The Crystal and Molecular Structure of the Iodine Monochloride Complex of 1-Oxa-4-selenacyclohexane, $C_4H_8OSe \cdot ICl$

BY CAROLYN KNOBLER AND J. D. McCULLOUGH

The 1:1 complex of 1-oxa-4-selenacyclohexane with ICl
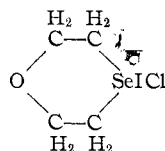
forms yellow-orange orthorhombic crystals with $a = 19.65$ Å ($\sigma = 0.01$ Å), $b = 9.256$ Å ($\sigma = 0.005$ Å), and $c = 8.962$ Å ($\sigma = 0.010$ Å). The space group symmetry is Pbca, there are eight molecules in the unit cell, and the measured and calculated densities are 2.6 and 2.554 g cm^{-3}, respectively. Diffraction data for 925 unique, observed reflections were collected by use of Cu Kα radiation and the multiple-film Weissenberg method. Intensities were estimated visually and were not corrected for absorption. A satisfactory trial structure was found by use of three-dimensional Patterson functions and was refined isotropically by use of three-dimensional, full-matrix, least-squares procedures to a final, conventional R value of 0.121. The molecule of the complex approximates the symmetry m with the six-membered ring in the chair configuration and with ICl bonded to Se in the axial position. The Se–I bond length of 2.630 Å ($\sigma = 0.005$ Å) is the shortest of its kind reported so far and the I–Cl distance of 2.73 Å ($\sigma = 0.01$ Å) is unusually long. The Se–I–Cl bond angle is 175.8° ($\sigma = 0.5°$). The average Se–C bond length is 1.98 Å ($\sigma = 0.03$ Å) and the bond angles around Se are: C–Se–C, 96° ($\sigma = 2°$); I–Se–C(1), 104° ($\sigma = 1°$); and I–Se–C(4),99° ($\sigma = 1°$). Selenium forms only the three bonds indicated above and is not involved in secondary bonding.

Introduction

In an earlier study, several addition compounds of 1-thia-4-selenacyclohexane (1,4-thiaselenane) with halogens and the interhalogens ICl and IBr were prepared and described.[1] The crystal and molecular structure of one of these, the 4,4-dibromide, has been reported,[2] and the structure of another, $C_4H_8SSe \cdot ICl$, was undertaken. However, the decomposition of the latter compound in the X-ray beam became a serious problem and the study was discontinued. In its place, a study of the isomorphous ICl complex of 1-oxa-4-selenacyclohexane (1,4-oxaselenane) was undertaken. Although this compound also decomposed in the X-ray beam, it was possible, by use of several crystals, to get sufficient data for a structure determination.

Experimental Section

1-Oxa-4-selenacyclohexane was synthesized and purified by the method reported earlier[3] and the ICl complex (I) was pre-

I
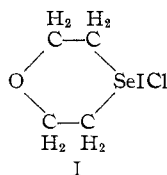
pared by mixing the components in a 1:1 molar ratio in ethylene chloride. Crystals for use in the X-ray study were grown by slow evaporation of a solution of the complex in the same solvent. The crystals are yellow-orange to light brown and the principal growth habit is that of plates on (100) bounded by (010) and (001).

There is a pronounced cleavage parallel to (100), and nearly all specimens display penetration twinning with a common orientation of the a axis. These properties greatly complicated the selection of specimens suitable for intensity measurements; also, because of volatility and reactivity toward moisture, all specimens used were sealed in thin-walled glass capillaries.

Precession and Weissenberg photographs indicated orthorhombic symmetry. The systematic absences of $0kl$ with k odd, $h0l$ with l odd, and $hk0$ with h odd are those of the space group Pbca. The lattice parameters obtained at 24 ± 1° with fresh crystals are $a = 19.65 \pm 0.01$ Å, $b = 9.256 \pm 0.005$ Å, and $c = 8.962 \pm 0.010$ Å based on Cu Kα = 1.5418 Å. The indicated uncertainties are the esd values of the observed quantities. The density observed by flotation is 2.6 g cm^{-3} while that calculated for eight molecules in the unit cell is 2.554 g cm^{-3}.

