

pressure determines which of two polymorphs will form. If (at constant temperature) increasing pressure is required with increasing atomic number to form one of the polymorphs, then 4f electrons are contributing to the bonding. If increasing pressure is required with decreasing atomic number, then 4f bonding is not involved.

The data in Table II show that the pressure requirement for synthesis varies directly with atomic number. In this case, the boundary exists between the compound and the elements, but this should have the same significance with respect to 4f bonding as a phase boundary between two polymorphs. Since increasing pressure is required to form  $\text{LTe}_{2-x}$  from the elements with increasing atomic number, it is likely that pressure is causing the 4f electrons of these heavier lanthanides to participate and, in effect, behave more like the higher lanthanides'.

Each of the new  $\text{LTe}_{2-x}$  compounds is silvery in appearance whereas  $\text{LuTe}_3$  is gold colored. Both types of compounds are unstable with respect to the elements. X-Ray spectra of  $\text{HoTe}_{2-x}$  show no decomposition after 15 days but complete decomposition after 80 days. When heated under vacuum,  $\text{HoTe}_{2-x}$  remained stable at  $260^\circ$  but decomposed at  $340^\circ$ . The shiny gold-colored  $\text{LuTe}_3$  was observed to lose its gold color after about 5–8 min. Complete decomposition occurred within 2 or 3 days. These compounds were stored in slip-capped plastic vials in the open atmosphere.

Scientists at the Battelle Memorial Institute, Columbus, Ohio, have been investigating the semiconduct-

ing properties of lanthanide metals and compounds.<sup>21–24</sup> Some of the  $\text{LTe}_{2-x}$  compounds (as well as other lanthanide–tellurium compounds) are included in their study. Although no study of the semiconducting properties of these new  $\text{LTe}_{2-x}$  compounds has been made, it is expected that their properties will be similar to those of the previously known analogs.

X-Ray studies have shown these new compounds to be isostructural with their lower molecular weight analogs. The points in Figures 4 and 5 show that the variation of lattice parameters *vs.* ionic radius follows the pattern set by the previously known analogous compounds. Lattice parameters are shown in Table III. X-Ray powder data are given in Table IV.

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## The Crystal Structure of Dipyrindinium(II) Oxytetrachloroselenate(IV), $\text{C}_{10}\text{H}_8\text{N}_2\text{H}_2^{2+}\text{SeOCl}_4^{2-}$ . A Highly Coordinated Selenium Compound<sup>1</sup>

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Crystals of dipyrindinium(II) oxytetrachloroselenate(IV),  $\text{C}_{10}\text{H}_8\text{N}_2\text{H}_2^{2+}\text{SeOCl}_4^{2-}$ , are monoclinic with  $a = 26.62$  (1) Å,  $b = 14.40$  (2) Å,  $c = 15.497$  (9) Å,  $\beta = 104.39$  (5)°,  $d_{\text{measd}} = 1.81$  (1) g cm<sup>-3</sup>, and  $d_{\text{calcd}} = 1.823$  (4) g cm<sup>-3</sup>. The space group is C2/c, with two formula units per asymmetric unit. Multiple-film Weissenberg methods yielded 4292 reflections (2731 observed). Full-matrix least-squares refinement included anisotropic temperature factors for Se and Cl and gave an  $R$  of 0.098. The structure consists of square-pyramidal  $\text{SeOCl}_4^{2-}$  units hydrogen bonded to the organic cations. The Se–O distances are 1.61 (1) and 1.65 (1) Å, and the Se–Cl distances are 2.525, 2.431, 2.246, 2.244, 2.445, 2.502, 2.980, and 2.990 Å (all  $\pm 0.004$  Å).

### Introduction

Structures of five-bonded selenium provide a bonding situation intermediate between compounds of four or fewer bonds, which are readily interpreted in terms of

ordinary molecular geometry treatments,<sup>3</sup> and the structurally anomalous hexahaloselenate dianions.<sup>4</sup> The recent structure of  $\text{R}^+\text{SeOCl}_3^-$  (R = 8-hydroxyquinolinium<sup>5</sup>) presented a selenium oxychloride ion

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which could be considered to contain five-bonded selenium, although some of the Se-Cl bonds, those to the bridging chlorines, were about 0.3 Å longer than normal Se-Cl bonds. The present structure contains another oxychloride ion, one with a different (4:1) Cl-Se stoichiometry, and provides new structural information on the stereochemistry of highly coordinated selenium.

### Experimental Section

**Preparation of the Crystals and Chemical Analysis.**—Selenium tetrachloride was prepared by passing chlorine gas over heated elemental selenium powder. 2,2'-Dipyridyl was purchased from K & K Laboratories, Inc., Plainview, N. Y., and was used without further purification.

In a typical reaction 0.25 g of SeCl<sub>4</sub> in 25 ml of acetonitrile was added to 0.18 g of dipyridyl in 25 ml of acetonitrile. Upon mixing, the clear, colorless compounds gave a pale yellow solution. About 0.5 hr after the mixing, white needlelike crystals began to appear.

An alternative method of making this compound was to bubble Cl<sub>2</sub> gas in 100 ml of acetonitrile which contained 0.65 g of selenium powder. After the black selenium powder completely disappeared into the solution, nitrogen gas was bubbled into the solution until it changed from deep yellow to pale yellow. A 25-ml portion of this solution was mixed with 0.2 g of bipyridyl in 40 ml of acetonitrile. The mixture was then allowed to absorb chlorine gas under a chlorine atmosphere. Needlelike crystals began to form about 1 hr later. Although reasonable precautions were taken to exclude moisture in the preparation, it is apparent that one water molecule per product molecule was introduced, probably through incomplete drying of the acetonitrile solvent.

The selenium and chlorine analyses were done by the sulfur dioxide reduction method and Volhard's method, respectively. The percentages of carbon and hydrogen were obtained using a Coleman Model 33 carbon-hydrogen analyzer. *Anal.* Calcd for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>H<sub>2</sub><sup>2+</sup>SeOCl<sub>4</sub><sup>2-</sup>: Se, 20.0; Cl, 35.9; C, 30.4; H, 2.6. Found: Se, 19.5; Cl, 39.3; C, 30.1; H, 2.7.

**The X-Ray Data Collection.**—One crystal was used for both the determination of the cell parameters and for collecting the intensity data. The approximately parallelepiped crystal had dimensions of 0.13 × 0.13 × 0.96 mm, with the long dimension parallel to the *b* axis. It was loaded in a Lindemann capillary because the crystals decompose upon exposure to the atmosphere.

