all.[20] On the other hand all five C–H stretching modes for the σ-C_5H_5 group of C_s symmetry are infrared active and the four associated with the olefinic hydrogens would be expected to occur at frequencies greater than 3000 cm^{-1}. Thus the 3000-cm^{-1} region offers a clear and simple choice to be made regarding the mode of bonding of C_5H_5 rings in these compounds, a point overlooked by Fritz[21] in his review of infrared spectra of metal–C_nH_n systems.

The infrared spectra of $(CH_3)_3SiC_5H_5$, $(CH_3)_3GeC_5H_5$, and $(CH_3)_3SnC_5H_5$ (Figure 5) all show several absorptions above 3000 cm^{-1}, consistent *only* with the σ-cyclopentadienyl geometry. We feel justified in concluding that $(CH_3)_3SnC_5H_5$ has a fluxional σ-bonded C_5H_5 ring but that the barrier to migration of the $(CH_3)_3Sn$ group around the ring is so low that even at −80° only one proton resonance can be observed. The suggestion by others[22,23] that the C_5H_5 rings in tin(IV)–cyclopentadiene compounds are π bonded has no basis in experimental fact.

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The Infrared Spectrum of the 3,5-Dimethyl-1,2-dithiolylium(I) Cation

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The infrared spectrum of bis(3,5-dimethyl-1,2-dithiolylium) tetrachloroferrate(II) has been recorded from 1700 to 300 cm^{-1}. Assignments for the in-plane vibrations of the cation were obtained by a normal coordinate analysis. A planar and cyclic structure adopted for the 3,5-dimethyl-1,2-diselenolylium(I) cation permitted vibrational assignments by the same normal-coordinate treatment. The nature of bonding in cyclic disulfides and diselenides is discussed.

Introduction

Under conditions which have favored the formation of dithioacetylacetone chelates[1] from ordinary metal salts, the reaction of iron(III) produced a compound[2] whose properties and structure were completely different. This compound was identified as bis(3,5-dimethyl-1,2-dithiolylium) tetrachloroferrate(II) by X-ray diffraction[3] and consists of planar, five-membered, cyclic disulfide cations and an anionic iron chloride species. In aqueous solution the cation has been reduced to a dithioacetylacetone species whose brief existence could only be recognized by the *in situ* formation of dithioacetylacetone chelates.[4] The disulfide cation may, therefore, be considered as a potential source of the unstable ligand and dithioacetylacetonates which have eluded previous synthetic attempts.

Although infrared spectra have been reported for various salts containing the disulfide cation, assignment of the frequencies was considered only tentative.[5,6] A normal-coordinate analysis of the cation has now been completed with good agreement between calculated and observed frequencies. Assignments for in-plane vibrations were accordingly made. The results of these calculations are reported here.

Experimental Section

Preparation of $(C_5H_7S_2)_2FeCl_4$.—Hydrogen chloride gas was bubbled through a solution of 18 g of anhydrous ferric chloride and 20 ml of acetylacetone in 300 ml of ethanol cooled to −10°. After 1 hr the hydrogen chloride was replaced by hydrogen sulfide and the bubbling was continued 1 hr. Dark red-violet crystals precipitated after dilution with 300 ml of anhydrous ether. The product was washed with ether and dried *in vacuo*. *Anal.* Calcd for $C_{10}H_{14}Cl_4S_4Fe$: Fe, 12.14. Found: Fe, 11.85.

Spectral Measurements

The spectrum was recorded with a Perkin-Elmer 521 infrared spectrophotometer over the range 1700–300 cm^{-1}. Potassium bromide and cesium bromide pellets and a Nujol mull were prepared. Calibration of frequency readings was performed with polystyrene film and water vapor.

Method of Calculation

The point symmetry of the planar 1,2-dithiolylium cation is C_{2v} if the methyl groups are considered as point masses as shown in Figure 1. This simplification

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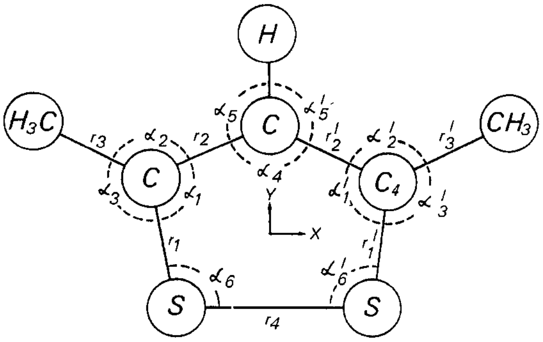

Figure 1.—Molecular model and internal coordinates.

has been successfully applied to the structurally related complexes of acetylacetone[7] and dithioacetylacetone.[1] These results were confirmed by an analysis[8] which included the methyl group hydrogen atoms in the molecular symmetries of copper(II), palladium(II), and iron(III) acetylacetonates. Bond distances and angles previously determined for this cation[3] were used in the calculations. The normal vibrations, $\Gamma = 7\ A_1 + 2\ A_2 + 3\ B_1 + 6\ B_2$, of the eight-atom model were divided into five out-of-plane, $2\ A_2 + 3\ B_1$, and thirteen in-plane, $7\ A_1 + 6\ B_2$, vibrations. Only the in-plane vibrations were analyzed in this normal-coordinate treatment.

