Structures of Fluorides. III. The Structure of the Mixed-Valence Fluoride Ge_5F_{12}

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Abstract: The mixed-valence halide Ge_5F_{12} is monoclinic with $a = 7.969$ (1) Å, $b = 7.590$ (1) Å, $c = 8.536$ (1) Å, $\beta = 93.03$ (3)°, and space group $P2_1/a$. The structure was determined from the three-dimensional Patterson function and difference syntheses and refined by least squares to a discrepancy index of 0.10 for 497 reflections collected with Mo Kα radiation. It was necessary to seal the very hygroscopic crystal in a quartz capillary and also cover the surface of the crystal with a thin film of Kel-F oil. The Ge^{IV} atom is in the center of a slightly distorted octahedron with Ge–F distances between 1.71 (2) and 1.80 (2) Å, and F–Ge–F angles between 87.5 (8) and 92.5 (8)°. The two crystallographically distinct Ge^{II} atoms have a very similar fluorine coordination, which is distorted square pyramidal with the Ge^{II} atoms at the apices of the pyramid and the Ge^{II} lone pair pointing away from the fluorine atoms forming the base of the pyramid. The overall structure is built up by means of fluorine bridging. The Ge^{II} coordination is in accord with the known stereochemistry of the group IVb metals.

The preparation of an unusual germanium fluoride has been reported recently.[1] The compound was thought to have the formula $(GeF_2)_x \cdot GeF_4$ with $x \sim 3$ and was prepared by allowing GeF_4 and Ge to react at 350°. The reaction could be controlled, producing either $(GeF_2)_x \cdot GeF_4$ or GeF_2, depending on whether the pressure of GeF_4 in the reactor was above or below 20 cm. The product from the Ge–GeF_4 reaction was mainly a powder, but in the final stages of reaction, when the GeF_4 pressure was dropping, some clear, needle-shaped crystals were formed. It was hoped that one of these crystals could be mounted and a single-crystal X-ray study undertaken, in an effort to elucidate the molecular structure of $(GeF_2)_x \cdot GeF_4$.

Experimental Section

The crystals, with an assumed empirical formula Ge_2F_5, were clear untwinned needles showing sharp extinction under polarized light. It was very difficult to prepare a specimen for single-crystal X-ray analysis. It was not possible to mount a crystal by the method of vacuum sublimation, as was the case in the X-ray study of GeF_2,[2] as the present compound was thermally unstable. Hydrolysis was rapid and bare crystals always hydrolyzed, even when sealed in quartz capillaries. A crystal was finally mounted by first dipping it in Kel-F oil and then sealing it in a capillary; the thin film of oil on the crystal prevented hydrolysis over the period of the experiment (4 weeks). The complete mounting operation was done in a drybox. After 1 week the oil diffused away from the crystal which became firmly attached to the capillary wall. Data collection was commenced at this stage, and no movement of the crystal in the tube was detected during the collection period.

The dimensions of the crystal, a nearly regular rectangular prism, were measured with a calibrated microscope and found to be 0.097 × 0.036 × 0.021 cm. The long axis was aligned along the capillary axis with the widest face adhering to the glass wall. The dimension 0.021 cm was not as accurate as the other two, because the oil film was thicker on the face away from the wall.

Weissenberg photographs of the (0–4) layers about the needle axis with Ni-filtered Cu K$\bar{\alpha}$ radiation ($\lambda = 1.5418$ Å) showed that this axis was the unique (b) axis of a monoclinic unit cell of dimensions 8.01 × 7.60 × 8.54 Å, with $\beta = 93°$. ($h0l$) reflections were absent for h odd. Further diffractometer measurements (see below) showed that ($0k0$) reflections were absent for k odd. The space group was thus uniquely established as No. 14: $P2_1/a$ (C_{2h}^5). Crystal face determinations from Weissenberg photographs and diffractometer data were in agreement. The faces were ±(010), ±($\bar{2}$01), and ±(102), with distances from the center of the crystal of 0.0485, 0.0105, and 0.0180 cm, respectively.