X-Ray data were obtained at 25° using Ni-filtered Cu K $\alpha$  radiation ( $\lambda$  1.5418 Å) and a Weissenberg camera with Kodak No-Screen medical X-ray films. The needle axis of the crystal was the rotation axis. For the determination of cell parameters, single-film equiinclination photographs of the layers  $0 \leq k \leq 6$  were recorded; for intensity measurements equiinclination photographs with  $0 \leq k \leq 6$  were recorded using multiple-film techniques (four or five films). The relative intensities were estimated visually on the upper half of the films using an intensity scale obtained from one of the zero-layer reflections of the same crystal. A total of 4292 independent reflections were assigned; 2731 of them were actually strong enough to be measured. The unobserved reflections were assigned maximum possible values; they were not included in the least squares or calculation of the residual unless the calculated *F* exceeded the observed *F*.

The unit cell is monoclinic. The cell dimensions and their standard deviations were calculated by a least-squares treatment of 58 measurements of the vertical displacement ( $\Upsilon$ ) of the reflections on zero and upper layer Weissenberg films. The cell constants are  $a = 26.62 \pm 0.01$  Å,  $b = 14.40 \pm 0.02$  Å,  $c = 15.497 \pm 0.009$  Å, and  $\beta = 104.39 \pm 0.05^\circ$ . The density calculated on the basis of 16 C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>H<sub>2</sub><sup>2+</sup>SeOCl<sub>4</sub><sup>2-</sup> formula units per unit cell is  $1.823 \pm 0.004$  g/cm<sup>3</sup>. The density found by flotation in a mixture of carbon tetrachloride and methyl iodide was  $1.81 \pm 0.01$  g/cm<sup>-3</sup>.

The systematic absences observed were *hkl* for  $h + k$  odd and  $h0l$  for  $h$  and  $l$  odd. The space group was therefore taken as C2/c.

The assignment of the intensity of the unobservable reflections, the assignment of standard deviations to each observed intensity, the averaging of the multiple readings, and the Lorentz and polarization corrections were made in the manner of the CRYM programs of Cal Tech.<sup>6</sup> A correction for spot elongation was also made. No absorption correction was made. From the linear absorption coefficient for Cu K $\alpha$  X-rays of 105 cm<sup>-1</sup> the estimated maximum correction factors for *F* would range from 1.58 to 2.18 for the zero layer and 1.67 to 2.43 for the ninth layer.

**The Determination of the Structure.**—Since the crystal has 16 molecules per unit cell, there are two crystallographically unrelated molecules in the unique part of the unit cell. A three-dimensional Patterson map revealed the positions of the two unrelated selenium atoms and their chlorine atoms.

Because of the location of the Se and Cl atoms either at  $y = 0$  or at the same  $x$  and  $z$  coordinates with one atom at  $+y$  and one at  $-y$ , these heavy atoms contributed only to reflections with  $l$  even. In order to deal with the heavy atoms first, reflections with  $l$  even were treated initially. The  $R_1$  ( $R_1 = \Sigma ||F_o - |F_c|| / \Sigma |F_o|$ ) value was 0.55 for reflections of  $l = 2n$  only. Positional shifts based on Fourier maps lowered this to 0.46.

Information concerning the orientations of the organic groups in the unit cell was supplied by a three-dimensional electron density map computed from 400 randomly selected reflections with  $l$  even. The crude orientations assumed for the two pyridine rings were then used to compute the positional parameters of the 12 nonhydrogen atoms in one of the two dipyridyl molecules in the asymmetric part of the unit cell. The other dipyridyl cation, according to the electron density map, was related to the first one by an inversion center at  $1/4, 1/4, 1/4$ . Although this inversion center is not a symmetry element of C2/c, it was temporarily used in the calculation of the positional parameters of the second dipyridyl ion. Introducing the carbon atoms (all ring atoms were temporarily treated as carbon) along with selenium and chlorine lowered  $R_1$  to 0.36.

The analysis of a series of difference Fourier maps located the oxygen atoms. At this time it was realized that the organic groups were not the only atoms which contributed to the odd  $l$  reflections, but the mirror plane symmetry at  $y = 0$  for the heavy atoms would have to be removed in order to obtain values of the proper magnitude for the odd  $l$  reflections. A three-dimensional Patterson map was constructed using the 500 most intense reflections with odd  $l$ . By comparing this map to the original Patterson map the symmetry about  $y = 0$  was broken. These positional parameters were then refined with Fourier and difference techniques using reflections with odd  $l$  until the  $R_1$  value was about 0.2. Then the reflections of even  $l$  and odd  $l$  were combined and least-squares refinement was applied.

Initial least-squares refinements were performed using a block-diagonal program weighted according to the standard deviations estimated from the original film readings. The final refinement was a full-matrix least-squares treatment. In the least-squares refinements, the function minimized was  $\Sigma w(|F_o| - |F_c|)^2$  where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure amplitudes,  $w$  is the weight defined as  $1/\sigma^2(F_o)$ , and  $\sigma(F_o)$  was the value assigned by the data-processing program. The atomic form factors were taken from Vol. II of the "International Tables of X-Ray Crystallography." No correction was made for anomalous dispersion.

The final refinement included 108 positional parameters and 86 temperature parameters. Anisotropic temperature factors were used for the selenium and chlorine atoms. The 16 hydrogen atoms (calculated positions) were added for the structure factor calculations but were not varied in the least-squares process.

(6) D. J. Duchamp, "User's Guide to the CRYM Crystallographic Computing Systems," California Institute of Technology, Pasadena, Calif., 1964. The equation for the  $\sigma$ 's assigned to the intensity readings is given by B. D. Sharma and J. F. McConnell, *Acta Crystallogr.*, **19**, 797 (1965).

After four cycles of full-matrix least-squares refinement  $R_1$  reached 0.098, the weighted discrepancy factor

$$R_2 = \left\{ \sum w [|F_o| - |F_c|]^2 / \sum w |F_o|^2 \right\}^{1/2}$$

where  $w = 1/\sigma(F)^2$  was 0.064, and the "goodness of fit" ( $= \sum w \cdot (F_o^2 - F_c^2)/(n - p)^{1/2}$ ) was 1.47. A final difference Fourier map did not produce any peaks larger than  $1.1 \text{ e}^-/\text{\AA}^3$ .

