. For atom numbering, see Figure 3. ^{b} Dependent parameter. ^{c} Not refined.

Table III. Results of the Electron Diffraction Analysis for $CF_3SF_3{}^a$

Geometric Parameters

$(S\text{–}F)_{mean}{}^b$	162.5 (3) (p_1)	$\angle F_e\text{–}S\text{–}F_a$	86.1 (10) (p_5)
ΔSF =	9.0 (10) (p_2)	$\angle C\text{–}S\text{–}F_a$	86.5 (7) (p_6)
$(S\text{–}F_a) - (S - F_e)$		$\angle F_a\text{–}S\text{–}F_a{}^c$	169.4 (13)
$S\text{–}F_e{}^c$	156.5 (8)	$\angle F_e\text{–}S\text{–}C$	98.4 (32) (p_7)
$S\text{–}F_a{}^c$	165.5 (5)	∠F–C–F	109.7 (8) (p_8)
S–C	188.7 (7) (p_3)	$\delta(F1CSF_e)^d$	21 (6) (p_9)
C–F	131.9 (3) (p_4)		

Interatomic Distances and Vibrational Amplitudes

	dist	amplitude		dist	amplitude
C–F	132	4.1 (3) (l_1)	$F_e{\cdot}C$	250	9.0^e
$S\text{–}F_e$	157	5.2 (6) (l_2)	S·F	263	7.3 (5) (l_5)
$S\text{–}F_a$	166		$F{\cdot}F_x{}^f$	226–269	23.0 (4) (l_6)
S–C	189	4.7 (8) (l_3)	$F{\cdot}F_x{}^f$	324–328	24.0 (7) (l_7)
F·F	215	6.6 (6) (l_4)	$F_a{\cdot}F_a{}'$	329	8.0^e
$F_a{\cdot}F_e$	220		$F{\cdot}F_x{}^f$	342–369	15.0^e
$F_a{\cdot}C$	243	7.0^e			

^{a} r_a distances in pm and $\angle_\alpha$ angles in deg. Figures in parentheses are 3σ values and refer to the last digit. For atom numbering, see Figure 4. ^{b} $(S\text{–}F)_{mean} = {}^1/_3[(S\text{–}F_e) + 2(S\text{–}F_a)]$. ^{c} Dependent parameter. ^{d} Effective torsional angle of CF_3 group, for $\tau = 0$ the C–F1 bond eclipses the $S\text{–}F_e$ bond. ^{e} Not refined. ^{f} F_x is F_a or F_e.

at −55 °C (CF_3SOF) and −73 °C (CF_3SF_3), and the inlet system and nozzle were maintained at room temperature. The purity of the samples was checked by IR gas spectra before and after the experiment. Two plates for each compound and camera distance were analyzed with the usual procedures.[38] Numerical values of the scattering intensities in the s-ranges 0.02–0.18 pm^{-1} and 0.08–0.35 pm^{-1} in steps of $\Delta s = 0.002$ pm^{-1} are available as supplementary material, and averaged molecular intensities are shown in Figures 1 and 2.

Structure Analysis

Preliminary structural models for both compounds were derived from the radial distribution curves (Figures 3 and 4), which were then refined by least-squares analyses. For this purpose, the molecular intensities were multiplied with diagonal weight matrices[38] and known scattering amplitudes and phases were applied.[39] Comparison of radial distribution curves calculated for various structural models with the experimental curve reveals that CF_3SF_3 possesses C_s symmetry with the CF_3 group in the equatorial position and eclipsing the equatorial S–F bond. The CF_3 group in CF_3SOF staggers the S=O and S–F bonds. For both compounds the CF_3 groups were constrained to C_{3v} symmetry with a possible tilt angle between the C_3 axis and the S–C bond direction. In the analysis for CF_3SF_3 the refined value for the tilt angle is smaller than the respective standard deviation and it was set to zero in further refinements. The fit of the experimental intensities improves slightly if the CF_3 group is allowed to deviate from the exact eclipsed position. This torsional angle is an effective value due to a large amplitude torsional motion and indicates a low barrier to internal rotation around the S–C bond. Vibrational amplitudes for closely spaced distances were collected in groups, and those for distances which make small contributions to the molecular intensities were set to fixed values (see Tables II and III). With these assumptions ten (CF_3SOF) and nine (CF_3SF_3) independent geometric parameters were refined simultaneously together with nine (CF_3SOF) and seven (CF_3SF_3) vibrational amplitudes. Several correlations between these parameters had values larger than |0.7|:

CF_3SOF: $p_4/p_8 = 0.80$, $p_6/p_7 = -0.90$, $p_6/p_9 = 0.75$, $p_6/p_{10} = 0.79$, $p_7/p_{10} = -0.92$, $p_1/l_1 = -0.82$, $p_4/l_2 = 0.71$, $p_6/l_7 = -0.83$, $p_6/l_8 = 0.85$, $p_7/l_8 = -0.78$, $p_9/l_7 = -0.98$, $p_9/l_8 = 0.75$, $l_1/l_2 = 0.87$, $l_7/l_8 = -0.82$

CF_3SF_3: $p_5/p_8 = 0.86$, $p_7/p_8 = -0.74$, $p_7/p_9 = 0.86$, $p_2/l_2 = -0.92$, $p_5/l_4 = -0.87$, $p_7/l_5 = 0.76$, $p_8/l_4 = -0.82$

Numbering of the geometric parameters p_i and vibrational amplitudes l_k and the final results are given in Tables II and III.

Discussion

The S–F bond length of CF_3SOF, which is of primary interest in this study, is not affected by high correlations and is thus well determined. It is only slightly shorter (159.1 (4) pm) than the "critical" value for chemical reactivity discussed in the Introduction (ca. 159.5 pm for sulfanes and sulfuranes). The experimental value conforms with the observation that this compound does not react by fluoride abstraction but forms adducts with Lewis acids. Within the combined error limits the S–F and S–C bond lengths are equal to those in F_2SO (S–F = 158.3 (3) pm)[7] and $(CF_3)_2SO$ (S–C = 188.5 (4) pm).[32] The bond angles around sulfur (∠O=S–F and ∠O=S–C), which are not well determined in this study because of high correlations between refined parameters, correspond within experimental uncertainties to those in F_2SO and $(CF_3)_2SO$.

Some geometric parameters of CF_3SF_3 which were derived in this study do not agree with those reported by Downs et al.[28] Their values for the S–F and S–C bond lengths are larger by 2–3 pm. This earlier study, however, has recently been revised (personal communication from D. W. H. Rankin), yielding parameters in agreement with ours. The mean S–F bond lengths in $R\text{–}SF_3$ compounds increase steadily with decreasing electronegativity of the equatorial substituent R, from $F\text{–}SF_3$ (160.9 (5) pm from electron diffraction,[22] 161.2 (3) pm from microwave spectroscopy[34]), to CF_3SF_3 (162.5 (3) pm), and to CH_3SF_3 (165.1 (2) pm[28]). This trend is in accordance with ab initio calculations (HF/4-21S*): $(S\text{–}F)_{mean} = 160.1$ pm in $F\text{–}SF_3$[8], 162.0 pm in CF_3SF_3,[28] and 164.2 pm in CH_3SF_3.[28] The experimental $(S\text{–}F)_{mean}$ bond lengths of $Me_2N\text{–}SF_3$ (163.4 (4) pm)[26] and $FS\text{–}SF_3$ (163.8 (5) pm)[40] are also intermediate between the two extremes $F\text{–}SF_3$ and CH_3SF_3. This effect of equatorial substituents is very similar to that in $R\text{–}PF_4$ compounds, indicating similar bonding properties in sulfuranes and phosphoranes. On the other hand, the CF_3-substituted sulfuranes CF_3SF_3 and $(CF_3)_2SF_2$ differ markedly from the analogous phosphoranes CF_3PF_4 and $(CF_3)_2PF_3$ with respect to their conformational properties. CF_3 groups in both sulfuranes occupy equatorial positions, and there is no experimental evidence for a conformer with axial CF_3 groups. Ab initio calculations for CF_3SF_3[28] predict the axial conformer to be higher in energy by 64.0 kJ mol^{-1} relative to the equatorial form. An electron diffraction study of CF_3PF_4, however, results in a mixture of equatorial and axial conformers in a ratio of 60:40,[41] in perfect agreement with a recent matrix isolation FTIR study.[42] The only

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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.

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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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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 (40 000 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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