Intensity variations over the films indicated that absorption by the glass and oil prohibited an effective analysis with Cu K$\bar{\alpha}$ radiation. Complete three-dimensional X-ray data to $\sin \theta/\lambda = 0.48$ Å^{-1} ($2\theta = 40°$) were therefore collected with the harder radiation Mo K$\bar{\alpha}$ (λ 0.7107 Å). The instrument used was a four-circle automatic X-ray diffractometer fitted with a graphite monochromator and a proportional counter with pulse height analysis. Bragg intensities in the range $0 < \sin \theta/\lambda < 0.36$ Å^{-1} were measured at two equivalent positions in different octants of reciprocal space; reflections in the range $0.36 < \sin \theta/\lambda < 0.48$ Å^{-1} were measured once. A standard reflection (005) was measured every 20 reflections, to allow for variations in tube intensity and possible hydrolysis (the latter was not appreciable), and the intensities were normalized to the first standard. A least-squares analysis of the measured 2θ values of 136 reflections (on the diffractometer) with the program of Mueller, Heaton, and Miller[3] gave the unit cell dimensions: $a = 7.969$ (1) Å, $b = 7.570$ (1) Å, $c = 8.536$ (1) Å, $\beta = 93.03$ (3)°.

At this stage, the precise number of Ge and F atoms in the unit cell was unkhown, and it was not possible to calculate the linear absorption coefficient, μ, of the crystal for Mo K$\bar{\alpha}$ radiation. It was initially assumed that $\mu_{\text{Mo K}\bar{\alpha}} = 157$ cm^{-1} (the value for GeF_2 used by Trotter, Akhtar, and Bartlett[2]). The raw intensity data were corrected for absorption by means of the program DRACULA,[4] and the X-ray transmission factors varied from 0.012 to 0.065. Corrections were not made for absorption by the oil film and silica capillary. The intensities were reduced to structure factors F_{hkl} and equivalent reflections were amalgamated by means of the same program. The standard deviations of the observed reflections included a statistical term and a proportional term to allow for systematic errors in the data. Intensities less than the observable limit $I_{\min}$ were labeled unobserved reflections, and these were all given intensities of $I_{\min}/3$ and standard deviations $I_{\min}/3$, essentially the procedure recommended by Hamilton.[5] The data reduction was repeated later when the true value of μ, 151.2 cm^{-1}, was revealed by the analysis of the structure. The final least-squares refinements were carried out with the latter set of F_{hkl} values. In all, 497 independent Bragg intensities were measured, of which 100 were unobservably small. The increase in the polarization factor due to the monochromator was zero at $2\theta = 0°$ and 0.5% at $2\theta = 45°$.[6] The extra polarization was therefore neglected. The crystal data are given in Table I.

Structure Analysis. The germanium atoms were located in the

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(1) G. P. Adams, J. L. Margrave, and P. W. Wilson, *J. Inorg. Nucl. Chem.*, **33**, 1301 (1971).

(2) J. Trotter, M. Akhtar, and N. Bartlett, *J. Chem. Soc.*, 30 (1966).

(3) M. H. Mueller, L. Heaton, and K. T. Miller, *Acta Crystallogr.*, **13**, 828 (1960).

(4) M. M. Elcombe, G. W. Cox, A. W. Pryor, and F. H. Moore, Report AAEC/TM 578, 1971.

(5) W. C. Hamilton, *Acta Crystallogr.*, 8, 185 (1955).

(6) L. V. Azaroff, *ibid.*, **8**, 701 (1955).

Table I. Crystal Data for Ge_5F_{12}

λ(Cu K$\bar{\alpha}$) 1.5418 Å, λ(Mo K$\bar{\alpha}$) 0.7107 Å
Ge_5F_{12} $M = 590.95$
Monoclinic, $a = 7.969$ (1), $b = 7.570$ (1), $c = 8.536$ (1) Å,
$\beta = 93.03$ (3)°, space group = $P2_1/a$ (C_{2h}^5)
$U = 514.2$ Å^3, $D_x = 3.816$ g cm^{-3}, $Z = 2$
μ(Mo K$\bar{\alpha}$) = 151.2 cm^{-1}

Table II. Positional and Thermal Vibration Parameters in Ge_5F_{12}[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ge(1)	3210 (4)	6278 (4)	1095 (3)	123 (7)	93 (7)	87 (5)	15 (5)	−37 (4)	−13 (4)
Ge(2)	$^1/_2$	$^1/_2$	$^1/_2$	120 (9)	54 (8)	50 (6)	−20 (7)	−54 (6)	7 (6)
Ge(3)	3763 (4)	0561 (4)	2976 (3)	196 (9)	86 (7)	63 (5)	−22 (6)	−84 (5)	12 (4)
F(1)	340 (2)	203 (2)	133 (2)	29 (4)	4 (3)	9 (2)	−5 (3)	−4 (3)	3 (2)
F(2)	268 (2)	872 (2)	159 (2)	12 (3)	14 (4)	21 (3)	1 (3)	−10 (3)	6 (3)
F(3)	110 (2)	86 (2)	347 (2)		B = 2.8 (3) Å^2				
F(4)	401 (2)	650 (2)	360 (2)	29 (5)	21 (4)	6 (2)	17 (4)	−6 (3)	−5 (3)
F(5)	342 (2)	350 (2)	465 (2)	20 (4)	15 (4)	17 (3)	−13 (3)	1 (3)	−3 (3)
F(6)	111 (2)	570 (2)	163 (2)	27 (5)	24 (4)	11 (3)	−2 (4)	8 (3)	7 (3)