### Results and Discussion

The final atomic coordinates and thermal parameters are listed in Tables I-IV. The thermal parameters and

TABLE I  
ATOMIC COORDINATES FOR  $\text{bipyH}_2 \cdot \text{SeOCl}_4^a$

Atom	X	Y	Z
Se(1)	0.13210 (5)	0.01216 (11)	0.33140 (9)
Se(2)	0.34343 (5)	0.01411 (12)	0.08903 (11)
Cl(1)	0.0891 (1)	-0.0011 (2)	0.4918 (2)
Cl(2)	0.1420 (1)	0.1861 (3)	0.3481 (2)
Cl(3)	0.1800 (2)	0.0163 (3)	0.2309 (3)
Cl(4)	0.1431 (1)	-0.1565 (3)	0.3405 (2)
Cl(5)	0.4141 (1)	-0.0081 (2)	-0.0316 (3)
Cl(6)	0.2662 (1)	-0.0088 (3)	-0.0314 (3)
Cl(7)	0.2933 (1)	-0.0022 (3)	0.1851 (3)
Cl(8)	0.4221 (1)	0.0015 (3)	0.2164 (3)
O(1)	0.0739 (4)	0.0121 (5)	0.2691 (6)
O(2)	0.3449 (6)	0.1280 (9)	0.0775 (9)
C(1)	-0.0231 (7)	0.2712 (13)	0.1318 (10)
C(2)	-0.0026 (6)	0.1833 (12)	0.1345 (9)
C(3)	0.0033 (6)	0.3500 (12)	0.1222 (11)
C(4)	0.0492 (6)	0.1730 (11)	0.1269 (9)
N(5)	0.0537 (5)	0.3338 (9)	0.1135 (8)
C(6)	0.0763 (4)	0.2505 (9)	0.1168 (7)
C(7)	0.1316 (5)	0.2511 (10)	0.1136 (9)
N(8)	0.1467 (4)	0.1771 (8)	0.0715 (7)
C(9)	0.1663 (5)	0.3188 (10)	0.1502 (9)
C(10)	0.1966 (6)	0.1674 (10)	0.0679 (10)
C(11)	0.2192 (6)	0.3081 (11)	0.1460 (10)
C(13)	0.2325 (6)	0.2343 (11)	0.1062 (9)
C(13)	0.2741 (6)	0.2660 (12)	0.3846 (10)
C(14)	0.2873 (6)	0.1945 (12)	0.3430 (11)
C(15)	0.3078 (6)	0.3368 (11)	0.4210 (10)
C(16)	0.3407 (5)	0.1850 (10)	0.3397 (9)
N(17)	0.3588 (4)	0.3284 (8)	0.4174 (7)
C(18)	0.3741 (5)	0.2560 (9)	0.3749 (8)
C(19)	0.4296 (5)	0.2541 (10)	0.3757 (8)
N(20)	0.4520 (5)	0.1729 (8)	0.3811 (7)
C(21)	0.4574 (6)	0.3314 (11)	0.3656 (9)
C(22)	0.5039 (6)	0.1597 (11)	0.3790 (10)
C(23)	0.5105 (6)	0.3239 (12)	0.3632 (10)
C(24)	0.5307 (6)	0.2374 (12)	0.3704 (9)
H(1)	-0.063	0.271	0.139
H(2)	-0.024	0.122	0.143
H(3)	-0.014	0.412	0.117
H(4)	0.066	0.108	0.129
H(9)	0.155	0.377	0.184
H(10)	0.207	0.111	0.034
H(11)	0.247	0.359	0.175
H(12)	0.272	0.231	0.107
H(13)	0.234	0.268	0.388
H(14)	0.261	0.141	0.317
H(15)	0.297	0.393	0.454
H(16)	0.352	0.130	0.306
H(21)	0.440	0.399	0.358
H(22)	0.520	0.094	0.385
H(23)	0.532	0.380	0.355
H(24)	0.572	0.229	0.370

<sup>a</sup> Estimated standard deviations for the last digit are given in parentheses. The hydrogen positions were calculated from the carbon parameters; their standard deviations are at least 0.001 in X, 0.002 in Y, and 0.002 in Z.

TABLE II

ANISOTROPIC THERMAL PARAMETERS FOR  $\text{bipyH}_2 \cdot \text{SeOCl}_4^a$ 

Atom	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^3\beta_{33}$	$10^3\beta_{12}$	$10^3\beta_{13}$	$10^3\beta_{23}$
Se(1)	91 (2)	521 (16)	350 (7)	5 (8)	103 (6)	28 (14)
Se(2)	96 (2)	713 (15)	416 (8)	4 (9)	149 (6)	-50 (16)
Cl(1)	129 (5)	448 (29)	340 (16)	-18 (20)	91 (15)	9 (32)
Cl(2)	119 (6)	379 (31)	580 (24)	-49 (20)	171 (19)	45 (39)
Cl(3)	154 (7)	840 (34)	416 (19)	-14 (25)	301 (19)	-20 (41)
Cl(4)	114 (6)	369 (30)	463 (21)	73 (19)	116 (18)	-1 (35)
Cl(5)	135 (6)	424 (30)	433 (18)	15 (20)	236 (16)	-36 (34)
Cl(6)	121 (6)	686 (33)	390 (17)	-63 (22)	8 (15)	-48 (37)
Cl(7)	121 (5)	801 (35)	432 (18)	-31 (22)	242 (17)	-63 (39)
Cl(8)	122 (6)	727 (35)	469 (20)	32 (23)	84 (17)	-61 (40)

<sup>a</sup> Estimated standard deviations  $\times 10^3$  are given in parentheses. The temperature factor is in the form:  $T_i = \exp[-\beta_{11}h^2 + \beta_{22}j^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl]_i$ .

TABLE III

VALUES OF THE TEMPERATURE FACTORS ( $\text{\AA}^2$ ) ALONG THE MAJOR, INTERMEDIATE, AND MINOR AXES OF THE ANISOTROPIC THERMAL ELLIPSOIDS<sup>a</sup>

Atom	B	Direction cosines		
Se(1)	4.33	0.000	0.995	0.099
	3.14	0.008	-0.102	0.962
	2.37	1.000	0.001	-0.256
Se(2)	5.94	0.018	0.995	-0.098
	3.77	0.170	0.092	0.908
	2.31	0.985	-0.033	-0.407
Cl(1)	3.80	-0.451	0.887	0.203
	3.42	0.881	0.460	-0.326
	3.05	0.141	-0.033	0.923
Cl(2)	5.24	-0.010	0.092	0.967
	3.51	-0.662	0.745	0.091
	2.64	0.749	0.660	-0.238
Cl(3)	6.97	-0.042	0.998	-0.034
	5.01	0.659	0.062	0.562
	2.12	0.751	0.001	-0.826
Cl(4)	4.20	-0.165	-0.090	0.992
	3.60	0.675	0.716	0.005
	2.47	-0.719	0.693	0.123
Cl(5)	4.48	0.539	-0.053	0.680
	3.56	0.197	0.978	-0.111
	2.50	0.819	-0.201	-0.725
Cl(6)	5.78	-0.192	0.981	0.030
	4.39	0.702	0.124	-0.854
	2.66	0.686	0.148	0.519
Cl(7)	6.69	-0.068	0.990	-0.100
	4.36	0.475	0.138	0.724
	2.18	0.878	0.002	-0.682
Cl(8)	6.12	0.137	0.977	-0.193
	4.32	-0.340	0.202	0.974
	3.21	0.930	-0.070	0.117

<sup>a</sup> The direction cosines of the ellipsoid axes with respect to the axes of the unit cell are given.

