from the plot of log ${}^1/_3K(1/T)$, yields a straight line which intercepts the origin of the Cartesian axes. If it is assumed that the dominant contribution to Q_t/Q_s comes only from the single Cu–Cu stretching vibration, ν, then

$$Q_t/Q_s = \left\{\frac{1 - \exp(-h\nu_s/kT)}{1 - \exp(-h\nu_t/kT)}\right\} \qquad (10)$$

The Cu–Cu stretching mode, ν_s, appears to be about 1.6 times higher in frequency than ν_t, since as $T \rightarrow \infty$, $\log (Q_t/Q_s) \rightarrow \log (\nu_s/\nu_t) = 0.2$. As an illustrative calculation, we take $\nu_s = 100$ cm^{-1} and $\nu_t = 63$ cm^{-1} to obtain the correction curve given in the lower part of Figure 2. The order of magnitude of the Cu–Cu vibrational correction is, in fact, sufficient to yield the expected intercept for the log ${}^1/_3K(1/T)$ plot (see dashed line of Figure 2). A necessary consequence of the correction is a slightly diminished value of $J = 840$ cal mole^{-1} (*i.e.*, $-2J_{12} = 294$ cm^{-1}).

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High-Pressure (70-kbar) Synthesis of New Crystalline Lead Dichalcogenides

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By subjecting mixtures of the elements or of lead monochalcogenides with excess sulfur and selenium to temperatures of 600–2400° and pressures of 20–70 kbars, we have synthesized the stable crystalline compositions $PbSe_2$, PbSSe, and two polymorphs of PbS_2, one of the latter appearing to be isomorphous with SnS_2. Until now, only crystalline PbS, PbSe, PbS·PbSe, or amorphous polysulfides and polyselenides had been reported.

Experimental Section

Starting materials consisted of compressed pellets of 99.9+% lead, 99.999+% sulfur, and 99+% selenium prepared at ambient conditions with chalcogenide:lead ratios of at least 3:1. Also pellets composed of mixtures of PbS + S, PbS + PbSe + S + Se, and PbSe + Se in ratios of 1:2, 1:1:2:2, and 1:2 were used in tetrahedral pyrophyllite sample holders with graphite heating elements described previously.[1] Thin-walled boron nitride sleeves were used to insulate the reaction mixture from the heater. A tetrahedral anvil apparatus of National Bureau of Standards design[2] was used for all syntheses. Discussion of temperature and pressure calibrations and experimental procedure have been reported earlier.[3]

Results and Discussion

Duncan and Ott[4] reported the synthesis and isolation of an amorphous lead disulfide which was quite unstable at ambient conditions. We have prepared two crystalline polymorphs of lead disulfide from elemental and PbS + S mixtures. One of these was prepared repeatedly at 20 kbars and 1600–1800°. Each time this synthesis was carried out, an explosion or blowout occurred so that the quantity of gray-black solid remaining in the sample cavity was sufficient only for X-ray characterization. The complete X-ray powder diffraction pattern we obtained for this product, which we shall call α-PbS_2, is shown in Table I. As indicated, the material appears to be isostructural with the CdI_2-type SnS_2 structure. The calculated lattice constants for α-PbS_2 based on hexagonal indexing are $a = 3.89$, $c = 5.91$ A. These constants seem reasonable when compared to the reported values $a = 3.63$ and $c = 5.86$ A for the tin sulfide,[5] which would be expected to occupy a smaller volume than PbS_2 considering the relative sizes of tin and lead radii. When we tried thicker BN capsules, Ni reaction vessels, or substituted pulse heating to maintain the reaction conditions without blowouts, we obtained either PbS or Ni_3PbS_2 as the only products indicated by X-ray analyses.

TABLE I
X-RAY POWDER DIFFRACTION PATTERNS

	SnS_2^a		α-PbS_2^b		
			d, A		
hkl	*d*, A	*I*	Obsd	Calcd	I^c
001	5.9	50	6.0	5.9	s
100	3.15	40			
101	2.78	100	2.85	2.83	s
102	2.14	50	2.13	2.18	m
110	1.82	50			
111	1.74	40			
103	1.66	13	1.68	1.67	s
201	1.52	20			
202	1.391	13			
113	1.334	10			
210	1.192	4	1.23	1.22	m
211	1.170	13			
114	1.146	8	1.16	1.16	w

[a] ASTM 1-1010. [b] Cu Kα radiation taken as 1.5418 A. [c] Visually estimated.