[a] Germanium parameters $\times 10^4$ and fluorine parameters $\times 10^3$.

unit cell by an analysis of the three-dimensional Patterson synthesis, in conjunction with a consideration of the intensities of the strongest reflections. The Ge atoms were found to lie in planes halfway between the $\{\bar{2}01\}$ planes, in an approximately hexagonal arrangement. Three crystallographically distinct Ge atoms were found, two in the fourfold positions 4(e) and one in the twofold position 2(b). Hence there were ten Ge atoms per cell. The Ge coordinates deduced were

Atom	Position	Coordinates
Ge(1)	4(e)	(0.289, 0.625, 0.087)
Ge(2)	2(b)	($^1/_2$, $^1/_2$, $^1/_2$)
Ge(3)	4(e)	(0.376, 0.046, 0.301)

The Patterson synthesis was not analyzed further since it was considered that the structure would be found more efficiently by the method of successive difference syntheses.

Structure factors were calculated with the program LINUS[7] for the Ge atoms alone, using the scattering curves for neutral Ge[8] and the anomalous dispersion terms for Ge of $\Delta f' = -0.2$ e and $\Delta f'' = 1.9$ e.[9] The Ge locations and individual isotropic temperature factors B were refined to an unweighted discrepancy index $R_U = \Sigma(|F_o| - S|F_c|)/\Sigma|F_o|$ of 0.38, where S is a scale factor. A difference synthesis with these structure factors revealed five probable fluorine atom locations, and inclusion of these five fluorine atoms, with neutral atom scattering curves[8] and isotropic least-squares refinement, gave $R_U = 0.21$. A further difference synthesis indicated a sixth fluorine location and confirmed the other five fluorine positions.

Least-squares refinement of the model, now $Ge_{10}F_{24}$, with first isotropic and finally anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + 2\beta_{12}hk + \ldots)]$ led to $R_U = 0.11$ and a weighted R factor, $R_W = (\Sigma w(F_o - S|F_c|)^2)^{1/2}/(\Sigma wF_o^2)^{1/2}$ of 0.10. The unobserved reflections were included in the calculation of R_U and R_W. The least-squares weighting factors were $w_{hkl} = [\sigma^2(F_{hkl})]^{-1}$. Initial cycles including an isotropic extinction coefficient g' showed that extinction was negligible in the crystal; hence g' was set at zero and not refined in the later cycles. The anisotropic temperature factors of one fluorine atom, F(3), were nonpositive definite, and this atom was therefore refined isotropically. The final criterion of fit, $\chi = (\Sigma w(F_o - S|F_c|)^2/(\mathrm{NO} - \mathrm{NV}))^{1/2}$, where NO is the number of observations and NV the number of variables, was 1.62.

In the final difference synthesis, the residual electron densities at the atomic sites were all less than $^1/_{12}$th of the corresponding peaks in the observed synthesis, and for seven of the nine atoms the residual was less than $^1/_{50}$th of the corresponding observed peak. There were no other peaks in the map which could possibly be fluorine atoms, and this difference map was thus a final confirmation of the structure.

The above crystal structure analysis thus established a unit cell content of $Ge_{10}F_{24}$; henceforth the crystal is referred to as Ge_5F_{12}. The formula Ge_5F_{12} is different from the formula Ge_2F_5 expected when the work was commenced.[1] To investigate this point further an X-ray powder diffraction pattern of a portion of the bulk sample was obtained. This showed the expected Ge_5F_{12} lines together with some extra lines which suggested the preparation was a mixture of two or more phases. Since the earlier work[1] had shown the bulk sample corresponded to the formula Ge_2F_5 or $(GeF_2)_3 \cdot GeF_4$, probably a mixture of the two members of the series $(GeF_2)_x \cdot GeF_4$, had been prepared, with $x = 3$ (Ge_2F_5) and $x = 4$ (Ge_5F_{12}). As noted earlier, the needle-like crystals formed mainly when the GeF_4 pressure was low. It was therefore reasonable that the ratio of GeF_2 to GeF_4 should be higher in the crystals than in the bulk sample.