TABLE IV

ISOTROPIC THERMAL PARAMETERS FOR THE STRUCTURE OF  $\text{bipyH}_2 \cdot \text{SeOCl}_4^a$ 

Atom	B, $\text{\AA}^2$	Atom	B, $\text{\AA}^2$	Atom	B, $\text{\AA}^2$
O(1)	3.4 (2)	O(2)	9.1 (4)	C(1)	5.1 (4)
C(2)	3.7 (3)	C(3)	4.7 (4)	C(4)	3.5 (3)
N(5)	3.9 (3)	C(6)	2.1 (2)	C(7)	3.2 (3)
N(8)	3.1 (2)	C(9)	3.5 (3)	C(10)	3.9 (3)
C(11)	4.2 (3)	C(12)	4.0 (3)	C(13)	4.9 (4)
C(14)	4.9 (4)	C(15)	4.4 (3)	C(16)	3.5 (3)
N(17)	3.0 (2)	C(18)	2.6 (2)	C(22)	2.9 (3)
N(20)	3.3 (2)	C(21)	3.7 (3)	C(22)	4.2 (3)
C(23)	4.2 (3)	C(24)	4.6 (4)	H	9.0

<sup>a</sup> Estimated standard deviations  $\times 10$  are given in parentheses.

TABLE V  
OBSERVED AND CALCULATED STRUCTURE FACTORS OF  $\text{bipyH}_2 \cdot \text{SeOCl}_4$

h	k	l	observed	calculated	h	k	l	observed	calculated
0	0	0	100	100	10	10	10	100	100
0	0	1	100	100	10	10	11	100	100
0	0	2	100	100	10	10	12	100	100
0	0	3	100	100	10	10	13	100	100
0	0	4	100	100	10	10	14	100	100
0	0	5	100	100	10	10	15	100	100
0	0	6	100	100	10	10	16	100	100
0	0	7	100	100	10	10	17	100	100
0	0	8	100	100	10	10	18	100	100
0	0	9	100	100	10	10	19	100	100
0	0	10	100	100	10	10	20	100	100
0	0	11	100	100	10	10	21	100	100
0	0	12	100	100	10	10	22	100	100
0	0	13	100	100	10	10	23	100	100
0	0	14	100	100	10	10	24	100	100
0	0	15	100	100	10	10	25	100	100
0	0	16	100	100	10	10	26	100	100
0	0	17	100	100	10	10	27	100	100
0	0	18	100	100	10	10	28	100	100
0	0	19	100	100	10	10	29	100	100
0	0	20	100	100	10	10	30	100	100
0	0	21	100	100	10	10	31	100	100
0	0	22	100	100	10	10	32	100	100
0	0	23	100	100	10	10	33	100	100
0	0	24	100	100	10	10	34	100	100
0	0	25	100	100	10	10	35	100	100
0	0	26	100	100	10	10	36	100	100
0	0	27	100	100	10	10	37	100	100
0	0	28	100	100	10	10	38	100	100
0	0	29	100	100	10	10	39	100	100
0	0	30	100	100	10	10	40	100	100
0	0	31	100	100	10	10	41	100	100
0	0	32	100	100	10	10	42	100	100
0	0	33	100	100	10	10	43	100	100
0	0	34	100	100	10	10	44	100	100
0	0	35	100	100	10	10	45	100	100
0	0	36	100	100	10	10	46	100	100
0	0	37	100	100	10	10	47	100	100
0	0	38	100	100	10	10	48	100	100
0	0	39	100	100	10	10	49	100	100
0	0	40	100	100	10	10	50	100	100
0	0	41	100	100	10	10	51	100	100
0	0	42	100	100	10	10	52	100	100
0	0	43	100	100	10	10	53	100	100
0	0	44	100	100	10	10	54	100	100
0	0	45	100	100	10	10	55	100	100
0	0	46	100	100	10	10	56	100	100
0	0	47	100	100	10	10	57	100	100
0	0	48	100	100	10	10	58	100	100
0	0	49	100	100	10	10	59	100	100
0	0	50	100	100	10	10	60	100	100
0	0	51	100	100	10	10	61	100	100
0	0	52	100	100	10	10	62	100	100
0	0	53	100	100	10	10	63	100	100
0	0	54	100	100	10	10	64	100	100
0	0	55	100	100	10	10	65	100	100
0	0	56	100	100	10	10	66	100	100
0	0	57	100	100	10	10	67	100	100
0	0	58	100	100	10	10	68	100	100
0	0	59	100	100	10	10	69	100	100
0	0	60	100	100	10	10	70	100	100
0	0	61	100	100	10	10	71	100	100
0	0	62	100	100	10	10	72	100	100
0	0	63	100	100	10	10	73	100	100
0	0	64	100	100	10	10	74	100	100
0	0	65	100	100	10	10	75	100	100
0	0	66	100	100	10	10	76	100	100
0	0	67	100	100	10	10	77	100	100
0	0	68	100	100	10	10	78	100	100
0	0	69	100	100	10	10	79	100	100
0	0	70	100	100	10	10	80	100	100
0	0	71	100	100	10	10	81	100	100
0	0	72	100	100	10	10	82	100	100
0	0	73	100	100	10	10	83	100	100
0	0	74	100	100	10	10	84	100	100
0	0	75	100	100	10	10	85	100	100
0	0	76	100	100	10	10	86	100	100
0	0	77	100	100	10	10	87	100	100
0	0	78	100	100	10	10	88	100	100
0	0	79	100	100	10	10	89	100	100
0	0	80	100	100	10	10	90	100	100
0	0	81	100	100	10	10	91	100	100
0	0	82	100	100	10	10	92	100	100
0	0	83	100	100	10	10	93	100	100
0	0	84	100	100	10	10	94	100	100
0	0	85	100	100	10	10	95	100	100
0	0	86	100	100	10	10	96	100	100
0	0	87	100	100	10	10	97	100	100
0	0	88	100	100	10	10	98	100	100
0	0	89	100	100	10	10	99	100	100
0	0	90	100	100	10	10	100	100	100

their estimated standard deviations are very possibly distorted by the lack of an absorption correction. The observed and calculated structure factors are presented in Table V. Bond lengths and bond angles derived

from the parameters of Table I are listed in Tables VI and VII. The bond lengths and bond angles of the anion unit are shown in Figure 1.