On exposure to X-rays the lattice parameters were observed to increase. Thus, after 600-hr exposure, the values $a = 19.71$ Å and $c = 8.996$ Å were obtained on one specimen, and after 1000 hr, another specimen showed values of $a = 19.73$ Å and $b = 9.295$ Å. During exposure, the crystals also darken in color and increase in macroscopic dimensions, especially in the direction of the a axis. In spite of these changes, the intensities and spot sizes did not change rapidly; however, as a precaution, specimens were changed several times during collection of the intensity data. The dimensions of the crystals used, in millimeters, as measured along a, b, and c, respectively, were 0.05 × 0.17 × 0.57 for $hk0$ through $hk4$, 0.07 × 0.11 × 0.23 for $hk5$ through $hk7$, and 0.057 × 0.20 × 0.10 for $h0l$ and $h1l$. Copper (Cu Kα) radiation was used to collect the intensity data, even though μ (390 cm^{-1}) is very high. The use of Mo Kα radiation involved other problems such as a much stronger background and bothersome overlapping of streaks caused by continuous radiation. Thus it was believed that Mo Kα radiation offered no net advantage in this case.

The intensity data were collected by use of the multiple-film, nonintegrated Weissenberg method, and the intensities were estimated visually. The observations on some 925 unique reflections were corrected by the usual factors and were scaled and

(1) J. D. McCullough, *Inorg. Chem.*, **3**, 1425 (1964).
(2) L. Battelle, C. Knobler, and J. D. McCullough, *ibid.*, **6**, 958 (1967).
(3) J. D. McCullough and A. Lefohn, *ibid.*, **5**, 150 (1966).

correlated by a least-squares method similar to that suggested by Rollett and Sparks.[4] Within the geometric limits covered by the observed data, an additional 655 possible reflections were below the observational level.

Although a program for absorption correction was available, it was not yet adapted to the UCLA computing system; hence no corrections for absorption were made. Consideration of the value of μ and the crystal dimensions indicates a ratio of the maximum to the minimum transmission factor of approximately 10. However, 90% of the observed reflections are within a range with a ratio of about 6.

It has been demonstrated in a number of cases[5–7] that failure to make absorption corrections (even in cases where μR exceeds the limits in the present study) does not result in errors in the positional parameters appreciably larger than the indicated esd values. The main effects of ignoring large absorption corrections appear to be (1) larger esd values for the positional parameters, (2) larger values of the usual R index, and (3) large shifts, usually downward, in the temperature coefficients. In fact, the latter may be in error by many times the implied esd values.

In the present study the refinement was carried out with isotropic temperature factors and the resulting B values are probably of little significance. On the other hand, it is firmly believed that the positional parameters, bond distances, and bond angles are valid to the degree indicated by their esd values.

Determination and Refinement of the Structure

A two-dimensional Patterson summation based on $hk0$ data indicated that the heavy atoms are lined up parallel to the c axis with approximately equal x and y parameters. This observation was confirmed by a three-dimensional Patterson summation which also gave approximate z parameters for the heavy atoms. On the assumption that the bonding order was Se–I–Cl, satisfactory trial positions for these atoms were derived. The remaining steps in the structure determination and refinement were as follows.

(1) The positions of the three heavy atoms were refined by least-squares procedures with isotropic temperature factors taken initially at 3 Å^2.

(2) A three-dimensional difference summation was prepared in which the heavy atoms were used for phasing but with their contributions otherwise subtracted. This summation clearly showed the positions of oxygen and the four carbon atoms.

(3) The positional parameters and isotropic B's for all atoms except hydrogen were refined by least-squares procedures based on the observed reflections only. In the final cycle the standard deviations were estimated and it was noted that the final shifts were much less than the corresponding esd values in all cases. The final positional and thermal parameters are given in Table I.

