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.

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

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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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Experimental Section

Selenacyclopentane and selenacyclohexane were prepared and purified by the method of McCullough and Lefohn.[4] The sources and methods of purification for iodine and carbon tetrachloride were the same as those given in ref 1.

Absorbance data[5] were measured on a Cary recording spectrophotometer, Model 11, with a thermostated cell compartment. Matched sets of absorption cells with lengths of 1.000, 9.998, 25.03, and 100.1 mm were used. Several recordings were made of each sample and the results were averaged. Absorbances were measured at wavelengths near the visible absorption maximum at 428 mμ for both complexes at each of three temperatures. An additional set of 20 measurements was made on the selenacyclopentane complex at 25.5° in the region of the ultraviolet absorption maximum at 322 mμ. The ultraviolet measurements showed considerably more scatter than those made at the visible maximum, especially for 10 points where iodine was in excess. For this reason, only data with the selenide concentration equal to or greater than that for iodine were used in the ultraviolet-band calculations. This behavior in the ultraviolet region was similar to that noted for another very stable complex, that of 1,4-diselenane.[6]

The equilibrium constants and molar absorptivities were computed from the absorbance data by the cyclic least-squares procedure described earlier.[7] Values of $\Delta H_c°$ for the complexes were computed from the change in K with temperature on the assumption that ϵ remains constant. Actually, the observed variation of ϵ with T was small; in no case did a value differ by more than 1.1 standard deviations from the appropriate mean value given in Table I.

TABLE I

VALUES OF MOLAR ABSORPTIVITY (ϵ) AND DISSOCIATION CONSTANT (K_c) FOR $D \cdot I_2$ AT VARIOUS WAVELENGTHS AND TEMPERATURES IN CARBON TETRACHLORIDE (ESTIMATED STANDARD DEVIATIONS IN PARENTHESES)

λ, mμ	ϵ	10^4K_c, M		
		15.0°	25.5°	40.0°
(a) D = Selenacyclopentane, C_4H_8Se Concentration Ranges: Selenide, 1.0×10^{-4} to 1.6×10^{-3} M; Iodine, 8.0×10^{-3} to 1.5×10^{-3} M				
415	3,070 (60)	2.44	4.85	11.5
420	3,230	2.45	4.83	11.4
425	3,330	2.45	4.81	11.4
430	3,350	2.49	4.81	11.3
Av		2.46 (0.05)	4.82 (0.07)	11.4 (0.2)
316	37,700 (700)		4.85	
320	39,600		4.89	
324	39,600		4.96	
328	38,100		4.91	
Av			4.90 (0.12)	
(b) D = Selenacyclohexane, $C_5H_{10}Se$ Concentration Ranges: Selenide and Iodine, 1.6×10^{-4} to 2.0×10^{-3} M				
415	3,030 (100)	4.05	7.49	16.0
420	3,160	4.09	7.47	15.7
425	3,210	4.11	7.44	15.7
430	3,200	4.15	7.47	15.9
Av		4.10 (0.08)	7.47 (0.06)	15.8 (0.4)

TABLE II

VALUES FOR THE DISSOCIATION CONSTANT (K_c), MOLAR FREE ENERGY ($\Delta G_c°$), MOLAR ENTHALPY ($\Delta H_c°$), AND MOLAR ENTROPY ($\Delta S_c°$) FOR THE DISSOCIATIONS IN CARBON TETRACHLORIDE AT 25°[a]

Complex[b]	10^4K_c, M	$\Delta G°$, kcal mole^{-1}	$\Delta H_c°$, kcal mole^{-1}	$\Delta S_c°$, cal deg^{-1} mole^{-1}
$C_4H_8SeI_2$	4.54	4.58	11.1	22
$C_5H_{10}SeI_2$	7.16	4.32	9.8	18
$C_4H_8SI_2$	55.0	3.10	8.7	19
$C_5H_{10}SI_2$	74.0	2.92	7.1	14

[a] Estimated standard deviations: $\Delta G_c°$, 0.03; $\Delta H_c°$, 0.3; $\Delta S_c°$, 1. [b] Values for sulfur compounds are from ref 3 and are included for comparison.

Results and Discussion

The equilibrium constants and molar absorptivities are given in Table I and the derived thermodynamic quantities in Table II. The small dissociation constants show that the iodine complexes of selenacyclopentane and selenacyclohexane are among the most stable compounds of this type. In keeping with this is the fact that both complexes are obtained as crystalline solids with melting points of 99 and 114°, respectively.[8,9] In contrast, attempts to isolate solid iodine complexes of the corresponding sulfides have been unsuccessful.

An X-ray diffraction study of the crystalline complex of selenacyclopentane[10] has shown a short Se–I bonded distance of 2.762 A which is only 0.26 A longer than the sum of the normal, single, covalent bond radii, 2.50 A. As a result of this relatively short bond that one iodine atom makes with selenium, the I–I distance is lengthened from the uncomplexed value of 2.66 to 2.914 A. These observed bond distances are in line with the high degree of stability found for the complex in solution.

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[5] The absorbance data have been deposited as Document No. 9379 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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Acetonitrile Exchange Rates in Solutions of Nickel(II) Ions by Nuclear Magnetic Resonance

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In a number of recent studies the rates of solvent exchange between the bulk solution and the ligand sphere of paramagnetic ions as determined by the effect

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