The angles between the ring planes in the biphenyl

TABLE V (Continued)

Table with multiple columns containing numerical data and labels such as H 1, H 2, H 3, H 4, H 5, H 6, H 7, H 8, H 9, H 10, H 11, H 12, H 13, H 14, H 15, H 16, H 17, H 18, H 19, H 20, H 21, H 22, H 23, H 24, H 25, H 26, H 27, H 28, H 29, H 30, H 31, H 32, H 33, H 34, H 35, H 36, H 37, H 38, H 39, H 40, H 41, H 42, H 43, H 44, H 45, H 46, H 47, H 48, H 49, H 50, H 51, H 52, H 53, H 54, H 55, H 56, H 57, H 58, H 59, H 60, H 61, H 62, H 63, H 64, H 65, H 66, H 67, H 68, H 69, H 70, H 71, H 72, H 73, H 74, H 75, H 76, H 77, H 78, H 79, H 80, H 81, H 82, H 83, H 84, H 85, H 86, H 87, H 88, H 89, H 90, H 91, H 92, H 93, H 94, H 95, H 96, H 97, H 98, H 99, H 100.

Within each column the three values are the h index, Fo, and Fe. A negative sign preceding Fo should be read "less than."

groups are 35.1 and 35.9°. There were no intermolecular atomic contacts with distances significantly shorter than the sum of the van der Waals radii, except as mentioned below. Views along the three different crystallographic axes are shown in Figures 2-4. In order to avoid overlap in the drawing, the depths of these views are restricted to one-fourth of the cell length. In Figure 3 the carbon

TABLE VI

BOND LENGTHS IN THE STRUCTURE OF  $\text{bipyH}_2 \cdot \text{SeOCl}_4^a$ 

Atoms	Dist, Å	Atoms	Dist, Å
Se(1)-Cl(1)	2.990 (4)	Cl(5)-N(5)	3.03 (1)
Se(1)-Cl(2)	2.525 (4)	Cl(5)-N(20)	3.03 (1)
Se(1)-Cl(3)	2.246 (4)	Se(2)-Cl(5)	2.980 (4)
Se(1)-Cl(4)	2.445 (4)	Se(2)-Cl(6)	2.431 (4)
Se(1)-O(1)	1.61 (1)	Se(2)-Cl(7)	2.244 (4)
C(1)-C(2)	1.37 (2)	Se(2)-Cl(8)	2.502 (4)
C(1)-C(3)	1.36 (2)	Se(2)-O(2)	1.65 (1)
C(2)-C(4)	1.42 (2)	C(24)-C(23)	1.35 (2)
C(3)-N(5)	1.40 (2)	C(24)-C(22)	1.35 (2)
C(4)-C(6)	1.36 (2)	C(23)-C(21)	1.43 (2)
N(5)-C(6)	1.34 (2)	C(22)-N(20)	1.40 (2)
C(6)-C(7)	1.48 (2)	C(21)-C(19)	1.37 (2)
C(7)-N(8)	1.36 (2)	N(20)-C(19)	1.31 (2)
C(7)-C(9)	1.37 (2)	C(19)-C(18)	1.48 (2)
N(8)-C(10)	1.35 (2)	C(18)-N(17)	1.35 (2)
C(9)-C(11)	1.43 (2)	C(18)-C(16)	1.37 (2)
C(10)-C(12)	1.38 (2)	N(17)-C(15)	1.38 (2)
C(11)-C(12)	1.32 (2)	C(16)-C(14)	1.44 (2)
Cl(1)-N(8)	3.06 (1)	C(15)-C(13)	1.38 (2)
Cl(1)-N(17)	3.02 (1)	C(14)-C(13)	1.31 (2)

<sup>a</sup> Estimated standard deviations for the last digit are given in parentheses.

TABLE VII

BOND ANGLES FOR THE STRUCTURE OF  $\text{bipyH}_2 \cdot \text{SeOCl}_4^a$ 

Atoms	Angle	Atoms	Angle
O(1)-Se(1)-Cl(1)	89.3 (4)	O(2)-Se(2)-Cl(5)	90.2 (5)
O(1)-Se(1)-Cl(2)	97.1 (3)	O(2)-Se(2)-Cl(6)	95.2 (5)
O(1)-Se(1)-Cl(3)	102.2 (4)	O(2)-Se(2)-Cl(7)	102.1 (5)
O(1)-Se(1)-Cl(4)	96.7 (3)	O(2)-Se(2)-Cl(8)	96.9 (5)
Cl(1)-Se(1)-Cl(2)	91.7 (1)	Cl(5)-Se(2)-Cl(6)	92.8 (1)
Cl(2)-Se(1)-Cl(3)	89.0 (1)	Cl(6)-Se(2)-Cl(7)	88.1 (1)
Cl(3)-Se(1)-Cl(4)	89.2 (1)	Cl(7)-Se(2)-Cl(8)	89.3 (1)
Cl(4)-Se(1)-Cl(1)	87.3 (1)	Cl(8)-Se(2)-Cl(5)	87.3 (1)
Cl(1)-Se(1)-Cl(3)	168.3 (1)	Cl(5)-Se(2)-Cl(7)	167.6 (1)
Cl(2)-Se(1)-Cl(4)	166.2 (1)	Cl(6)-Se(2)-Cl(8)	168.0 (1)
C(2)-C(1)-C(3)	123.9 (16)	C(23)-C(24)-C(22)	124.2 (16)
C(1)-C(2)-C(4)	118.7 (15)	C(24)-C(23)-C(21)	116.3 (15)
C(1)-C(3)-N(5)	113.8 (5)	C(24)-C(22)-N(20)	116.0 (15)
C(2)-C(4)-C(6)	118.5 (14)	C(23)-C(21)-C(19)	120.7 (14)
C(3)-N(5)-C(6)	125.4 (13)	C(22)-N(20)-C(19)	123.9 (13)
C(4)-C(6)-N(5)	119.6 (12)	C(21)-C(19)-N(20)	118.9 (3)
N(5)-C(6)-C(7)	115.8 (12)	N(20)-C(19)-C(18)	117.3 (13)
C(4)-C(6)-C(7)	124.6 (13)	C(21)-C(19)-C(18)	123.6 (13)
C(6)-C(7)-N(8)	115.1 (12)	C(19)-C(18)-N(17)	115.7 (12)
C(6)-C(7)-C(9)	124.4 (13)	C(19)-C(18)-C(16)	122.4 (12)
N(8)-C(7)-C(9)	120.5 (13)	N(17)-C(18)-C(16)	121.7 (12)
C(7)-N(8)-C(10)	120.8 (12)	C(18)-N(17)-C(15)	120.5 (12)
C(7)-C(9)-C(11)	118.4 (13)	C(18)-C(16)-C(14)	117.4 (13)
N(8)-C(10)-C(12)	119.4 (13)	N(17)-C(15)-C(13)	117.7 (14)
C(9)-C(11)-C(12)	119.2 (14)	C(16)-C(14)-C(13)	118.8 (16)
C(10)-C(12)-C(11)	121.6 (15)	C(15)-C(13)-C(14)	123.6 (17)