(4) A final set of structure factors was computed and is listed as Table II. The final value of the usual index, $R = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$, was 0.121 for the 925 observed reflections and 0.170 for all 1580 possible reflections listed in Table II. In the latter calculation, unobserved reflections were given the tabulated values

TABLE I
FINAL ATOMIC POSITIONAL AND THERMAL PARAMETERS IN $C_4H_8OSeICl$[a]

Atom	x	y	z	B, Å^2
I	0.3365 (1)	0.4437 (2)	0.5047 (3)	1.96 (5)
Se	0.3327 (2)	0.4347 (5)	0.7979 (5)	1.97 (7)
Cl	0.3318 (6)	0.4412 (13)	0.2001 (13)	3.6 (2)
O	0.466 (1)	0.638 (3)	0.853 (3)	2.2 (5)
C(1)	0.340 (2)	0.635 (5)	0.856 (5)	3.2 (8)
C(2)	0.410 (2)	0.702 (5)	0.792 (5)	3.4 (9)
C(3)	0.479 (2)	0.496 (4)	0.784 (5)	2.0 (6)
C(4)	0.431 (2)	0.383 (4)	0.837 (5)	2.6 (7)

[a] Numbers in parentheses here and in succeeding tables are the standard deviations in the least significant digits.

of F_o which were taken as $\sqrt{2}/2$ times the minimum observable values.

(5) A final three-dimensional difference Fourier was computed. As could have been predicted, this did not indicate the positions of the hydrogen atoms; neither did it show maxima or minima greater than twice the esd of the electron density, 0.82 e Å^{-3}.

The Patterson and difference summations were computed by use of UCLAFOUR written by P. K. Gantzel, Håkon Hope, and Carolyn Knobler, and the least-squares refinement was carried out by use of UCLALS4, written mainly by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood. The latter program minimizes the weighted sum of the squares of the quantity ($KF_o - GF_c$) by a full-matrix routine where K and G are scale factors. The weighting scheme used for observed reflections was that of Hughes[8] and the atomic scattering factors were the neutral atom values given in Table 3.3.1A of the "International Tables for X-Ray Crystallography."[9] The factors for I, Se, and Cl were corrected for dispersion for Cu Kα radiation by use of the $\Delta f'$ values given in Table 3.3.2B of ref 9.

Discussion of the Structure

Projections of the structure down the crystallographic b and c axes are shown in Figures 1 and 2, respectively, and the structurally interesting bond distances, bond angles, packing distances, etc., are given in Tables III–VI. Although the $C_4H_8OSeICl$ molecule is not required crystallographically to have any symmetry, mirror symmetry m is approximated. Deviations from mirror symmetry in the molecule are indicated by differences in corresponding pairs of bond distances, bond angles, and dihedral angles in the tables.

The 1,4-oxaselenane ring has the expected chair conformation, but the heteroatoms cause marked deviations from the usual shape of a cyclohexane ring. In general, the structural features of the ring found in the present study agree well with those found in the iodine complex of 1,4-oxaselenane, $C_4H_8OSeI_2$.[10] Observations on the iodine complex are included in some of the tables for comparison purposes.

Ideally, the four carbon atoms should be coplanar and this was found to be the case within the standard

(4) J. S. Rollett and R. A. Sparks, *Acta Cryst.*, **13**, 273 (1960).

(5) G. D. Christofferson, R. A. Sparks, and J. D. McCullough, *ibid.*, **11**, 782 (1958).

(6) P. Werner, *Acta Chem. Scand.*, **18**, 1851 (1964).

(7) R. C. Srivastava and E. C. Lingafelter, *Acta Cryst.*, **20**, 918 (1966).