A modified Urey–Bradley force field[9] which included stretch–stretch, stretch–bend, and bend–bend interactions was used to form the F matrix. F matrix elements and force field coefficients used appear in Tables IX and X. By use of the eighteen coordinates a G matrix was constructed according to previously outlined methods.[10]

Of the six redundant coordinates produced, three were expressed as sums of angles about each of the three ring carbon atoms and were removed by an orthogonal similarity transformation.[11] A fourth redundancy which represented the sum of the five angles in the ring was eliminated in the transformation from internal to symmetry coordinates. The set of symmetry coordinates established appears in Table I. After a high-frequency separation[10] of the carbon–hydrogen stretching vibration, the partitioned secular determinant $|GF - E\lambda| = 0$ was solved separately for A_1 and B_2 representations. The last two redundancies generated zero frequencies. The normalized eigenvectors are given in Table II. Assignment of vibrational modes was made by deriving the potential energy distribution[12] in each characteristic frequency as shown in Table III.

Table I

Symmetry Coordinates for In-Plane Vibrations

Coordinate	Vibrational mode
A_1 Species	
$S_1 = \Delta r_4$	$\nu(\text{S—S})$
$S_2 = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_1')$	$\nu(\text{C}\overset{\cdots}{-}\text{S})$
$S_4 = \frac{1}{\sqrt{2}}(\Delta r_2 + \Delta r_2')$	$\nu(\text{C}\overset{\cdots}{-}\text{C})$
$S_6 = \frac{1}{\sqrt{2}}(\Delta r_3 + \Delta r_3')$	$\nu(\text{C—CH}_3)$
$S_8 = \Delta r_5$	$\nu(\text{C—H})$
$S_9 = \frac{1}{\sqrt{2}}(\Delta\alpha_2 - \Delta\alpha_3 + \Delta\alpha_2' - \Delta\alpha_3')^{a}$	$\delta(\text{C—CH}_3)$
$S_{13} = \frac{1}{2}(\Delta\alpha_1 + \Delta\alpha_1' - \Delta\alpha_6 - \Delta\alpha_6')$	Ring def
$S_{16} = \frac{1}{\sqrt{20}}(-\Delta\alpha_1 - \Delta\alpha_1' - \Delta\alpha_6 - \Delta\alpha_6' + 4\Delta\alpha_4)$	Ring def
B_2 Species	
$S_3 = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_1')$	$\nu(\text{C}\overset{\cdots}{-}\text{S})$
$S_5 = \frac{1}{\sqrt{2}}(\Delta r_2 - \Delta r_2')$	$\nu(\text{C}\overset{\cdots}{-}\text{C})$
$S_7 = \frac{1}{\sqrt{2}}(\Delta r_3 - \Delta r_3')$	$\nu(\text{C—CH}_3)$
$S_{10} = \frac{1}{\sqrt{2}}(\Delta\alpha_2 - \Delta\alpha_3 - \Delta\alpha_2' + \Delta\alpha_3')^{a}$	$\delta(\text{C—CH}_3)$
$S_{11} = \Delta\alpha_5 - \Delta\alpha_5'^{a}$	$\delta(\text{C—H})$
$S_{14} = \frac{1}{2}(\Delta\alpha_1 - \Delta\alpha_1' + \Delta\alpha_6 - \Delta\alpha_6')$	Ring def
$S_{15} = \frac{1}{2}(\Delta\alpha_1 - \Delta\alpha_1' - \Delta\alpha_6 + \Delta\alpha_6')$	Ring def

[a] Not normalized.

Jacobian matrix elements[13] which express the rate of change of frequency with force constant are tabulated in Table IV. The force constant which yielded the greatest rate of change of a particular frequency represented the stable solution, *i.e.*, the predominant contribution to the normal mode. The latter results agree with the assignments based on the potential energy distribution.

Since there were more force constants than observed frequencies, six force constants, $H(\text{CCH})$, $H(\text{CCC})$, $H(\text{CCCH}_3)$, $F(\text{C}\cdots\text{H})$, $F(\text{C}\cdots\text{C})$, and $F(\text{C}\cdots\text{CH}_3)$, were constrained with values obtained for the same constants in the analysis of dithioacetylacetone chelates.[1] To attain optimum agreement between observed and calculated frequencies, the remaining ten force constants were treated as variables in a least-squares force constant adjustment routine.[14] Final values of force constants are listed in Table V. Since the average error between twelve observed and calculated frequencies in Table VI is 3.2%, the agreement is considered satisfactory.