<sup>a</sup> Estimated standard deviations  $\times 10$  are given in parentheses.

atoms are not shown. The broken lines between some atoms indicate the weak interactions between these atoms (see the following discussion).

As shown in Figure 4, the structure is composed of a chainlike arrangement of Cl-N-N-Cl hydrogen-bond linkages with  $\text{SeOCl}_3^-$  units linked to this framework by Se-Cl interactions. The Cl-N distances in the framework are about 3.0 Å (Table V), which is almost 0.3 Å shorter than the sum of van der Waals radii of chlorine and nitrogen (3.30 Å). Comparing the Cl-N distances (3.002, 3.014, 3.030, and 3.096 Å) in this compound with the N-H...Cl hydrogen-bond lengths usually found,<sup>7</sup> it is seen that strong hydrogen bonding exists between the chlorine and nitrogen atoms of this structure. As seen from Figure 4, each chlorine is hy-

(7) J. Lindgren and I. Olovsson, *Acta Crystallogr.*, **24**, 554 (1968).

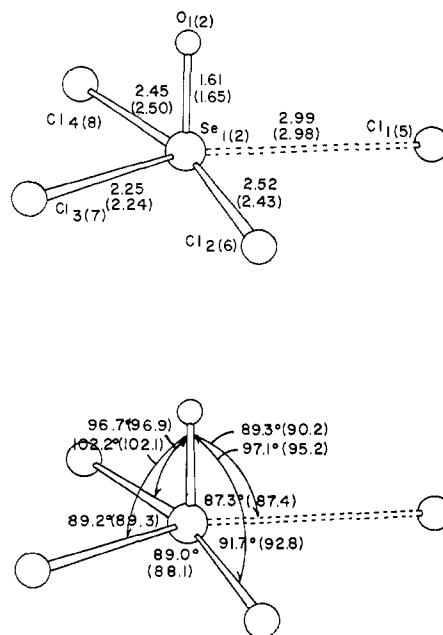


Figure 1.—Bond distances and bond angles in the  $\text{SeOCl}_4^{2-}$  units. The top part of the figure gives the distances in ångströms; the lower part, the angles. Atom numbering is shown in the top figure. The atom numbers in parentheses are for the second unit in the unique part of the cell, and the distances and angles in parentheses correspond to the atom numbers in parentheses. When only one distance or angle is given, it means that the parameter was the same for both of the units.

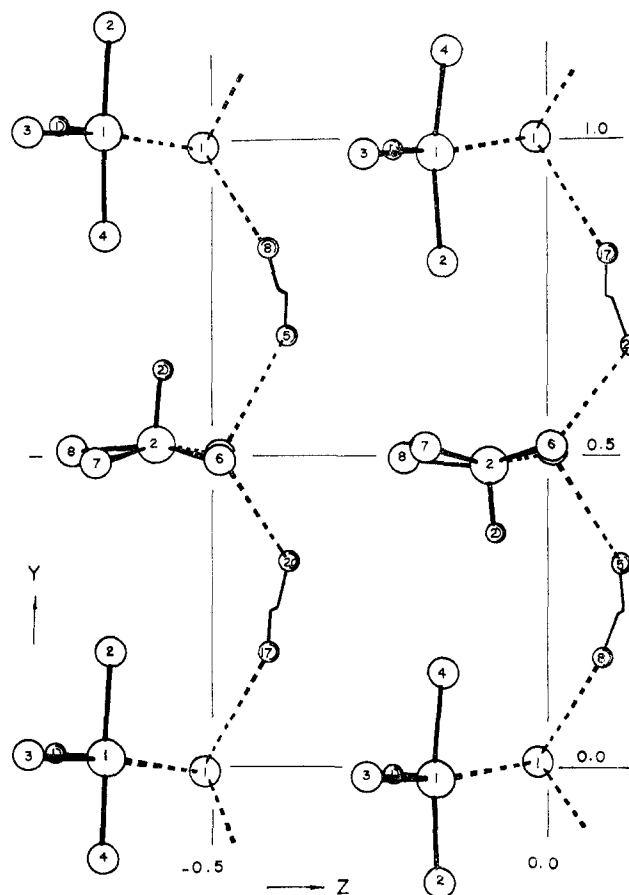
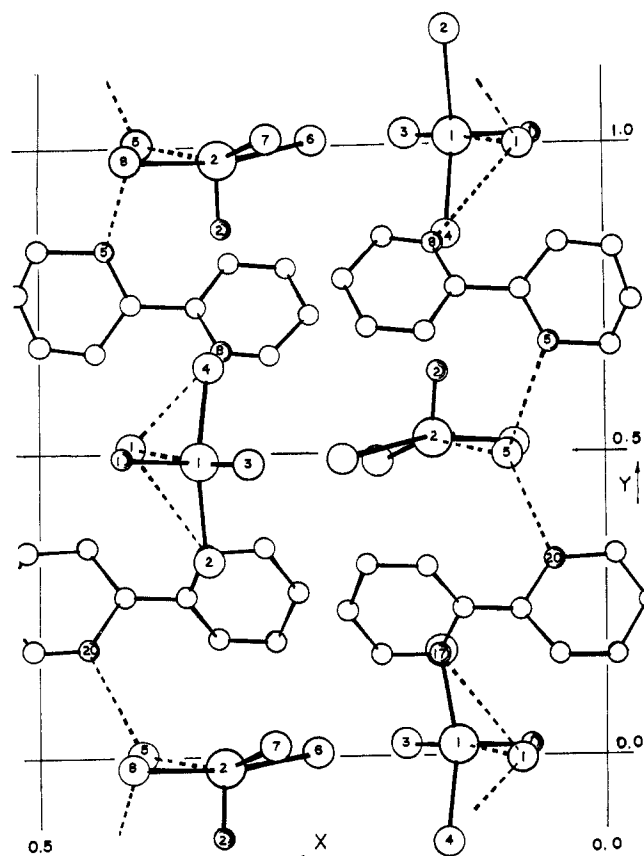


Figure 2.—View down the *a* axis. The carbon atoms are not shown.