The other crystalline products were prepared from Pb–S, Pb–S–Se, and Pb–Se elemental mixtures in atomic ratios of 1:3, 1:1.5:1.5, and 1:4, respectively. Successful syntheses were also carried out with mixtures of the monochalcogenides and excess sulfur and/or selenium. The strongest lines of the X-ray powder diffraction patterns obtained for these are listed in Table II. The patterns could be indexed on the basis of a tetragonal KN_3 structure type with average lattice constants as follows: β-PbS_2, $a = 6.10 \pm 0.10$, $c = 7.48 \pm 0.10$ A; PbSSe, $a = 6.27$ [illegible] 0.01, $c = 7.57 \pm 0.02$ A; and $PbSe_2$, $a = 6.36 \pm 0.08$, $c = 7.63 \pm 0.10$ A. The increasing lattice constants with increasing

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(1) H. T. Hall, *Science*, **128**, 446 (1958).

(2) E. C. Lloyd, U. O. Hutton, and D. P. Johnson, *J. Res. Natl. Bur. Std.*, **C63**, 59 (1959).

(3) J. R. Soulen and M. S. Silverman, *J. Polymer Sci.*, **A1**, 823 (1963).

(4) W. E. Duncan and E. Ott, *J. Am. Chem. Soc.*, **53**, 3940 (1931).

(5) R. W. G. Wyckoff, "The Structure of Crystals," 2nd ed, The Chemical Catalog Co., Inc., New York, N. Y., 1931, p 239.

TABLE II

X-RAY POWDER DIFFRACTION PATTERNS

	β-PbS_2		PbSSe		$PbSe_2$	
hkl	*d*, A[a]	*I*[b]	*d*, A	*I*	*d*, A	*I*
110	4.30	75	4.44	60	4.56	60
111	3.73	25	3.79	25	3.86	10
200	3.07	50	3.15	60	3.22	50
112	2.83	100	2.89	100	2.94	100
211	2.58	5	2.63	50	2.70	50
202	2.38	50	2.42	60	2.47	60
220	2.17	25	2.22	50	2.27	25
310	1.93	50	1.98	60	2.04	60
222	1.87	60	1.91[c]	50	1.96	25
004	...	...	1.87	25	1.92[c]	50
312	1.72	60	1.75	50	1.79	25
114	...	...	...	...	1.77	10
321	1.65	5	1.70	25	1.74	25
204	1.60	25	1.62	50	1.65	25
330	1.44	10	1.48	10	...	...
402	...	...	1.45[c]	50	1.48	50
323, 224	1.41	50	...	...	1.47	25
NI[d]	...	...	1.40	10	...	...
420	1.365	5	...	...	1.438	25
332	1.345	50	1.375[c]	50	1.407	25
314	...	...	1.353	10	1.397	50
NI	...	...	1.337	10	1.357	10
422	1.280	25	1.316	25	1.346	25
510	1.200	25	1.231	25	1.261	25

[a] Copper Kα radiation taken as 1.5418 A. KCl internal standard used for all; however, only intensities were corrected for KCl presence. [b] The intensities of the diffraction lines were measured as peak heights above background using a densitometer. They are expressed as percentages of the intensity of the strongest line. [c] Broad line. [d] Not indexed.

selenium content are consistent with the relative atomic sizes of S and Se. The measured densities were 5.51 g/cc for β-PbS_2 and 7.48 g/cc for $PbSe_2$ compared to 6.47, 7.15, and 7.86 g/cc calculated for four molecules per unit cell for PbS_2, PbSSe, and $PbSe_2$ respectively.

Conditions favorable for at least partial conversion to the tetragonal dichalcogenides were found to be above 30 kbars and 650° in most cases. At 45 kbars, 1500°, essentially quantitative conversions were obtained in 5 min. Microscopic examination of the homogeneous products revealed charcoal-gray, elongated, rodlike crystals usually radiating toward the center of the reaction pellet. No β-PbS_2 was found below 600° and only PbS formed between 10 and 30 kbars and 600 and 1200°. $PbSe_2$ and PbSSe also required temperatures above 500–600° for their formation. Excess sulfur was removed by successive washings with CS_2 followed by ether rinsing and vacuum drying. An aqueous solution of 10% Na_2S separated elemental Se from the selenide without decomposing the lead compound, as indicated by the X-ray pattern of the dried solute.

Anal. Calcd for β-PbS_2: Pb, 76.4; S, 23.6. Found: Pb, 71.8, 74.1; S, 27.2, 24.7. Calcd for PbSSe: Pb, 65.1; S, 10.1; Se, 24.8. Found: Pb, 58.3; S, 10.5; Se, 25.2. Calcd for $PbSe_2$: Pb, 56.7; Se, 43.3. Found: Pb, 57.6, 51.1, 55.2; Se, 42.4 (by difference), 45.1, 44.8 (by difference).