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TABLE II
NORMALIZED L MATRIX ELEMENTS

A_1 species	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6
S_1	0.004	0.009	0.054	0.190	0.203	−0.044
S_2	0.191	−0.186	0.196	−0.067	0.018	−0.021
S_4	−0.339	−0.084	0.051	−0.025	−0.050	0.033
S_6	0.080	0.354	0.042	−0.092	−0.028	0.018
S_9	0.616	−0.152	0.111	0.144	−0.045	0.286
S_{13}	−0.003	0.320	0.162	0.176	0.109	−0.040
S_{16}	0.311	−0.322	−0.181	−0.060	−0.058	−0.013
B_2 species	λ_7	λ_8	λ_9	λ_{10}	λ_{11}	λ_{12}
S_3	0.026	0.176	−0.232	−0.153	−0.071	0.030
S_5	−0.404	−0.174	0.038	−0.078	0.006	0.018
S_7	0.171	0.015	0.303	−0.162	−0.025	−0.037
S_{10}	0.080	0.369	−0.252	−0.355	0.369	−0.092
S_{11}	1.271	−1.466	−0.518	−0.198	−0.172	−0.018
S_{14}	0.108	−0.058	0.126	0.131	0.042	−0.042
S_{15}	0.263	0.054	0.183	−0.041	0.035	0.240

TABLE III
POTENTIAL ENERGY DISTRIBUTION, $F_{ii}L_{iN}^2$ (PER CENT CONTRIBUTION)

A_1 species	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6
S_1	0.000	0.000	0.049	1.000	1.000	0.123
S_2	0.221	0.308	1.000	0.191	0.012	0.045
S_4	1.000	0.090	0.098	0.038	0.134	0.155
S_6	0.034	1.000	0.041	0.321	0.026	0.028
S_9	0.288	0.026	0.040	0.111	0.010	1.000
S_{13}	0.000	0.270	0.200	0.393	0.132	0.047
S_{16}	0.165	0.259	0.239	0.043	0.035	0.005
Predominant modes	$\nu(\mathrm{C\overset{\cdots}{-}C})$	$\nu(\mathrm{C{-}CH_3})$	$\nu(\mathrm{C\overset{\cdots}{-}S})$	$\nu(\mathrm{S{-}S})$	$\nu(\mathrm{S{-}S})$	$\delta(\mathrm{C{-}CH_3})$
B_2 species	λ_7	λ_8	λ_9	λ_{10}	λ_{11}	λ_{12}
S_3	0.003	0.248	0.657	0.996	0.293	0.051
S_5	1.000	0.313	0.023	0.338	0.002	0.024
S_7	0.124	0.002	1.000	1.000	0.033	0.072
S_{10}	0.004	0.135	0.096	0.674	1.000	0.061
S_{11}	0.447	1.000	0.191	0.098	0.101	0.001
S_{14}	0.016	0.008	0.057	0.216	0.031	0.031
S_{15}	0.097	0.007	0.121	0.021	0.021	1.000
Predominant modes	$\nu(\mathrm{C\overset{\cdots}{-}C})$	$\delta(\mathrm{C{-}H})$	$\nu(\mathrm{C{-}CH_3})$ + $\nu(\mathrm{C\overset{\cdots}{-}S})$	$\nu(\mathrm{C{-}CH_3})$ + $\nu(\mathrm{C\overset{\cdots}{-}S})$	$\delta(\mathrm{C{-}CH_3})$	Ring def

TABLE IV
JACOBIAN MATRIX ELEMENTS, $(1/\lambda_N)(\partial\lambda_N/\partial K_j)$

Force constant	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6
$K(\mathrm{S{-}S})$	0.000	0.000	0.010	0.184	0.320	0.033
$K(\mathrm{C\overset{\cdots}{-}S})$	0.035	0.042	0.137	0.023	0.002	0.008
$K(\mathrm{C\overset{\cdots}{-}C})$	0.111	0.009	0.009	0.003	0.019	0.019
$K(\mathrm{C{-}CH_3})$	0.006	0.153	0.006	0.043	0.006	0.005
Force constant	λ_7	λ_8	λ_9	λ_{10}	λ_{11}	λ_{12}
$K(\mathrm{C\overset{\cdots}{-}S})$	0.001	0.033	0.084	0.072	0.042	0.010
$K(\mathrm{C\overset{\cdots}{-}C})$	0.129	0.033	0.002	0.019	0.000	0.004
$K(\mathrm{C{-}CH_3})$	0.023	0.000	0.143	0.081	0.005	0.016