Figure 3.—View down the *c* axis.

drogen bonded to two bipyridyl molecules and each bipyridyl molecule is bonded to two chlorines by two Cl-N hydrogen bonds. The organic units function as the bridges connecting the different  $\text{SeOCl}_4^{2-}$  units along the *b* axis in the crystal.

The formation of bipyridinium ions in the present compound may be confirmed by the increase of the C-N-C angle in the organic units from the  $116^\circ$  angle found in the structure of the neutral 2,2'-bipyridyl molecule, as expected because of the reduction of the repulsive force from the nitrogen's lone pair electrons on protonation.<sup>8</sup>

As shown in Figures 2-4, the two symmetry-unrelated  $\text{SeOCl}_3^-$  units are linked to the in-chain chlorine atoms with different orientations. The difference may be described roughly as that one  $\text{SeOCl}_3^-$  unit has been rotated  $90^\circ$  along the Se-Cl linkage with respect to the other  $\text{SeOCl}_3^-$  unit. The environments of these two  $\text{SeOCl}_3^-$  units are thus considerably different.

It is interesting to notice that the geometries of these two different  $\text{SeOCl}_4^{2-}$  units are similar; both have short Se-O bond distances, and both units contain Se-Cl bond distances of three drastically different lengths: one short, two medium, and one long.

The selenium-oxygen bond distances ( $1.61 \pm 0.01$  and  $1.65 \pm 0.01 \text{ \AA}$ ) are comparable to those  $1.61 \pm 0.03 \text{ \AA}$  Se-O bonds found in gas-phase  $\text{SeO}_2$ ,<sup>9</sup>  $\text{C}_2$ -

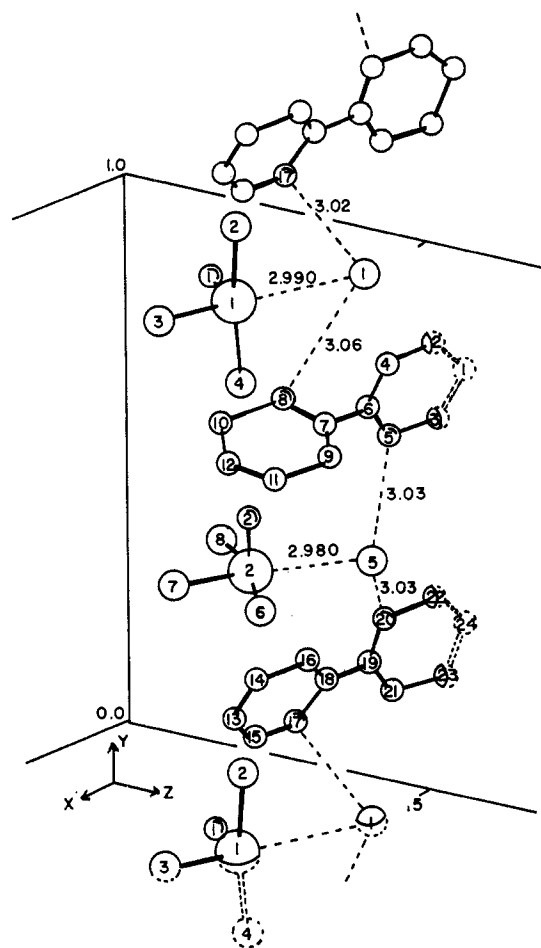


Figure 4.—Illustration of one of the chain units in the unit cell.

$\text{H}_4\text{O}_3\text{Se}_2$ ,<sup>10</sup> and  $\text{H}_2\text{SeO}_4$ .<sup>11</sup> These short Se-O bonds have been recognized as having a considerable amount of double-bond character. The difference in bond distance ( $0.04 \text{ \AA}$ ) between the two selenium-oxygen bonds, Se(1)-O(1) and Se(2)-O(2), is equal to four standard deviations. This difference may be caused by the different van der Waals forces that each oxygen atom experiences. The second oxygen, O(2), is located in a position that is almost on the axis of one pyridyl ring plane at about  $3.6\text{-\AA}$  distance from each of the ring atoms and thus has nine closest neighbors, while O(1) has only four closest neighbors.

According to the bond lengths, the four selenium-chlorine bonds in each  $\text{SeOCl}_4^{2-}$  unit can be grouped into three categories, those about 2.2, 2.5, and  $3.0 \text{ \AA}$ . The  $3.0\text{-\AA}$  type bonds,  $2.990 \pm 0.004$  and  $2.980 \pm 0.004 \text{ \AA}$ , are comparable to those long Se-Cl bonds found in  $\text{SbCl}_6 \cdot \text{SeOCl}_2$  ( $3.01 \pm 0.01$  and  $3.05 \pm 0.01 \text{ \AA}$ ),<sup>12</sup>  $\text{SnCl}_4 \cdot \text{SeOCl}_2$  ( $3.01 \pm 0.01 \text{ \AA}$ ),<sup>13</sup>  $(\text{CH}_3)_4\text{NCl} \cdot 5\text{SeOCl}_2$  ( $2.93\text{-}3.09 \pm 0.01 \text{ \AA}$ ),<sup>14</sup> and  $\text{C}_9\text{H}_9\text{NO} \cdot \text{SeOCl}_3^-$  ( $2.992$  and  $2.963 \pm 0.003 \text{ \AA}$ ).<sup>5</sup> These distances have been interpreted as some type of ion-dipole association.<sup>5,14</sup> From this point of view the present compound may be described by the formula  $\text{RH}_2^{2+}, \text{Cl}^-, \text{SeOCl}_3^-$ .

(10) E. S. Gould and B. Post, *ibid.*, **78**, 5161 (1956).(11) M. Bailey and A. F. Wells, *J. Chem. Soc.*, 968 (1951).(12) Y. Hermodsson, *Acta Chem. Scand.*, **21**, 1313 (1967).(13) Y. Hermodsson, *Acta Crystallogr.*, **13**, 656 (1960).(14) Y. Hermodsson, *Acta Chem. Scand.*, **21**, 1328 (1967).(8) R. J. Gillespie and R. S. Nyholm, *Quart. Rev. Chem. Soc.*, **11**, 339 (1957).(9) K. J. Palmer and N. Elliott, *J. Amer. Chem. Soc.*, **60**, 1309 (1938).

