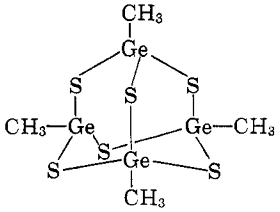
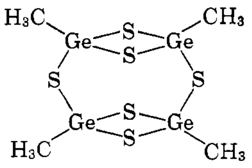


I



II

thought to be more likely than structure II, which involves strained four-atom germanium–sulfur rings. The single proton nuclear magnetic resonance (nmr) signal observed for solutions of tetra(methylgermanium) hexasulfide is in accord with either I or II. The infrared spectrum is simple. A structure of the type of I has been suggested for the tetra(alkylsilicon) hexasulfide and the tetra(alkylsilicon) hexaselenide[7] on the basis of such spectroscopic data.

ADDED IN PROOF.—A single crystal X-ray study of $(CH_3GeS_{1.5})_4$ as well as of $(CH_3SiS_{1.5})_4$ showed that both compounds are isomorphous and isostructural with a monoclinic space group Cc or C2/c, with the latter more probable. For the space group C2/c the molecule has either a center of symmetry or a twofold axis. Unfortunately this does not permit one to distinguish between I and II. Structure II may have a center of symmetry or a twofold axis while I may have a twofold axis.

Experimental Section

Materials.—Methyltribromogermane was prepared by a modified version of the direct synthesis;[2,3] triethylamine was obtained from Matheson Coleman and Bell, and hydrogen sulfide, from Matheson Co.

Preparation and Characterization.—Methyltribromogermane (22.2 g, 0.068 mole) and triethylamine (20.7 g, 0.204 mole) were dissolved in 0.5 l. of dry benzene in a three-necked flask fitted with a reflux condenser, stirrer, and gas-inlet tube. Hydrogen sulfide was passed over phosphorus pentoxide and bubbled into the solution until no more precipitate was formed. After 1 hr at reflux temperature, the solution was filtered, yielding 37.4 g (0.195 mole) of triethylamine hydrobromide (mp 250°). The resulting clear benzene solution was evaporated to dryness *in vacuo* yielding a slightly yellow solid product, which upon recrystallization from benzene melted at 345–346°; yield, 7.8 g (84%). The product is soluble in benzene and chloroform.

Anal. Calcd for $(CH_3GeS_{1.5})_4$: C, 8.85; H, 2.23; Ge, 53.49; S, 35.43; mol wt, 543. Found: C, 9.04; H, 2.24; Ge, 53.39; S, 35.38; mol wt, 529 (osmometric in chloroform).

The proton nmr spectrum in chloroform consists of a very sharp singlet at −1.316 ppm relative to internal tetramethylsilane. The infrared spectrum (as a KBr pellet) shows absorptions at 1235 (s), 1213 (w), 1035 (w), 870 (sh), 805 (vs), and 755 (w) cm^{-1} and thus resembles quite closely that reported[7] for the analogous silicon compound, $(CH_3SiS_{1.5})_4$. In the fragmentation pattern in the mass spectrometer, the largest fragment was seen at *m/e* 541 with additional predominant ions at *m/e* 491, 479, 417, 405, 343, and 149.

ADDED IN PROOF.—The unit cell data for $(CH_3GeS_{1.5})_4$ are the following (with the corresponding data for $(CH_3SiS_{1.5})_4$ listed in parentheses): a = 9.40 (9.38), b = 16.72 (16.51), c = 10.57 (10.58) A; β = 108° (107.2°). Assuming four molecules of the tetramer in the unit cell, the molecular weight was found to be 531 (calcd 543) for the germanium compound and 368 (calcd 365) for the silicon compound.

Acknowledgment.—The author wishes to thank Dr. J. J. Daly of Monsanto Research S.A. for the X-ray structure study and the Physical Sciences Center of Monsanto Co. for the analytical and mass data.