TABLE V
FORCE CONSTANTS (10^5 DYN/CM) OF THE 3,5-DIMETHYL-1,2-DITHIOLYLIUM(I) CATION

Stretching		Bending		Repulsive	
$K(\mathrm{S{-}S})$	2.20	$H(\mathrm{SSC})$	0.14	$F(\mathrm{S\cdots C})$	0.44
$K(\mathrm{C\overset{\cdots}{-}S})$	3.40	$H(\mathrm{SCC})$	0.18	$F(\mathrm{S\cdots C})$	0.40
$K(\mathrm{C\overset{\cdots}{-}C})$	4.70	$H(\mathrm{SCCH_3})$	0.33	$F(\mathrm{S\cdots CH_3})$	0.45
$K(\mathrm{C{-}CH_3})$	3.30	$H(\mathrm{CCCH_3})$	0.35	$F(\mathrm{C\cdots CH_3})$	0.20
		$H(\mathrm{CCH})$	0.20	$F(\mathrm{C\cdots H})$	0.45
		$H(\mathrm{CCC})$	0.35	$F(\mathrm{C\cdots C})$	0.40

Results and Discussion

The infrared spectrum of bis(3,5-dimethyl-1,2-dithiolylium) tetrachloroferrate(II) is shown in Figure 2 with the cation denoted as $\mathrm{DTAA^+}$ in the formula. Frequencies and force constants for the disulfide ring vibrations are similar to those in certain other sulfur-containing compounds.[15–17] Absorption bands which appear near 557 and 435 $\mathrm{cm^{-1}}$ were assigned to ν(S–S) and have a counterpart in the spectrum of $\mathrm{S_8}$[15] in which the stretching frequency occurs at 465 $\mathrm{cm^{-1}}$. The value of the stretching force constant in elemental sulfur, 2.04 mdyn/Å, is 0.16 mdyn/Å less than that of K(S–S) in $\mathrm{DTAA^+}$. In view of the magnitude of the force constants and the valence force field used in calculations for $\mathrm{S_8}$, the difference is probably too small to confirm the existence of important S–S multiple

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TABLE VI

CALCULATED AND OBSERVED FREQUENCIES (CM^{-1}) OF THE 3,5-DIMETHYL-1,2-DITHIOLYLIUM(I) CATION

	Calcd	Obsd	Assignment
		In-Plane Modes	
		A_1 Species	
ν_1	1327	1318	$\nu(\mathrm{C\overset{\cdots}{-}C})$
ν_2	1181	1204	$\nu(\mathrm{C—CH_3})$
ν_3	692	697	$\nu(\mathrm{C\overset{\cdots}{-}S})$
ν_4	576	557	$\nu(\mathrm{S—S})$
ν_5	469	435	$\nu(\mathrm{S—S})$
ν_6	315	~342	$\delta(\mathrm{C—CH_3})$
		B_2 Species	
ν_7	1466	1476	$\nu(\mathrm{C\overset{\cdots}{-}C})$
ν_8	1257	1232	$\delta(\mathrm{C—H})$
ν_9	1044	1092	$\nu(\mathrm{C—CH_3}) + \nu(\mathrm{C\overset{\cdots}{-}S})$
ν_{10}	741	712	$\nu(\mathrm{C—CH_3}) + \nu(\mathrm{C\overset{\cdots}{-}S})$
ν_{11}	451	457	$\delta(\mathrm{C—CH_3})$
ν_{12}	382	370	Ring def
		Methyl Group and Out-of-Plane Modes	
		1426 1399	$\mathrm{CH_3}$ deg def
		1371 1351	$\mathrm{CH_3}$ sym def
		1019 1006 995 980	$\rho_r(\mathrm{CH_3})$
		861	$\pi(\mathrm{C—H})$
		525	$\pi\left(\mathrm{SC}<^{\mathrm{C}}_{\mathrm{C}}\right)$

TABLE VII

OBSERVED AND CALCULATED FREQUENCIES (CM^{-1}) OF THE 3,5-DIMETHYL-1,2-DISELENOLYLIUM(I) CATION

	Calcd DSeAA$^+$	Obsd^a (DSeAA)$_2$-CoCl$_4$-	Obsd^a (DSeAA)I	Predominant modes
		In-Plane Modes		
		A_1 Species		
ν_1	1321	1355	1340	$\nu(\mathrm{C\overset{\cdots}{-}C})$
ν_2	1154	1178	1170	$\nu(\mathrm{C—CH_3})$
ν_3	601	615	600	$\nu(\mathrm{C—Se})$
ν_4	499	525	517	$\nu(\mathrm{C—CH_3})$ + ring def
ν_5	341	320	320	$\delta(\mathrm{C—CH_3}) + \nu(\mathrm{Se—Se})$
ν_6	290			Ring def + $\nu(\mathrm{Se—Se})$
		B_2 Species		
ν_7	1467	1465	1465	$\nu(\mathrm{C\overset{\cdots}{-}C})$
ν_8	1247	1240	1240	$\delta(\mathrm{C—H})$
ν_9	1003	1005	1000	$\nu(\mathrm{C—CH_3}) + \nu(\mathrm{C—Se})$
ν_{10}	703		700	$\delta(\mathrm{C—CH_3}) + \nu(\mathrm{C—Se})$
ν_{11}	390	400	410	$\delta(\mathrm{C—CH_3})$
ν_{12}	284			Ring def
		Methyl Group and Out-of-Plane Modes		
		1420 1400	1420 1395	$\mathrm{CH_3}$ deg def
		1365	1365	$\mathrm{CH_3}$ sym def
		1005	1000	$\rho_r(\mathrm{CH_3})$
		877	840	$\pi(\mathrm{C—H})$

[a] Reference 6.

bonding. A higher K(S–S) in DTAA$^+$ would be in accord with results of X-ray studies[3] which indicated significant double-bond character in the S–S bond of the cation.