It was apparent from the formula Ge_5F_{12} that the crystal was a mixed-valence compound. As the two Ge(2) atoms were surrounded by a nearly regular octahedron of fluorine atoms, while Ge(1) and Ge(3) both had fluorine coordination very similar to the coordination in GeF_2,[2] atom Ge(2) was a Ge^{IV} atom and atoms Ge(1) and Ge(3) were Ge^{II} atoms. The formula Ge_5F_{12} thus corresponded to $[(Ge^{II}F_2)_4 \cdot Ge^{IV}F_4]$.

The final positional and thermal parameters in Ge_5F_{12} are given in Table II. The observed and calculated structure factors are included in the microfilm edition of this journal.[10] The interatomic distances and angles are given in Table III.

Discussion

The Crystal Structure of Ge_5F_{12}. Ge_5F_{12} is a mixed-valence binary fluoride containing Ge^{II} and Ge^{IV} atoms in the ratio of 4:1, and the formula can be written as $(Ge^{II}F_2)_4 \cdot Ge^{IV}F_4$. The overall crystal structure is illustrated in Figure 1. The Ge^{IV} atoms, labeled Ge(2) in Figure 1, are surrounded by a slightly distorted octahedron of fluorine atoms, with Ge(2)–F distances between 1.71 (2) and 1.80 (2) Å and F–Ge(2)–F angles between 87.5 (8) and 92.5 (8)°.

The octahedra are linked, by fluorine bridging involving F(4) and F(3), to the two crystallographically distinct Ge^{II} atoms, labeled Ge(1) and Ge(3) in Figure 1. It can be seen from Figure 1 that the atoms are clustered into layers which are parallel to the $\{\bar{2}01\}$ planes (one such layer is defined by the series of atoms labeled F(1), Ge(1), F(2), Ge(3), F(4), Ge(2), . . . in Figure 1). The fluorine bridges are of two kinds: (a) intralayer

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(7) P. Coppens and W. C. Hamilton, *Acta Crystallogr., Sect. A*, **26**, 71 (1970).

(8) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1962, p 201.

(9) C. H. Dauben and D. H. Templeton, *Acta Crystallogr.*, 8, 841 (1955).

(10) Observed and calculated structure factor tables will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-1834. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

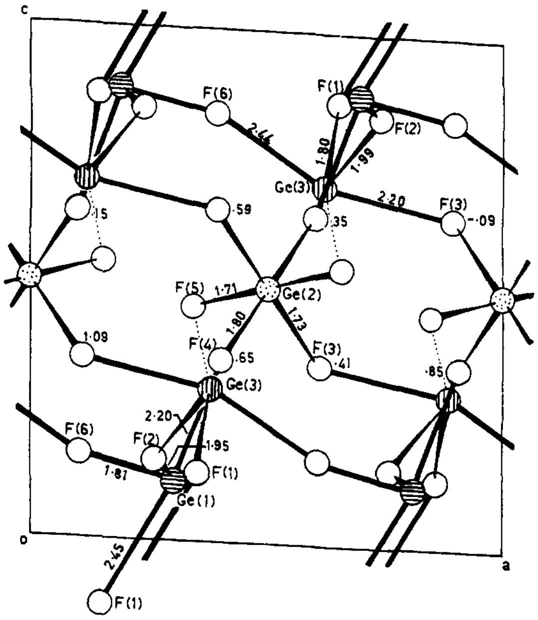

Figure 1. The crystal structure of Ge_5F_{12} as viewed down the *b* axis. The $Ge^{IV}F_6$ octahedron is in the center of the diagram. Atoms Ge(1) and Ge(3) are Ge^{II} atoms. The height convention of the bonds is given by the *y* coordinates of attachment to the octahedral fluorines F(3) and F(4). The dotted line is the weaker Ge(3)–F(5) interaction of 2.67 (2) Å.