Since the change in *d* spacings shown in Table II for each *hkl* value is nearly linearly related to composition, possibly there exists a whole solid solution range of compositions such as $PbS_{2-x}Se_x$ where *x* varies from 0 to 2. Our attempts to prepare the intermediate compositions Pb_2S_3Se and Pb_2Se_3S from the appropriate atomic ratio mixtures containing excess S and Se, however, yielded only PbS and PbSe, respectively, plus a few unidentified lines, according to the X-ray patterns.

Thermogravimetric analysis (tga) of purified β-PbS_2 in pure, dry O_2 showed a weight gain of 12.8% compared to 11.7% calculated for oxidation of the disulfide to $PbSO_4$. The residue had an X-ray powder diffraction pattern characteristic of $PbSO_4$ plus a few weak unidentified lines. The initial weight gain started at 235° and leveled off at 462°. In N_2, β-PbS_2 showed an initial weight loss at 150° leveling off at 317°. The reaction, purposely interrupted at the first plateau in the tga curve, yielded PbS only. This mode of decomposition is typical of group IVa disulfides and was also the same for PbSSe and $PbSe_2$, which decomposed initially to PbS·PbSe and PbSe, respectively. The weight loss of the diselenide began at 344° and leveled off at 513°.

The distinct differences between β-PbS_2 reported here and the lead disulfide reported by Duncan and Ott[4] are as follows: (1) Weak PbS lines only were present on their original X-ray films from fresh samples and this pattern became more intense as samples were exposed. The products we obtained including the mixed selenide and diselenide showed no trace of the monochalcogenide X-ray powder patterns after 8 months of storage at room temperature. (2) The density of their amorphous product increased from 4.47 to 5.49 g/cc after air exposure for 1 week (6.8 g/cc is the calculated density of a PbS–S 1:1 mixture). In the same period of time the density of β-PbS_2, 5.51 g/cc, was virtually unchanged. (3) Tetragonal β-PbS_2 analyzed close to this stoichiometry after air exposure for 1 week, whereas the amorphous disulfide decomposed to $PbS_{1.4}$ after remaining at ambient conditions overnight. (4) Duncan and Ott reported that some decomposition took place at temperatures as low as 50° in contrast to our tga results mentioned previously. (5) The color of all of our lead products was charcoal-gray, whereas most of the amorphous disulfides were maroon or reddish brown, although a few were reported to be black.

Some preliminary electrical resistance measurements were taken with increasing pressure from 10 to 70 kbars on $PbSe_2$. No significant changes were observed, indicating that the basic character of the compound is covalent. Chemical behavior of the tetragonal disulfide was as follows: no reaction in water or ethanol, partial solubility in 0.1 *N* NaOH, vigorous reaction in concentrated HCl with H_2S evolution, and immediate reaction in concentrated HNO_3 to yield a precipitate. Tetragonal $PbSe_2$ did not superconduct above 0.3°K,[6] the lowest temperature at which tests were run.

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(6) D. B. McWhan, private communication.

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Fluorine-19 Chemical Shifts in Nuclear Magnetic Resonance Spectra of Fluorosulfate-Containing Compounds

BY FREDERICK A. HOHORST AND JEAN'NE M. SHREEVE

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Since the synthesis of peroxydisulfuryl difluoride ($S_2O_6F_2$) by Dudley and Cady,[1] the number of compounds containing the fluorosulfate group, OSO_2F, has increased rapidly inasmuch as reactions of the former or its derivatives provide a facile route to the introduction of this group into fluoroolefins and simple inorganic molecules. In characterizing some of these fluorosulfates, the chemical shift of the fluorine bonded to sulfur was reported with respect to an internal or an external standard. The literature reports no attempts to compare the magnitudes of the chemical shifts as a function of chemical or molecular environment. However, it has been stated that resonances in the -50-ppm region are diagnostic of the fluorine in fluorosulfate since the frequency in organic molecules seems to be relatively constant.[2] In order to study this relationship, several of these compounds have been synthesized and their nuclear magnetic resonance spectra have been measured with trichlorofluoromethane as the internal reference.

Experimental Section

The compounds examined were prepared through the use of conventional methods. A Varian Model 4311B high-resolution spectrometer equipped with a 40-Mc oscillator was used to determine the nuclear magnetic resonance spectra. Reproducibility of chemical shift values was about ±0.1 ppm for consecutive measurements on the same or different preparations of a compound or for measurements separated by 24 hr. The samples were contained in sealed 5-mm o.d. Pyrex tubes heated to 35° prior to use to check pressure stability. Roughly 50% solutions (by volume) were prepared with CCl_3F, which had been dried over P_2O_5, as the reference compound. In the case of $HOSO_2F$, because of immiscibility with CCl_3F, an external reference was used. CCl_3F was sealed into a 2-mm o.d. tube, and this was placed in the liquid $HOSO_2F$. External references were also used with $ClOSO_2F$ and $BrOSO_2F$.