CONTRIBUTION NO. 1244 FROM THE CENTRAL RESEARCH
DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE
NEMOURS AND COMPANY, WILMINGTON, DELAWARE

Mössbauer Effect Studies of $(CH_3)_4Sn_3Fe_4(CO)_{16}$ and $(CH_3)_4Sn_2Fe_2(CO)_8$

BY M. THOMAS JONES[1]

Received September 2, 1966

Mössbauer effect (ME) studies of $(CH_3)_4Sn_3Fe_4(CO)_{16}$ and $(CH_3)_4Sn_2Fe_2(CO)_8$ were performed to gain a better understanding of the bonding and electronic structure of these compounds and to demonstrate the chemical applications of the Mössbauer effect. An additional reason for initiating the study is that iron and tin, two ME nuclei, are rarely found in the same compound. The two primary pieces of data, of most interest to chemists, which one obtains from a ME experiment[2] are the isomer shift (δ) and the quadrupolar splitting (Δ).

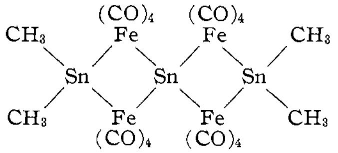
The isomer shift is proportional to $|\psi_s(0)|_A^2 - |\psi_s(0)|_S^2$, where $|\psi_s(0)|^2$ is the electron density at the Mössbauer nucleus, A denotes the absorber, and S the source. Therefore, the isomer shift is dependent upon such factors as affect the electron density at the nucleus, for example, the oxidation state and the extent of covalent and π bonding of the Mössbauer nucleus.

The quadrupolar splitting for ^{57}Fe is given by[3]

$$\Delta = (1/2)e^2qQ[1 + (\eta^2/3)]^{1/2}$$

The electric field gradient in the z direction is represented by eq, *i.e.*, $\partial^2 V/\partial x^2 = V_{zz}$.[4] Q and η are the quadrupole moment and asymmetry parameter, respectively. Hence, the quadrupolar splitting is a direct measure of the electric field gradient at the site of the Mössbauer nucleus.

The structural formulas of the compounds studied are



I

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[7] J. A. Forstner and E. L. Muetterties, *Inorg. Chem.*, **5**, 552 (1966).

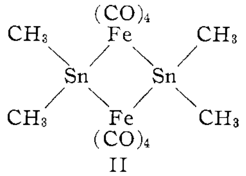
(1) Department of Chemistry, St. Louis University, St. Louis, Mo.

(2) One also observes magnetic hyperfine splitting in magnetically ordered materials. However, that will not be of concern with respect to the compounds studied here.

(3) R. Ingalls, *Phys. Rev.*, **133**, A787 (1964).

(4) Strictly, for the electric field gradient in the z direction, $eq = -V_{zz}$. For convenience many people redefine $eq = V_{zz}$ as has been done here. See M. H. Cohen and F. Reif, *Solid State Phys.*, **5**, 321 (1957).

and



II

Occasionally, a problem arises in determining the values of isomer shifts and quadrupolar splittings because of poor resolution sometimes associated with the Mössbauer effect. The line widths are frequently large with respect to differences in isomer shifts and quadrupolar splittings, which results in overlap. A particularly useful device has been found to aid in the decomposition of overlapped spectra, of which those recorded in this study are typical. It is the prototype of the Du Pont 310 curve resolver which is an analog computer device.[5]

Experimental Section

The synthesis of the compounds studied has been described as has the crystal structure of I.[6] Since these compounds are reactive toward oxygen, they were studied under vacuum conditions.

The ME spectra were obtained with an NSEC-AM-1 spectrometer equipped with a cryostat.[7] The γ rays were detected with a Reuter–Stokes RG-30, Kr–N$_2$-filled proportional counter. The proportional counter was connected to a RIDL amplifier–analyzer which fed into a Nuclear Data ND-180, 512 channel analyzer. The data stored in the multichannel analyzer could be read out *via* a Teletype printer and tape punch or a Moseley X–Y point plotter. The spectra shown were plotted by the X–Y plotter.

The iron spectra were obtained at room temperature *vs.* a source of ^{57}Co diffused into copper foil. The scans were calibrated with a polycrystalline sample of Na$_2$Fe(CN)$_5$NO·2H$_2$O with respect to which all of the iron isomer shifts are reported.