The carbon–sulfur stretching frequency at 697 cm^{-1} in the cation can be compared with $\nu(\mathrm{C\overset{\cdots}{-}S})$ at 730 cm^{-1} in uncomplexed thiourea and at 700 cm^{-1} in thiourea–metal complexes.[16] The decrease upon complexation was attributed to a reduction in carbon–sulfur double-bond character. The carbon–sulfur single-bond and double-bond stretching force constants of diethyl thioether,[17] 2.50 mdyn/Å, and thiourea, 3.20 mdyn/Å, respectively, are less than the value of the disulfide cation, 3.40 mdyn/Å. The existence of considerable π character in the carbon–sulfur bond of the 1,2-dithiolylium ion, first suggested from iterated Hückel calculations,[18] is further supported. A comparison of the carbon–carbon stretching force constant in benzene,[19] 5.46 mdyn/Å, with that of the cyclic

TABLE VIII

POTENTIAL ENERGY DISTRIBUTION, $F_{ii}L_{iN}{}^2$ (PER CENT CONTRIBUTION)

A_1 species	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6
S_1	0.000	0.000	0.014	0.021	0.826	0.967
S_2	0.154	0.196	1.000	0.306	0.302	0.061
S_4	1.000	0.030	0.062	0.326	0.180	0.003
S_6	0.063	1.000	0.003	1.000	0.069	0.015
S_9	0.262	0.057	0.142	0.006	1.000	0.642
S_{13}	0.000	0.330	0.214	0.573	0.002	0.243
S_{16}	0.139	0.351	0.318	0.354	0.052	1.000
Predominant modes	$\nu(\mathrm{C\overset{\cdots}{-}C})$	$\nu(\mathrm{C—CH_3})$	$\nu(\mathrm{C—Se})$	$\nu(\mathrm{C—CH_3})$ + ring def	$\delta(\mathrm{C—CH_3}) + \nu(\mathrm{Se—Se})$	Ring def + $\nu(\mathrm{Se—Se})$
B_2 species	λ_7	λ_8	λ_9	λ_{10}	λ_{11}	λ_{12}
S_3	0.006	0.145	0.397	0.767	0.434	0.235
S_5	1.000	0.289	0.056	0.193	0.009	0.028
S_7	0.122	0.010	1.000	0.559	0.087	0.050
S_{10}	0.002	0.108	0.108	1.000	1.000	0.111
S_{11}	0.445	1.000	0.085	0.087	0.012	0.000
S_{14}	0.021	0.003	0.045	0.184	0.062	0.049
S_{15}	0.097	0.004	0.148	0.021	0.316	1.000
Predominant modes	$\nu(\mathrm{C\overset{\cdots}{-}C})$	$\delta(\mathrm{C—H})$	$\nu(\mathrm{C—CH_3}) + \nu(\mathrm{C—Se})$	$\delta(\mathrm{C—CH_3}) + \nu(\mathrm{C—Se})$	$\delta(\mathrm{C—CH_3})$	Ring def

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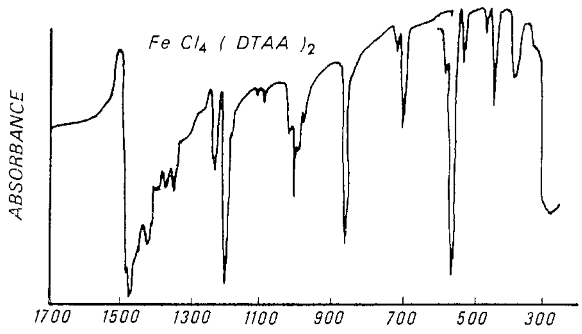

Figure 2.—Infrared spectrum of bis(3,5-dimethyl-1,2-dithiolylium) tetrachloroferrate(II) in potassium bromide. Below 600 cm^{-1} the matrix is cesium bromide.