(8) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

(9) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

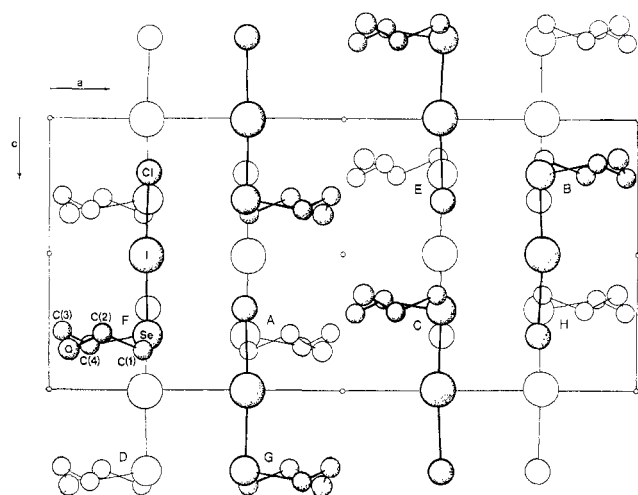(10) H. Maddox and J. D. McCullough, *Inorg. Chem.*, **5**, 522 (1966).

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

(Table of numerical structure factor data — columns of h, F₀, and Fₒ values grouped by common k and l)

[a] The data are separated into groups having common values of k and l. The three columns in each group list values of h, F_o, and F_o, in that order. Unobserved reflections are indicated by an asterisk and the values of F_o given correspond to $\sqrt{2}/2$ times the minimum observable values.

deviations involved. The displacements of the ring atoms from a least-squares plane fit to the carbon atoms are, in Å: C(1), 0.01; C(2), −0.01; C(3), 0.01; C(4), −0.01; O, 0.73; Se, −0.84 (σ = 0.05 Å for C and O, 0.02 Å for Se). In the iodine complex, the displacements of O and Se were found to be 0.761 and −0.942 Å, respectively.

An interesting feature of the packing in the ICl complex is the alignment of the nearly linear Se–I–Cl groups into columns parallel to the c axis. Packing distances between these columns and between the groups in a given column are just slightly less (~0.2 Å) than the sums of the usual van der Waals radii of the atoms involved. Hence it is assumed that intermolecular forces are relatively weak. In a given column, the

Se–I–Cl groups are lined up head-to-tail and each column makes contact with two others at about the same distance. The result is a series of folded sheets of Se–I–Cl groups with intercolumnar dihedral angles of 110°. All of the Se–I–Cl groups in a given sheet are oriented in the same direction and the general orientation of the sheets is parallel to (100). In Figure 2 the structure is viewed down the columns while in Figure 1 the view is perpendicular to the columns and parallel to the general orientation of the sheets.

The bonding and packing around selenium is shown in Figure 3 as viewed perpendicular to the c axis and parallel to the pseudo-mirror of the molecule. Selenium is bonded to two carbon atoms at an average distance of 1.98 Å and one iodine atom at 2.630 Å. The Se atom

Figure 1.—Projection of the structure of $C_4H_8OSeICl$ down the b axis. The capital letters A–H designate the positions given in the footnote to Table VI.
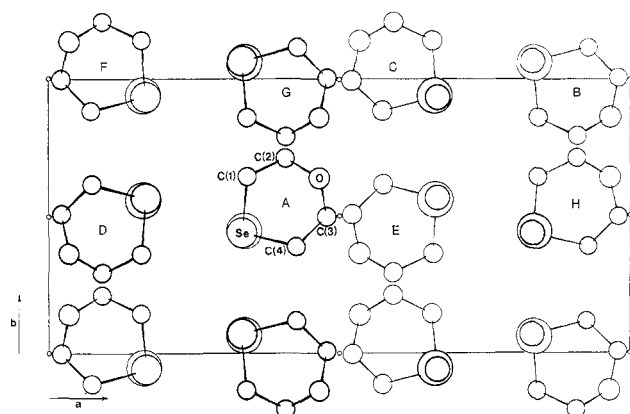

Figure 2.—Projection of the structure of $C_4H_8OSeICl$ down the c axis. The capital letters A–H designate the positions given in the footnote to Table VI.
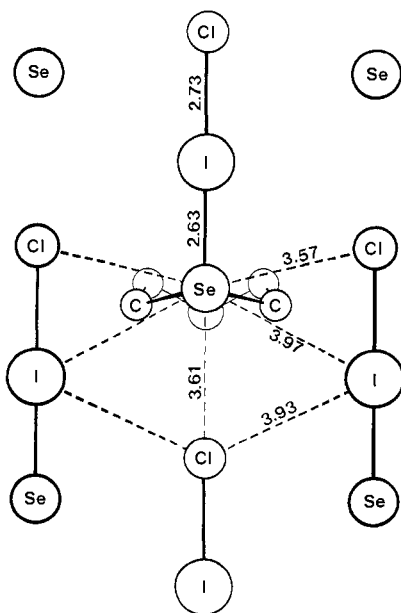

Figure 3.—View showing the bonding and packing about selenium. The pseudo-mirror plane through the $C_4H_8OSeICl$ molecule divides the idealized figure right and left.