The tin spectra were obtained *vs.* a source of ^{119m}SnO$_2$. Both source and sample were at 77°K. The isomer shifts are reported *vs.* SnO$_2$ at 77°K. However, it should be noted that a slight difference between line centers for an absorber of SnO$_2$ at room temperature *vs.* the source at 77°K was measured. The velocity scans were calibrated with Na$_2$Fe(CN)$_5$NO·2H$_2$O and the ^{57}Co source described above.

Different individual samples were used for the iron and tin measurements. However, they were taken from the same batches and contained 5 mg of Fe/cm^2 and 14 mg of Sn/cm^2, respectively.

The error introduced into the Sn Mössbauer parameters by the use of the curve resolver is estimated to be ±0.1 mm/sec.

Results

A. (CH$_3$)$_4$Sn$_3$Fe$_4$(CO)$_{16}$. Tin ME.—A single asymmetric absorption line was observed, as shown in Figure 1. This spectrum was resolved into its components by the use of the prototype of the Du Pont 310 curve resolver. The line shape used for the trial functions was Lorentzian. The spectrum consists of a pair of quadrupolar split lines with δ +1.45 mm/sec and Δ 1.24 mm/sec and a single line with δ +2.20 mm/sec. The quadrupolar split lines, which comprise 64% of the area under the curve, arise from the two tin atoms bonded to the methyl groups, and the single line arises from the central tin atom.

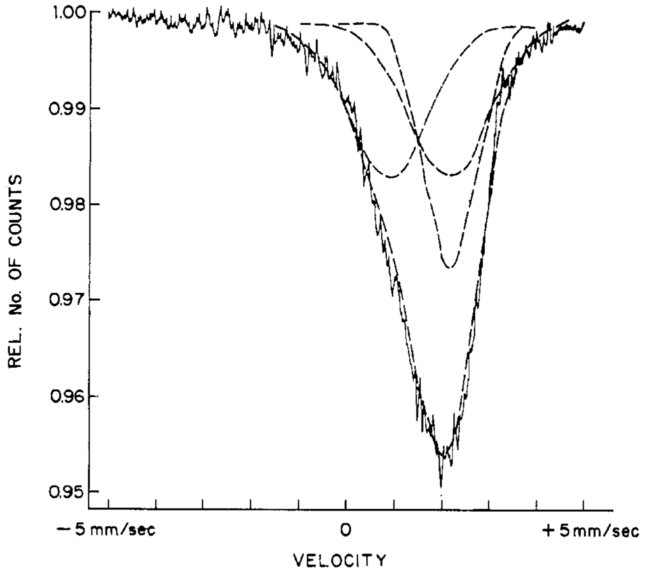


Figure 1.—Sn ME spectrum of (CH$_3$)$_4$Sn$_3$Fe$_4$(CO)$_{16}$ *vs.* ^{119m}SnO$_2$ at 77°K.

Iron ME.—The iron spectrum consists of a poorly resolved pair of quadrupolar split lines with δ +0.16 (±0.02) mm/sec and Δ 0.30 mm/sec.

B. (CH$_3$)$_4$Sn$_2$Fe$_2$(CO)$_8$. Tin ME.—A single broad absorption was observed which was resolved into a pair of quadrupolar split lines with the curve resolver. The parameters which describe the spectrum are δ +1.47 mm/sec and Δ 1.22 mm/sec.

Iron ME.—A single broadened absorption was observed, which could be resolved into a pair of quadrupolar split lines with the curve resolver. The line shape used was that displayed by Na$_2$Fe(CN)$_5$NO·2H$_2$O at room temperature. The parameters which describe the spectra are δ 0.15 (±0.02) mm/sec and $\Delta \approx 0.15$ mm/sec.