Table IX

F Matrix Elements

A$_1$ Species

$$F(1,1) = K_1 + 2t_1{}^2F_1' + 2s_1{}^2\mathrm{F}_1$$
$$F(1,2) = \sqrt{2}(-t_1t_2F_1' + s_1s_2F_1)$$
$$F(1,6) = r_1(t_1s_2F_1' + t_2s_1F_1)$$
$$F(1,7) = (1/\sqrt{5})F(1,6)$$
$$F(2,2) = K_2 + t_3{}^2F_2' + s_3{}^2F_2 + t_5{}^2F_3' + s_5{}^2F_3 + t_2{}^2F_1' + s_2{}^2F_1$$
$$F(2,3) = -t_3t_4F_2' + s_3s_4F_2$$
$$F(2,4) = -t_5t_6F_3' + s_5s_6F_3$$
$$F(2,5) = -\frac{1}{2}r_3(t_5s_6F_3' + t_6s_5F_3)$$
$$F(2,6) = (1/\sqrt{2})r_2(t_3s_4F_2' + t_4s_3F_2) - (1/2\sqrt{2})r_3(t_5s_6F_3' + t_6s_5F_3) - (1/\sqrt{2})r_4(t_2s_1F_1' + t_1s_2F_1)$$
$$F(2,7) = -(1/\sqrt{10})r_2(t_3s_4F_2' + t_4s_3F_2) + (1/2\sqrt{10}) \times r_3(t_5s_6F_3' + t_6s_5F_3) - (1/\sqrt{10})r_4(t_2s_1F_1' + t_1s_2F_1)$$
$$F(3,3) = K_3 + 2s_{11}{}^2F_6 + t_9{}^2F_5' + s_9{}^2F_5 + t_4{}^2F_2' + s_4{}^2F_2 + t_8{}^2F_4' + s_8{}^2F_4$$
$$F(3,4) = -t_8t_7F_4' + s_8s_7F_4$$
$$F(3,5) = \frac{1}{2}r_3(t_8s_7F_4' + t_7s_8F_4)$$
$$F(3,6) = (1\sqrt{2})r_1(t_4s_3F_2' + t_3s_4F_2) - (1/2\sqrt{2})r_3(t_8s_7F_4' + t_7s_8F_4)$$
$$F(3,7) = -(1/\sqrt{10})r_1(t_4s_3F_2' + t_3s_4F_2) + (1/2\sqrt{10}) \times r_3(t_8s_7F_4' + t_7s_8F_4) + (4/\sqrt{10})r_2(t_{11}s_{11}F_6' + t_{11}s_{11}F_6) - (2/\sqrt{10})r_5(t_9s_{10}F_5' + t_{10}s_9F_5)$$
$$F(4,4) = K_4 + t_6{}^2F_3' + s_6{}^2F_3 + t_7{}^2F_4' + s_7{}^2F_4$$
$$F(4,5) = \frac{1}{2}r_2(t_7s_8F_4' + t_8s_7F_4) - \frac{1}{2}r_1(t_6s_5F_3' + t_5s_6F_3)$$
$$F(4,6) = -(1/2\sqrt{2})r_2(t_7s_8F_4' + t_8s_7F_4) - (1/2\sqrt{2})r_1(t_6s_5F_3' + t_5s_6F_3)$$
$$F(4,7) = -(1/\sqrt{5})F(4,6)$$
$$F(5,5) = \frac{1}{4}r_1r_3(H_3 - s_5s_6F_3' + t_5t_6F_3) + \frac{1}{4}r_2r_3(H_4 - s_7s_8F_4' + t_7t_8F_4)$$
$$F(5,6) = (1/4\sqrt{2})r_1r_3(H_3 - s_5s_6F_3' + t_5t_6F_3) - (1/4\sqrt{2}) \times r_2r_3(H_4 - s_7s_8F_4' + t_7t_8F_4)$$
$$F(5,7) = -(1/\sqrt{5})F(5,6)$$
$$F(6,6) = \frac{1}{2}r_1r_4(H_1 - s_1s_2F_1' + t_1t_2F_1) + \frac{1}{2}r_1r_2(H_2 - s_3s_4F_2' + t_3t_4F_2) + \frac{1}{8}r_1r_3(H_3 - s_5s_6F_3' + t_5t_6F_3) + \frac{1}{8}r_2r_3(H_4 - s_7s_8F_4' + t_7t_8F_4)$$

A$_1$ Species (*Continued*)

$$F(6,7) = (1/2\sqrt{5})r_1r_4(H_1 - s_1s_2F_1' + t_1t_2F_1) - (1/2\sqrt{5})r_1r_2(H_2 - s_3s_4F_2' + t_3t_4F_2) - (1/8\sqrt{5}) \times r_1r_3(H_3 - s_5s_6F_3' + t_5t_6F_3) - (1/8\sqrt{5})r_2r_3(H_4 - s_7s_8F_4' + t_7t_8F_4)$$
$$F(7,7) = \frac{1}{10}F(6,6) + \frac{2}{5}r_2r_5(H_5 - s_9s_{10}F_5' + t_9t_{10}F_5) + \frac{4}{5}r_2{}^2(H_6 - s_{11}{}^2F_6' + t_{11}{}^2F_6)$$