Table III. Interatomic Distances and Angles in Ge_5F_{12}

Bonds, Å		Angle, deg	
	(a)	About Ge(1)	
Ge(1)–F(1)	2.45 (2)	F(2)–Ge(1)–F(1)	81.6 (7)
	3.22 (2)	F(2)–Ge(1)–F(4)	76.7 (8)
Ge(1)–F(2)	1.95 (2)	F(1)–Ge(1)–F(6)	79.8 (8)
	3.06 (2)	F(2)–Ge(1)–F(6)	87.7 (10)
Ge(1)–F(4)	2.20 (2)	F(4)–Ge(1)–F(6)	89.7 (9)
Ge(1)–F(5)	3.69 (2)	F(4)–Ge(1)–F(1)	156.3 (7)
Ge(1)–F(6)	1.81 (2)		
	3.27 (2)		
Ge(1)–Ge(1)	3.99 (1)		
	(b)	About Ge(2)	
Ge(2)–F(3)	1.73 (2)	F(3)–Ge(2)–F(4)	92.5 (8)
Ge(2)–F(4)	1.80 (2)		87.5 (8)
Ge(2)–F(5)	1.71 (2)	F(3)–Ge(2)–F(5)	91.0 (9)
			89.0 (9)
		F(4)–Ge(2)–F(5)	90.6 (10)
			89.4 (10)
	(c)	About Ge(3)	
Ge(3)–F(1)	1.80 (2)	F(1)–Ge(3)–F(3)	88.2 (9)
Ge(3)–F(2)	1.99 (2)	F(1)–Ge(3)–F(6)	88.4 (8)
Ge(3)–F(3)	2.20 (2)	F(2)–Ge(3)–F(1)	85.7 (7)
Ge(3)–F(3)	3.30 (2)	F(2)–Ge(3)–F(3)	78.0 (7)
Ge(3)–F(4)	3.12 (2)	F(2)–Ge(3)–F(6)	76.6 (7)
Ge(3)–F(5)	2.67 (2)	F(3)–Ge(3)–F(6)	154.6 (7)
Ge(3)–F(6)	2.44 (2)		
Ge(3)–Ge(3)	3.98 (1)		

through the system

$$\begin{array}{l}\mathrm{Ge(2)} \overset{1.80}{\text{——}} \mathrm{F(4)} \overset{2.20}{\text{——}} \mathrm{Ge(1)} \overset{1.95}{\text{——}} \mathrm{F(2)} \overset{1.99}{\text{——}} \mathrm{Ge(3)} \\ \qquad\qquad\qquad\quad \backslash \, 2.45 \\ \qquad\qquad\qquad\quad \mathrm{F(1)} \\ \qquad\qquad\qquad\qquad \backslash \, 1.80 \\ \qquad\qquad\qquad\qquad \mathrm{Ge(3)}\end{array}$$

and (b) interlayer through the system

$$\mathrm{Ge(2)} \overset{1.73}{\text{——}} \mathrm{F(3)} \overset{2.20}{\text{——}} \mathrm{Ge(3)} \overset{2.44}{\text{——}} \mathrm{F(6)} \overset{1.81}{\text{——}} \mathrm{Ge(1)}$$

The two systems are connected by the common Ge^{II} atoms, and together they form a three-dimensional network. The overall bridging scheme is complex, but is fully specified by Figure 1.

In GeF_2,[2] there are two kinds of infinite bridge systems: (i) type (1) the "strong" system

$$\text{——}\ \mathrm{Ge} \overset{1.91\ \text{Å}}{\text{——}} \mathrm{F(2)} \overset{2.09\ \text{Å}}{\text{——}} \mathrm{Ge} \text{ —— } \mathrm{F(2)} \text{ —— } \mathrm{Ge} \text{ ——}$$

in the *b* direction of the orthorhombic cell and (ii) type (2) the "weak" system

$$\text{——}\ \mathrm{Ge} \overset{2.57\ \text{Å}}{\text{——}} \mathrm{F(1)} \overset{1.79\ \text{Å}}{\text{——}} \mathrm{Ge} \text{ —— } \mathrm{F(1)} \text{ —— } \mathrm{Ge}$$

The interlayer bridges in Ge_5F_{12} are of the weak type 2. The only strong bridge in Ge_5F_{12} is the nonextensive grouping

$$\begin{array}{l}\text{——}\ \mathrm{Ge(1)} \overset{1.95}{\text{——}} \mathrm{F(2)} \overset{1.99}{\text{——}} \mathrm{Ge(3)} \\ \ \ / \end{array}$$

The {001} planes in Ge_5F_{12} are planes across which only weak Ge(1)–F(1) bonds of length 2.44 Å occur (Figure 1); these would be likely cleavage planes.

There must be considerable covalent character in the Ge–F bonds in Ge_5F_{12}. Using the data of Pauling,[11a] the sum of the covalent radii of Ge and F corrected for the electronegativity difference is 1.73 Å, close to the shortest Ge–F distances observed. On the basis of the electronegativity difference a Ge–F single bond should have 50% ionic character.[11b]

Stereochemistry of the Ge^{II} Atoms in Ge_5F_{12}. The environments of the two kinds of Ge^{II} atom, labeled Ge(1) and Ge(3), are illustrated in Figures 2 and 3. The Ge(1) and Ge(3) atoms have a similar fluorine coordination which may be described as a distorted square pyramid with the Ge^{II} atom at the apex. The Ge–F distances to the four basal fluorines are 1.80, 2.00, 2.20, and 2.45 Å for both Ge(1) and Ge(3). The F–Ge–F apical angles also show correspondence and are about 90°. These $Ge^{II}F_4$ units also have quite similar bridge-bonding schemes to three nearby Ge^{II} atoms of the other kind and one nearby Ge^{IV} atom. There is a fifth fluorine, F(5), which is distant 2.67 Å from Ge(3). All other Ge–F distances are 3.06 Å or greater.