The ME. parameters associated with the very similar compound (C$_4$H$_9$)$_4$Sn$_2$Fe$_2$(CO)$_8$ have just been reported.[8] The increase in the tin isomer shift in going from the methyl- to the butyl-substituted compound parallels those observed for other such pairs, for example,[8] L$_2$Sn(OCOC$_6$H$_5$)$_2$ and L$_2$SnCl$_2$. It is gratifying to observe that the tin quadrupolar splittings are so similar because the spectrum for (CH$_3$)$_4$Sn$_2$Fe$_2$(CO)$_8$ was decomposed without knowledge of the results reported in ref 8. The isomer shifts for the Fe in the two compounds cannot be compared because of the difference in temperature at which they were obtained. The magnitude and the direction of the isomer shifts as a function of temperature for these compounds (*i.e.*, (C$_4$H$_9$)$_4$Sn$_2$Fe$_2$(CO)$_8$ and (CH$_3$)$_4$Sn$_2$Fe$_2$(CO)$_8$) are not known. The quadrupolar splittings are in fair agreement with each other. They should display little if any temperature dependence.

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(5) E. I. du Pont de Nemours and Co., Instrument Products Division, Wilmington, Del. 19898.

(6) R. M. Sweet, C. J. Fritchie, Jr., and R. A. Schunn, *Inorg. Chem.*, **6**, 749 (1967).

(7) Nuclear Science and Engineering Corp., Pittsburgh, Pa 15236

(8) R. H. Herber in "Applications of the Mössbauer Effect in Chemistry and Solid-State Physics," International Atomic Energy Agency, Vienna, 1966, p 121.

Discussion and Conclusions

As one would expect, the methylated tin atoms in both compounds yield similar ME parameters. Furthermore, it is interesting to note that the isomer shift found for tin in this situation is rather close to that observed for $(CH_3)_2SnCl_2$. It has been pointed out that, in quite a variety of Sn compounds, δ is roughly a linear function of the electronegativity of the attached ligands.[9] Therefore, as a gross approximation it would appear that the iron tetracarbonyl group possesses about the same electronegativity as a chlorine atom.

Greenwood's rule[10] appears to be satisfied for the methylated tin atoms; *i.e.*, any atom bonded directly to the tin atoms possessing nonbonding pairs of electrons produces a quadrupolar splitting, whereas any atom with no nonbonding pairs does not.

The central tin atom in $(CH_3)_4Sn_3Fe_4(CO)_{16}$ shows no quadrupolar splitting as expected from its pseudotetrahedral environment and a more positive isomer shift consistent with its being bonded to four metal atoms. One notes that its isomer shift falls in the same region as $FeSn_2$ and β-Sn.

TABLE I

SUMMARY OF Sn ME PARAMETERS[a]

Compound	δ^b	Δ^b	$Lw^{b,c}$
SnO_2 (298°K)	−0.080	. . .	2.30
$(CH_3)_4Sn_3Fe_4(CO)_{16}$ (77°K)			
A	+2.20	. . .	1.37
B	+1.45	1.24	1.72
$(CH_3)_4Sn_2Fe_2(CO)_8$ (77°K)	+1.47	1.22	1.95
$(C_4H_9)_4Sn_2Fe_2(CO)_8{}^d$ (77°K)	+1.70	1.26	. . .
$(CH_3)_2SnCl_2{}^e$	+1.44[f]	3.41	. . .
$FeSn_2{}^g$	+2.1[f]	~2.5	

[a] Source: $^{119m}SnO_2$ at 77°K. [b] Units: mm/sec. [c] Full width at half-maximum. [d] Reference 8. [e] Reference 9. [f] Adjusted for source temperature of 77°K. [g] V. I. Nikolaev, Yu. I. Shcherbina, and A. I. Karchevskii, *Soviet Phys. JETP*, **17**, 524 (1963).