TABLE III

BOND DISTANCES IN $C_4H_8OSeICl$ COMPARED WITH THOSE IN $C_4H_8OSeI_2$

Bond	Distance, Å $C_4H_8OSeICl$	$C_4H_8OSeI_2$
I–I	...	2.956 (3)
I–Cl	2.73 (1)	...
Se–I	2.630 (5)	2.755 (4)
Se–C(1)	1.93 (4)	1.93 (3)
Se–C(4)	2.02 (4)	1.98 (3)
O–C(2)	1.36 (5)	1.42 (4)
O–C(3)	1.47 (5)	1.41 (4)
C(1)–C(2)	1.61 (6)	1.53 (4)
C(3)–C(4)	1.49 (6)	1.52 (4)
Se···O[a]	3.26 (4)	3.24 (3)
Se–C av	1.98 (3)	1.96 (2)
O–C av	1.42 (4)	1.42 (3)
C–C av	1.55 (5)	1.53 (3)

[a] Across the ring.

TABLE IV

BOND ANGLES IN $C_4H_8OSeICl$ COMPARED WITH THOSE IN $C_4H_8OSeI_2$

Atoms	Angle, deg $C_4H_8OSeICl$	$C_4H_8OSeI_2$
I(1)–I(2)–Se	...	174.8 (3)
Cl–I–Se	175.8 (5)	...
I–Se–C(1)	104 (1)	107 (1)
I–Se–C(4)	99 (1)	102 (1)
C(1)–Se–C(4)	96 (2)	94 (2)
Se–C(1)–C(2)	110 (2)	112 (2)
Se–C(4)–C(3)	113 (2)	110 (2)
C(1)–C(2)–O	112 (3)	109 (3)
C(4)–C(3)–O	113 (3)	110 (3)
C(2)–O–C(3)	111 (3)	111 (3)

TABLE V

DIHEDRAL OR TORSION ANGLES IN THE 1,4-OXASELENANE RING IN $C_4H_8OSeICl$ (esd ∼4°)

Atoms	Angle, deg	Atoms	Angle, deg
Se–C(1)–C(2)–O	64	Se–C(4)–C(3)–O	58
C(1)–Se–C(4)–C(3)	42	C(4)–Se–C(1)–C(2)	42
C(2)–O–C(3)–C(4)	76	C(3)–O–C(2)–C(1)	78

TABLE VI

SHORTEST INTERMOLECULAR PACKING DISTANCES IN $C_4H_8OSeICl$

First atom (position A)	Second atom, position,[a] and lattice translation			Distance, Å
I	Se	G	0$\bar{1}$0	3.96
I	Se	D	00$\bar{1}$	3.97
I	Cl	D	000	3.89
I	Cl	G	0$\bar{1}$0	3.97
I	C(1)	D	00$\bar{1}$	3.80
I	C(4)	G	0$\bar{1}$0	3.85
Se	Cl	D	000	3.54
Se	Cl	G	0$\bar{1}$0	3.59
Se	Cl	A	001	3.61
Cl	C(1)	A	00$\bar{1}$	3.57
Cl	C(1)	D	00$\bar{1}$	3.73
Cl	C(2)	G	00$\bar{1}$	3.73
Cl	C(4)	G	0$\bar{1}\bar{1}$	3.78
O	C(4)	E	001	3.45
O	C(4)	C	000	3.49
C(2)	C(3)	C	000	3.56