B$_2$ Species

$$F(1,1) = F(2,2)^{\mathrm{A}_1}$$
$$F(1,2) = F(2,3)^{\mathrm{A}_1}$$
$$F(1,3) = F(2,4)^{\mathrm{A}_1}$$
$$F(1,4) = F(2,5)^{\mathrm{A}_1}$$
$$F(1,6) = (1/\sqrt{2})r_2(t_3s_4F_2' + t_4s_3F_2) - (1/2\sqrt{2})r_3(t_5s_6F_3' + t_6s_5F_3) + (1/\sqrt{2})r_4(t_2s_1F_1' + t_1s_2F_1)$$
$$F(1,7) = F(2,6)^{\mathrm{A}_1}$$
$$F(2,2) = K_3 + 2t_{11}{}^2F_6' + t_9{}^2F_5' + s_9{}^2F_5 + t_4{}^2F_2' + s_4{}^2F_2 + t_8{}^2F_4' + s_8{}^2F_4$$
$$F(2,3) = F(3,4)^{\mathrm{A}_1}$$
$$F(2,4) = F(3,5)^{\mathrm{A}_1}$$
$$F(2,5) = (1/\sqrt{2})r_5(t_9s_{10}F_5' + t_{10}s_9F_5)$$
$$F(2,6) = F(3,6)^{\mathrm{A}_1}$$
$$F(2,7) = F(3,6)^{\mathrm{A}_1}$$
$$F(3,3) = F(4,4)^{\mathrm{A}_1}$$
$$F(3,4) = F(4,5)^{\mathrm{A}_1}$$
$$F(3,6) = F(4,6)^{\mathrm{A}_1}$$
$$F(3,7) = F(4,6)^{\mathrm{A}_1}$$
$$F(4,4) = F(5,5)^{\mathrm{A}_1}$$
$$F(4,6) = F(5,6)^{\mathrm{A}_1}$$
$$F(4,7) = F(5,6)^{\mathrm{A}_1}$$
$$F(5,5) = \frac{1}{2}r_2r_5(H_5 - s_9s_{10}F_5' + t_9t_{10}F_5)$$
$$F(6,6) = F(6,6)^{\mathrm{A}_1}$$
$$F(6,7) = \frac{1}{2}r_1r_4(H_1 + s_1s_2F_1' + t_1t_2F_1) + \frac{1}{2}r_1r_2(H_2 - s_3s_4F_2' + t_3t_4F_2) + \frac{1}{8}r_1r_3(H_3 - s_5s_6F_3' + t_5t_6F_3) + \frac{1}{8}r_2r_3(H_4 - s_7s_8F_4' + t_7t_8F_4)$$
$$F(7,7) = F(6,6)^{\mathrm{A}_1}$$

disulfide ion, 4.70 mdyn/Å, suggests a lower carbon–carbon π-bond order for the latter compound.

In-plane frequencies other than those assigned to stretching modes involving nuclei in the dithiolylium ring are similar to the same frequencies in the complexes of dithioacetylacetone.[1] The low-frequency vibrations ν_6, ν_{11}, and ν_{12} were assigned on the basis of Mikami's analyses of the corresponding vibrations of copper(II) acetylacetonate.[8]

Methyl group and out-of-plane vibrations were assigned by comparison with similar modes in metal dithioacetylacetonates.[1] It was possible to compare these assignments with those obtained from a normal-coordinate analysis of methyl group vibrations in dimethyl sulfide.[20] For the latter compound the methyl symmetric and antisymmetric deformations were shown to occur at 1322 and 1433 cm^{-1}, respectively. These modes appear near 1351, 1371 and 1399, 1426 cm^{-1} in the 1,2-dithiolylium cation.

Since tetrachloroferrate(II) vibrations[21] do not appear above 300 cm^{-1}, these did not interfere with those calculated for DTAA$^+$. The infrared spectra of the tetrachloroferrate and iodide[6] salts of the 1,2-dithiolylium ion are essentially the same except differences do exist in the character of the methyl deformation and rocking bands. The small variations