TABLE II

SUMMARY OF Fe ME PARAMETERS[a]

Compound	$\delta^{b,c}$	Δ^b	$Lw^{b,d}$
$(CH_3)_4Sn_3Fe_4(CO)_{16}$ (298°K)	+0.16 (±0.02)	0.30	~0.30
$(CH_3)_4Sn_2Fe_2(CO)_8$ (298°K)	±0.15 (±0.02)	~0.15	~0.34
$(C_4H_9)_4Sn_2Fe_2(CO)_8{}^e$ (78°K)	+0.24	~0.2	. . .
$Na_2Fe(CN)_5NO \cdot 2H_2O$	0	1.712	0.195
$Na_2Fe(CO)_4{}^f$	+0.010	. . .	. . .
$NaFe_3(CO)_{11}H^f$			
A	+0.18[g]	. . .	
B	+0.16[g]	1.32	
$Fe_3(CO)_{12}{}^h$			
A	+0.22[i]	. . .	~0.36
B	+0.25[i]	0.94	~0.27

[a] Source: ^{57}Co in copper foil at 298°K. [b] Units: mm/sec. [c] δ *vs.* $Na_2Fe(CN)_5NO \cdot 2H_2O$ at 298°K. [d] Full width at half maximum. [e] Reference 8. [f] N. E. Erickson and A. W. Fairhall, *Inorg. Chem.*, **4**, 1320 (1965). [g] Adjusted for isomer shift relative to $Na_2Fe(CN)_5NO \cdot 2H_2O$. Note error: on the scale used in *f*, $Na_2Fe(CN)_5NO \cdot 2H_2O$ should have an isomer shift of −0.261 at 298°K relative to the source used. [h] E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 277 (1963). [i] Linearly extrapolated to $T = 298$°K, using data in *h*.

While one would expect the iron ME parameters to be similar for compounds I and II, it is surprising that they do not show greater differences. A larger electric field gradient in compound I than in II is observed, most likely because of a somewhat lower local symmetry at the iron as expected. It is interesting to note that the isomer shifts for compounds I and II fall between those for $Na_2Fe(CO)_4$ and the unique iron atom in $Fe_3(CO)_{12}$[11] and near that reported for $NaFe_3(CO)_{11}H$. Thus it appears that the electronic configuration of the iron in these compounds is such that the charge on the iron atom is more negative than Fe^0 but less than Fe^{2-}.

The ME parameters are summarized in Tables I and II.

Acknowledgments.—The author wishes to thank Dr. R. A. Schunn for providing the compounds and for valuable and interesting discussions about their chemistry. He also wishes to thank Dr. Jack Fritsch of the Monsanto Co. for allowing the use of their Du Pont 310 curve resolver to check a point raised by a referee.

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[9] R. H. Herber, H. A. Stöckler, and W. T. Reichle, *J. Chem. Phys.*, **42**, 2447 (1965).

[10] T. C. Gibb and N. N. Greenwood, *J. Chem. Soc., Sect. A*, 43 (1966).

[11] C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966).

CONTRIBUTION NO. 1843 FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA AT LOS ANGELES,
LOS ANGELES, CALIFORNIA 90024

Spectrophotometric Studies of the Dissociation of the Iodine Complexes of Selenacyclopentane and Selenacyclohexane

BY J. D. MCCULLOUGH AND ASTRID BRUNNER

Received October 20, 1966

Spectrophotometric studies of the iodine complexes of cyclic sulfides, $(CH_2)_nS$, show that these are the most stable in the sulfur series.[1-3] The order of stability of the complexes was established as thiacyclopentane > thiacyclohexane > thiacyclobutane > ethylene sulfide. In the present study, measurements have been extended to two members of the selenium series, selenacyclopentane and selenacyclohexane. Unfortunately, selenacyclobutane and selenacyclopropane are very difficult to prepare because the syntheses go almost exclusively to polymeric products. Also the tendency of iodine to induce polymerization, noted to some degree with thiacyclobutane,[1] is much more pronounced in the three- and four-membered rings of the selenium series. Thus it has not been possible to determine the dissociation constants of the iodine complexes of the latter selenides.

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[1] J. D. McCullough and D. Mulvey, *J. Am. Chem. Soc.*, **81**, 1291 (1959).

[2] M. Tamres and S. Searles, *J. Phys. Chem.*, **66**, 1099 (1962).

[3] J. D. McCullough and I. C. Zimmermann, *ibid.*, **66**, 1198 (1962).