The only other structure involving Ge^{II} which is directly comparable is GeF_2.[2] The Ge^{II} atom in GeF_2 is surrounded by four fluorine atoms in nearly the same configuration as in Ge_5F_{12}. The close correspondence between the bond lengths and angles in the $Ge^{II}F_4$ groups in Ge_5F_{12} and GeF_2 is shown in Table IV. Ge^{II} possesses a lone pair of valence electrons, and it is well known[12] that lone pairs are sterically active and occupy space and coordination positions for atoms with valence configuration ns^2. There is a large region of empty space behind the Ge^{II} atoms in Ge_5F_{12} and on the line away from the pyramid no fluorine atoms approach. The main interaction in this direction is the approach of a Ge^{II} atom of similar type (Ge(1)–Ge(1) = 4.00 Å, Ge(3)–Ge(3) = 3.98 Å). It is assumed, therefore, that the lone pair occupies a fifth coordination position in the Ge^{II} polyhedron, above the apex of the distorted

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(11) (a) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960; (b) N. B. Hannay and C. P. Smythe, *J. Amer. Chem. Soc.*, 68, 171 (1946).

(12) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, Chapter XXIV.

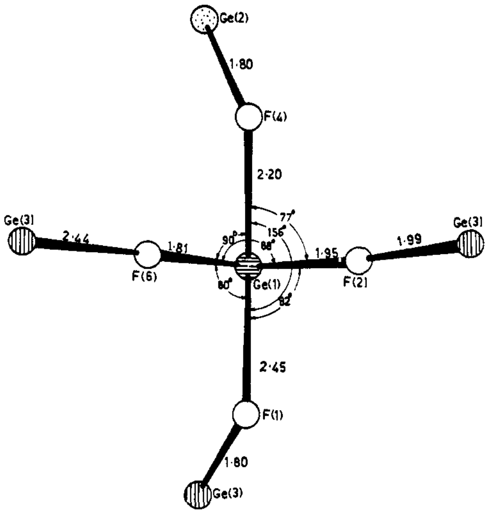

Figure 2. The environment of the Ge^{II} atom Ge(1).

Table IV. Comparison of the Geometry of the $Ge^{II}F_4$ Coordination Groups in Ge_5F_{12} and GeF_2[a]

Bond length (Å) or angle (deg)	Ge^{II} atom: Ge(1) in Ge_5F_{12}	Ge(3) in Ge_5F_{12}	Ge in GeF_2
Ge-a	1.81 (2)	1.80 (2)	1.79 (2)
Ge-b	1.95 (2)	1.99 (2)	1.91 (2)
Ge-c	2.20 (2)	2.20 (2)	2.09 (2)
Ge-d	2.45 (2)	2.44 (2)	2.57 (2)
a-Ge-b	87.7 (10)	85.7 (7)	91.6 (8)
c-Ge-d	156.3 (7)	154.6 (7)	162.8 (8)
a-Ge-c	89.7 (9)	88.2 (9)	85.6 (8)
b-Ge-c	76.7 (8)	78.0 (7)	85.0 (8)
a-Ge-d	79.8 (8)	88.4 (8)	82.4 (8)
b-Ge-d	81.6 (7)	76.6 (7)	83.1 (8)

[a] a, b, c, and d denote the fluorine atoms in order of their decreasing Ge-F bond strength (*i.e.*, increasing Ge-F distance).

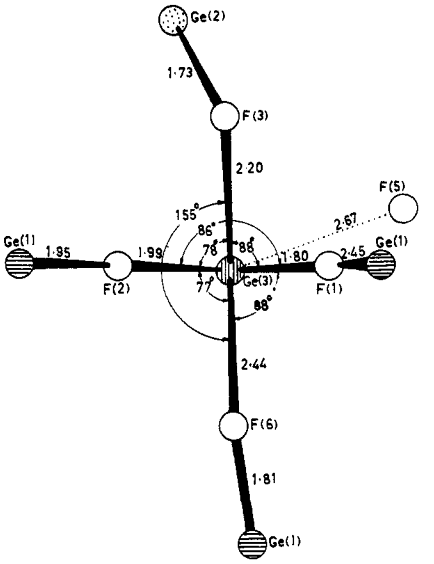

Figure 3. The environment of the Ge^{II} atom Ge(3).