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TABLE X

FORCE FIELD COEFFICIENTS

$$t_1 = r_1 \sin \alpha_6/q_1 \qquad s_1 = (r_4 - r_1 \cos \alpha_6)/q_1$$
$$t_2 = r_4 \sin \alpha_6/q_1 \qquad s_2 = (r_1 - r_4 \cos \alpha_6)/q_1$$
$$t_3 = r_2 \sin \alpha_1/q_2 \qquad s_3 = (r_1 - r_2 \cos \alpha_1)/q_2$$
$$t_4 = r_1 \sin \alpha_1/q_2 \qquad s_4 = (r_2 - r_1 \cos \alpha_1)/q_2$$
$$t_5 = r_3 \sin \alpha_3/q_3 \qquad s_5 = (r_1 - r_3 \cos \alpha_3)/q_3$$
$$t_6 = r_1 \sin \alpha_3/q_3 \qquad s_6 = (r_3 - r_1 \cos \alpha_3)/q_3$$
$$t_7 = r_2 \sin \alpha_2/q_4 \qquad s_7 = (r_3 - r_2 \cos \alpha_2)/q_4$$
$$t_8 = r_3 \sin \alpha_2/q_4 \qquad s_8 = (r_2 - r_3 \cos \alpha_2)/q_4$$
$$t_9 = r_5 \sin \alpha_5/q_6 \qquad s_9 = (r_2 - r_5 \cos \alpha_5)/q_6$$
$$t_{10} = r_2 \sin \alpha_5/q_6 \qquad s_{10} = (r_5 - r_2 \cos \alpha_5)/q_6$$
$$t_{11} = r_2 \sin \alpha_4/q_5 \qquad s_{11} = (r_2 - r_2 \cos \alpha_4)/q_5$$
$$q_1{}^2 = r_4{}^2 + r_1{}^2 - 2r_4r_1 \cos \alpha_6 \qquad q_4{}^2 = r_2{}^2 + r_3{}^2 - 2r_2r_3 \cos \alpha_2$$
$$q_2{}^2 = r_1{}^2 + r_2{}^2 - 2r_1r_2 \cos \alpha_1 \qquad q_5{}^2 = r_2{}^2 + r_2{}^2 - 2r_2r_2 \cos \alpha_4$$
$$q_3{}^2 = r_1{}^2 + r_3{}^2 - 2r_1r_3 \cos \alpha_3 \qquad q_6{}^2 = r_2{}^2 + r_5{}^2 - 2r_2r_5 \cos \alpha_5$$
$$q_1 = q_{\mathrm{C}\cdots\mathrm{S}} \quad q_2 = q_{\mathrm{C}'\cdots\mathrm{S}} \quad q_3 = q_{\mathrm{R}\cdots\mathrm{S}}$$
$$q_4 = q_{\mathrm{C}'\cdots\mathrm{R}}, \quad q_5 = q_{\mathrm{C}\cdots\mathrm{C}}, \quad q_6 = q_{\mathrm{C}\cdots\mathrm{H}}$$

observed possibly arise from changes in methyl group environment in the different lattices.

The results of the normal-coordinate analysis are consistent with the absence of iron–sulfur bonding shown by X-ray diffraction studies.

An opportunity to apply the normal-coordinate treatment developed for DTAA$^+$ to another compound possibly of identical structure was provided by the recent synthesis of salts of the 3,5-dimethyl-1,2-diselenolylium ion hereafter denoted as DSeAA$^+$. After carbon–selenium and selenium–selenium bond lengths for this cation were estimated, bond angles for a planar five-membered diselenide ring were adjusted by reference to molecular parameters of DTAA$^+$ which were common to DSeAA$^+$. Except for K(C–Se) and K(Se–Se), which were varied to obtain a best fit between observed and calculated frequencies, the force constants used were transferred from the disulfide cation. Assignments based on potential energy distributions which appear in Table VIII were supported by calculation of Jacobian terms. Based on the model adopted good agreement was obtained between calculated and observed frequencies as recorded in Table VII.

The weak band near 600 cm^{-1} was assigned to the carbon–selenium stretching vibration. It was of interest to note the corresponding force constant, 2.80 mdyn/Å, almost equals 2.78 mdyn/Å, which is the value for K(C–Se) in the metal chelates of diethyldiselenocarbamic acid.[22] Although a pure selenium–selenium stretching vibration was not predicted, an absorption band close to 320 cm^{-1} and one predicted near 290 cm^{-1} were assigned to coupled modes which contain that vibration. In the series of selenium–selenium bonded compounds—dimethyl selenide, $Se_4{}^{2+}$, and Se_2—the intermediate value, 2.20 mdyn/Å, for $Se_4{}^{2+}$ has been considered[23] to indicate the existence of a degree of multiple bonding. Since the corresponding force constant is 2.00 mdyn/Å for the diselenide ion, the selenium double-bond character of the two ions is probably similar.

The carbon–selenium stretching force constant in the diselenolylium ion is less than the carbon–sulfur constant in the dithiolylium ion. Similar decreases were observed in the pairs of compounds selenourea, thiourea and selenoacetamide, thioacetamide.[24] These trends conform to the usual expectation for differences in selenium and sulfur bond energies.

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The Preparation and Properties of Diorganoselenium Difluorides

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The synthesis of a number of alkyl- and aryldiorganoselenium difluorides is reported from the reaction of silver(II) fluoride with diorganoselenides. Diorganoselenium difluorides are liquids or low-melting solids which are monomers in benzene solution. Infrared and ^{19}F and ^1H nmr data are presented and discussed with regard to bonding and fluorine exchange in these compounds.

Some years ago it was suggested that higher organochalcogen fluorides were unstable.[1] However, Sheppard[2] has demonstrated the stability of organosulfur tri- and pentafluorides. In a continuing study of organoselenium halides[3] we have found further evidence for the stability of organochalcogen fluorides. We have communicated the synthesis of the first reported example of a diorganoselenium difluoride, dimethylselenium difluoride,[4] from the reaction of dimethyl selenide with

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