Within the  $\text{SeOCl}_4^{2-}$  units, the short Se-Cl bonds,  $2.246 \pm 0.004$  and  $2.244 \pm 0.004$  Å, are comparable to those found in  $(\text{C}_6\text{H}_5)_2\text{SeCl}_2$  ( $2.30 \pm 0.05$  Å),<sup>15</sup>  $(\text{CH}_3\text{-C}_6\text{H}_4)_2\text{SeCl}_2$  ( $2.38 \pm 0.02$  Å),<sup>16</sup>  $\text{C}_4\text{H}_8\text{Se}_2\text{Cl}_4$  ( $2.24 \pm 0.02$  Å),<sup>17</sup> and  $\text{C}_9\text{H}_8\text{NO}^+\text{SeCl}_3^-$  ( $2.234 \pm 0.004$  and  $2.271 \pm 0.004$  Å).<sup>5</sup> These Se-Cl bonds are usually considered as single covalent bonds. The other selenium-chlorine bonds, the 2.5-Å bonds ( $2.445$  and  $2.525$ ,  $2.502$  and  $2.431$  Å, all  $\pm 0.004$  Å) are rather unique. They are about the same as the average value of the bond lengths of the short and long Se-Cl bonds ( $2.39 \pm 0.02$  and  $2.57 \pm 0.02$  Å) found in  $\text{SeOCl}_2 \cdot 2\text{py}$ .<sup>18</sup>

The intermolecular environments of corresponding chlorine atoms for the two asymmetric units are very similar. Thus the packing features of Cl(1) and Cl(5) are dominated by the hydrogen bonding, and the remaining chlorine atoms have shortest intermolecular contacts with ring atoms of the cations. The one note-

(15) J. D. McCullough and G. Hamburger, *J. Amer. Chem. Soc.*, **64**, 508 (1942).

(16) J. D. McCullough and R. E. Marsh, *Acta Crystallogr.*, **3**, 41 (1950).

(17) A. Amendola, E. S. Gould, and B. Post, *Inorg. Chem.*, **3**, 1199 (1964).

(18) I. Lindquist and G. Nahringsbauer, *Acta Crystallogr.*, **12**, 638 (1959).

worthy exception is a 3.28-Å distance between Cl(3) and Cl(7).

The immediate environment of the selenium atoms can thus be considered a distorted square-pyramidal  $\text{SeOCl}_4^{2-}$  unit as shown in Figure 1 or a  $\text{SeOCl}_3^-$  unit which is approximately trigonal bipyramidal with axial chlorines at 2.5 Å, the oxygen, the chlorine at 2.2 Å, and a lone pair of electrons all being equatorial.

The occurrence of the three different Se-Cl lengths in the  $\text{SeOCl}_4^{2-}$  units is certainly the most significant feature of the structure. The explanation of the difference in bond character is very likely related to the manner in which the bonding orbitals on the selenium atom are being used, because there do not seem to be any structural features which would prevent the attainment of equal Se-Cl bond distances. Further aspects of the bonding in this and related selenium studies will be the subject of a future paper.

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## The Crystal and Molecular Structure of Sorbic Acid-Iron Tricarbonyl. Hybridization of the Butadiene Group in Metal Complexes

BY ROGER EISS

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The crystal and molecular structure of sorbic acid-iron tricarbonyl,  $(\text{C}_8\text{H}_8\text{O}_2)\text{Fe}(\text{CO})_3$ , has been determined from an X-ray diffraction study, with all hydrogen atoms being located and included in the least-squares refinement. The hybridization of all carbon atoms in the butadiene group is essentially  $sp^2$ , with a twist of about  $8.5^\circ$  about the terminal C-C bonds of the group in a direction to increase overlap between the  $\pi$ -electron orbitals of the butadiene group and the metal orbitals. The sorbic acid ligand consequently has four coplanar carbon atoms (those of the butadiene skeleton) and systematic deviations from the plane for the other ligand atoms, as predicted by Gutowsky, *et al.*, from  $^{13}\text{C}$  nmr. The presence of two crystallographically independent and essentially identical molecules in the unit cell gives strong evidence for the lack of distortion of bond lengths and bond angles within the monomeric unit by packing forces. The triclinic unit cell, space group  $P\bar{1}$ , contains two molecular dimers, each having a center of symmetry and held together by hydrogen-bonded carboxyl groups. Unit cell constants are  $a = 7.493$  (1),  $b = 22.885$  (5),  $c = 7.236$  (1) Å;  $\alpha = 81.70$  (1),  $\beta = 122.23$  (1),  $\gamma = 95.58$  (1)°. The observed density was  $1.60$  g/cm<sup>3</sup>, in agreement with  $1.61$  g/cm<sup>3</sup> calculated assuming four molecular units per unit cell. The structure was solved using 2086 statistically significant unique reflections collected by a counter method and refined to a final  $R$  factor of 0.047.

### Introduction

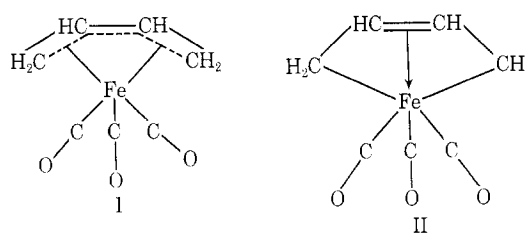
Since the synthesis of butadiene-iron tricarbonyl in 1930 by Rheilen, *et al.*,<sup>1</sup> and the subsequent treatment of bonding by Hallam and Pauson,<sup>2</sup> a great deal of attention has been directed to the elucidation of the nature of the very stable bond between the butadiene group and iron atom.<sup>3</sup>

(1) H. Rheilen, A. Gruhl, G. Hessling, and O. Pfrengle, *Justus Liebig's Ann. Chem.*, **482**, 161 (1930).

(2) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958).

(3) (a) M. Cais in "The Chemistry of Alkenes," S. Patai, Ed., Wiley-Interscience, New York, N. Y., 1964, p 335; (b) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 1 (1964); (c) M. R. Churchill and R. Mason, *ibid.*, **5**, 93 (1967).

The two leading models for the bonding in butadiene-iron tricarbonyl complexes are represented as I and II.



In I, the carbon atoms of the butadiene group have  $sp^2$  hybridization and the bonding to iron is *via* the de-