Table V. Rms Components of Thermal Displacement (in Å) along the Principal Axes R1, R2, and R3 of the Vibration Ellipsoids and the Orientation of the Ellipsoids in the Unit Cell

Atom	Rms displacement along: R1	R2	R3	Angle (deg) of R3 with: a	b	a × b
Ge(1)	0.146 (8)	0.160 (9)	0.231 (7)	39 (4)	76 (4)	125 (3)
Ge(2)	0.083 (17)	0.122 (12)	0.230 (9)	31 (3)	100 (4)	119 (3)
Ge(3)	0.087 (12)	0.154 (8)	0.288 (7)	28 (2)	98 (2)	117 (2)
F(1)	0.08 (6)	0.17 (3)	0.32 (3)	18 (9)	101 (7)	103 (9)
F(2)	0.11 (5)	0.21 (3)	0.32 (3)	120 (9)	77 (11)	33 (7)
F(4)	0.13 (4)	0.15 (4)	0.38 (3)	39 (6)	54 (6)	103 (6)
F(5)	0.11 (5)	0.25 (3)	0.31 (3)	39 (11)	127 (7)	80 (23)
F(6)	0.13 (4)	0.28 (3)	0.31 (3)	31 (40)	80 (53)	61 (21)

tetragonal pyramid. A similar description can be applied to the Ge^{II} atom in GeF_2.[2]

The chemistry of Ge^{II} is very similar to the chemistry of Sn^{II} and Pb^{II}, also group IVb elements. Sn^{II} and Pb^{II} also have an outer lone pair and a complex stereochemistry. There has been little attempt to clarify the complex behavior shown until the recent review of the chemistry of Sn^{II} by Donaldson,[13] who showed that the structures of Sn^{II} compounds could be described either in terms of hybridization or crystal field theory. Depending on the number of ligands, sp, sp^2, sp^3, sp^3d, or sp^3d^2 hybridization was suggested, with the lone pair occupying a coordination position. Alternatively, the arrangement was described as an unsymmetrical distortion of an octahedron giving extra crystal field stability by s-p mixing.[14] The trigonal-pyramidal arrangements in SnS, SnSe, $SnCl_2$, SnF_2, $SnSO_4$, and $NaSn_2F_5$ and square-pyramidal arrangements in blue-black SnO were discussed by Donaldson in terms of sp^3 and sp^3d hybridization. Few Ge^{II} compounds were listed but GeS and GeSe are isostructural with the Sn^{II} analogs while GeO is pyramidal. CF_2 and SiF_2 are not solid at room temperature and form C-C and Si-Si bonds readily.[15]

It is apparent from the above that the stereochemistry of the Ge^{II} atoms in Ge_5F_{12} is analogous to that of the other group IVb metals.

Thermal Motion. The rms components of thermal displacement along the principal axes of the vibration ellipsoids, for all atoms except F(3), are shown in Table V, together with their orientation with respect to Cartesian axes, defined with respect to the unit cell edges. In Table VI, the angles between the principal tensor axes corresponding to the largest mean square vibration and the normal to the ($\bar{2}01$) plane are given. As these angles are generally small, the vibrations in the crystal are largely in a direction normal to the ($\bar{2}01$) plane.

(13) J. D. Donaldson, *Progr. Inorg. Chem.*, 8, 287 (1967).

(14) L. E. Orgel, *J. Chem. Soc.*, 3815 (1959).

(15) G. P. Adams, J. L. Margrave, R. P. Steiger, and P. W. Wilson, *J. Chem. Thermodyn.*, 3, 297 (1971).

Table VI. Angles (ϕ) between the Principal Tensor Axes R3[a] and the Normal to the ($\bar{2}01$) Plane

Atom	ϕ, deg	Atom	ϕ, deg
Ge(1)	19 (1)	F(2)	144 (4)
Ge(2)	11 (1)	F(4)	37 (3)
Ge(3)	7 (1)	F(5)	51 (9)
F(1)	17 (1)	F(6)	55 (17)

[a] Corresponding to the largest mean square vibration.