In Table I, the fluorosulfate compounds are listed with the respective chemical shifts given in ppm.

TABLE I

F^{19} CHEMICAL SHIFTS OF OSO_2F IN FLUOROSULFATE-CONTAINING COMPOUNDS RELATIVE TO CCl_3F

Compound	Shift, ppm	Compound	Shift, ppm
$ClOSO_2F$[a]	-33.9[h]	FO_2SOSO_2F[b]	-48.8
$FOSO_2F$[b]	-36.3	$CF_2(OSO_2F)_2$[e]	-48.7
CF_3OOSO_2F	-37.9	$C_2F_5OSO_2F$[a]	-49.6
FO_2SOOSO_2F[b]	-40.4	$O_2S(OSO_2F)_2$	-49.6
$BrOSO_2F$	-41.3[h]	$NF_2CF_2CF_2OSO_2F$[f]	-50.4
$FOOSO_2F$[b]	-42.6	$C_2F_4(OSO_2F)_2$	-50.7
NF_2OSO_2F	-44.1	$CF_3CBrFCF(OSO_2F)CF_3$[g]	-51.0
CF_3OSO_2F	-46.8	$CF_3CF_2CF(OSO_2F)CF_3$[c]	-51.2
$CF_3C(O)OSO_2F$[c,d]	-47.4	$HOSO_2F$	-65.6[h]
$CClF_2OSO_2F$[d]	-48.0		

[a–g] For comparison with previously reported shifts, consult the following: (a) W. P. Gilbreath and G. H. Cady, *Inorg. Chem.*, **2,** 496 (1963); (b) G. Franz and F. Neumayr, *ibid.*, **3,** 921 (1964); (c) J. J. Delfino and J. M. Shreeve, *ibid.*, **5,** 308 (1966); (d) D. D. DesMarteau and G. H. Cady, *ibid.*, **5,** 169 (1966); (e) see ref 2; (f) M. Lustig and J. K. Ruff, *Inorg. Chem.*, **4,** 1441 (1965); (g) B. L. Earl, B. K. Hill, and J. M. Shreeve, *ibid.*, in press. [h] External reference.

Although the observed shifts as a function of the substituent group cannot be simply related to any single factor, the data, in general, appear to be internally consistent, which makes some interesting comparisons possible. (1) Introduction of CF_2 group(s) shifts resonances to lower field: $FOSO_2F > CF_3OSO_2F > C_2F_5OSO_2F$; $ClOSO_2F > ClCF_2OSO_2F$; $FO_2SOOSO_2F > FO_2SOCF_2OSO_2F > FO_2SOC_2F_4OSO_2F$; $NF_2OSO_2F > NF_2C_2F_4OSO_2F$. (2) Substitution of SO_3F for fluorine shifts to lower field: $FO_2SOSO_2F > FO_2SOSO_2OSO_2F$; $CF_3OSO_2F > FO_2SOCF_2OSO_2F$; $FOSO_2F > FO_2SOOSO_2F$. (3) Substitution of a halogen or pseudo-halogen for a fluorine may shift to lower field: $CF_3OSO_2F > ClCF_2OSO_2F$; $FOSO_2F > NF_2OSO_2F$; $FOSO_2F > BrOSO_2F$; or to higher field: $FOSO_2F < ClOSO_2F$. (4) Introduction of an oxygen atom varies: $FOSO_2F > FOOSO_2F$, while $CF_3OSO_2F < CF_3OOSO_2F$.

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[1] F. B. Dudley and G. H. Cady, *J. Am. Chem. Soc.*, **79,** 513 (1957).

[2] M. Lustig, *Inorg. Chem.*, **4,** 1828 (1965).

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Trimethylsiloxydimethylgold

BY HUBERT SCHMIDBAUR AND MANFRED BERGFELD

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We wish to report the synthesis of trimethylsiloxydimethylgold, a heterosiloxane species[1] containing the Si–O–Au linkage.

Trimethylgold, prepared according to a method described by Gilman and Woods,[2] was converted to

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[1] H. Schmidbaur, *Angew. Chem.*, **77,** 206 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4,** 201 (1965).

[2] H. Gilman and L. A. Woods, *J. Am. Chem. Soc.*, **70,** 550 (1948).