Ge_5F_{12} as a Mixed-Valence Compound. The subject of mixed-valence chemistry has been reviewed by Robin and Day,[16] who list few mixed-valence binary halides. The structure of Cr_2F_5 ($CrF_2 \cdot CrF_3$) is known,[17] the environment around Cr^{II} being distorted octahedral and around Cr^{III} regular octahedral. No binary mixed-valence halides are given for the group IVb metals. Pb_3O_4[16] contains an octahedrally coordinated Pb^{IV} atom and a Pb^{II} atom at the apex of a trigonal pyramid; the bonding in Pb_3O_4 has been discussed in covalent terms by Dickens.[18]

Ge_5F_{12} is colorless, showing no additional absorption in the visible region; this is normal when the two types of metal atom are in sites of different symmetry and ligand field strength.[16]

It is interesting to speculate on the possibility of preparing other members of the $(GeF_2)_x \cdot GeF_4$ series. The compounds with $x = 3$ and $x = 4$ were prepared when the pressure of GeF_4 was less than 1 atm. It may be possible to prepare the compounds with $x = 1$ or $x = 2$ by using pressures of GeF_4 exceeding 1 atm, in a slightly modified reactor.[1] It may also be possible to prepare compounds the type $(GeF_2)_x \cdot MF_4$ where M is Si, Sn, or Pb. Obviously, M could not be C since lack of available d subshells precludes occupation of an octahedral crystal site. It may also prove possible to prepare compounds of the type $(M'F_2)_x \cdot M''F_4$ where M′ is not Ge; however, for reasons listed elsewhere,[1] this is unlikely.

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[16] M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, 10, 248 (1967).

[17] H. Steinfink and J. H. Burns, *Acta Crystallogr.*, 17, 823 (1964).

[18] B. Dickens, *J. Inorg. Nucl. Chem.*, 27, 1509 (1965).

Molybdenocene and Tungstenocene. New "Carbene" Intermediates in Reactions with Hydrogen, Nitrogen, Carbon Monoxide, Olefins, and Acetylenes

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Abstract: The generation and reactions of $(C_5H_5)_2Mo$, $[C_5(CH_3)_5]_2Mo$, and $(C_5H_5)_2W$ are described. Carbon monoxide and N_2 complexes of the above metallocenes as well as dimethyl derivatives of molybdenocene and tungstenocene have been characterized. The role of 14- and 16-electron species in nitrogen reduction reactions is discussed. $(C_5H_5)_2Mo(C_2H_4)$, $(C_5H_5)_2Mo(CH_3CCCH_3)$, $(C_5H_5)_2Mo(CH_2CHCHCH_2)$, $(C_5H_5)_2Mo(CF_3CCCF_3)$, and some similar complexes of tungstenocene have been prepared. Metallocyclopropane and metallocyclopropene structures are proposed for the olefin and acetylene complexes, respectively. Hydrolysis of some of these complexes resulted in reduction of the complexed hydrocarbon. Similarities to nitrogenase are noted. A systematic comparison of the reaction chemistry of $(C_5H_5)_2Mo$ and $(C_5H_5)_2W$ to carbenes was undertaken and revealed an unprecedented parallelism of reactivities and product stabilities.

Interest in the preparation of molybdenocene and tungstenocene resulted from a search for isolatable compounds that would coordinate and lead to reduction of molecular nitrogen. Previous studies with titanocene[1] and other titanium species[2] suggested that such a compound would be coordinatively unsaturated and electron deficient. Molybdenocene and tungstenocene satisfied these conditions. Interest in molybdenocene is especially high since molybdenum is one of the two metals known to be present in the nitrogenase enzyme.[3]

With the exception of group VIII, metallocenes of the second- and third-row transition metals are unknown.[4] Thus, while chromocene is stable and readily prepared,[5] neither molybdenocene nor tungstenocene has ever been synthesized. A very inert bis(pentaphenylcyclopentadienyl)molybdenum(II) has been reported,[6] and a few symmetrically bound olefin and acetylene complexes have been prepared by insertion of the hydrocarbon into $(C_5H_5)_2MoH_2$.[7] Tungstenocene has been postulated as an intermediate in the formation of aryl hydrides and some olefin complexes of that metallocene.[8,9] Recent investigations in these laboratories have led to the generation of molybdenocene as a highly reactive species and

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[1] J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 94, 1219 (1972).

[2] E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Akermark, *ibid.*, 91, 1551 (1969), and references therein.

[3] J. R. Postgate, "The Chemistry and Biochemistry of Nitrogen Fixation," Plenum Press, London, 1971, p 181.

[4] R. B. King, "Transition-Metal Organometallic Chemistry," Academic Press, New York, N. Y., 1969, p 18.

[5] G. Wilkinson, F. A. Cotton, and J. M. Birmingham, *J. Inorg. Nucl. Chem.*, 2, 95 (1956).

[6] W. Hubel and R. Merenyi, *J. Organometal. Chem.*, 2, 213 (1964).

[7] A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, 94, 1886 (1972).

[8] B. R. Francis, M. L. H. Green, and G. G. Roberts, *Chem. Commun.*, 1290 (1971).

[9] M. L. H. Green and P. R. Knowles, *J. Chem. Soc. A*, 1508 (1971).