[a] Positions: A = (x, y, z), B = $(^1/_2 + x, ^3/_2 - y, 1 - z)$, C = $(1 - x, ^1/_2 + y, ^3/_2 - z)$, D = $(^1/_2 - x, 1 - y, ^1/_2 + z)$, E = $(1 - x, 1 - y, 1 - z)$, F = $(^1/_2 - x, ^1/_2 + y, z)$, G = $(x, ^3/_2 - y, ^1/_2 + z)$, and H = $(^1/_2 + x, y, ^3/_2 - z)$.

also makes contacts with three Cl atoms at 3.54–3.61 Å and with two I atoms at 3.97 Å. Although these contacts are about 0.2 Å short of the sums of the usual van der Waals radii, they cannot be considered to be bonds. Thus selenium forms three strong bonds and there is no indication of secondary bonding of the type found in $C_4H_8OSeI_2$[10] and in $C_4H_8SeI_2$.[11] The Se–I bond of 2.630 Å is the shortest reported thus far, and, presumably, as a result, the I–Cl bond is lengthened from its uncomplexed value of 2.32 to 2.73 Å. This situation

(11) H. Hope and J. D. McCullough, *Acta Cryst.*, **17**, 712 (1964).

and the fact that the chlorine forms no other bonds than the weak one to iodine suggest that there is considerable ionic character in the I–Cl bond. This is a step in the direction of the formation of a selenonium salt, $[C_4H_8OSeI]^+Cl^-$.

Ceric Ion Equilibrium in Aqueous Acetic Acid[1]

BY KENNETH B. WIBERG AND PETER C. FORD[2]

The equilibria among cerium(IV) species in aqueous acetic acid have been studied spectrophotometrically. In contrast to earlier studies, the principal equilibrium was found to involve monomeric and trimeric cerium(IV) species with the dimer being relatively unimportant. This equilibrium responds to the inverse cube of the acid concentration.

Introduction

The oxidation of aldehydes, ketones, and similar compounds having an α-hydrogen using a variety of oxidizing agents usually leads to attack at the α position. In fact, many oxidants such as copper(II), iron(III), and thallium(III) do not react with benzaldehyde or pivalaldehyde under ordinary conditions. Ceric ion is interesting in that it is capable of effecting oxidation at the carbonyl function and readily oxidizes benzaldehyde to benzoic acid. In order to interpret the data obtained in studying the latter reaction, it was necessary to study the nature of the cerium(IV) species present in solution. Since most interesting organic substrates are at best sparingly soluble in water, aqueous acetic acid was chosen as the solvent. This solvent is relatively inert to oxidants and has frequently been used in the study of oxidation reactions.

A number of studies have been made on the equilibria between various forms of cerium(IV) in aqueous solution. Smith and Goetz[3] found the oxidation potential of the Ce(III)–Ce(IV) couple to increase with increasing perchloric acid concentration. Sherrill, King, and Spooner[4] showed the increase in potential to be independent of the perchlorate ion concentration and concluded that neither Ce(III) nor Ce(IV) reacts with perchlorate and that Ce(IV) is hydrolyzed even in strongly acidic solution. They estimated an equilibrium constant for the second hydrolysis reaction

$$CeOH^{3+} + H_2O = Ce(OH)_2^{2+} + H^+$$
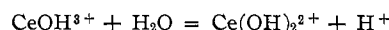
However, their constant did not include a correction for the presence of polymeric Ce(IV) species which were observed in later investigations.

Heidt and Smith, in studying the photooxidation of water by ceric perchlorate, concluded that cerium(IV) dimers must have been present.[5] King and Pandow[6] observed deviations from Beer's law in the spectral range 440–530 mμ for 4×10^{-4} to 0.1 M cerium(IV) solutions in aqueous perchloric acid. Hardwick and Robinson observed similar deviations from Beer's law from 395 to 430 mμ.[7] Their quantitative study for solutions in 0.2–2.0 M perchloric acid appeared consistent with the model

$$Ce^{4+} + H_2O = CeOH^{3+} + H^+ \tag{1}$$
$$2CeOH^{3+} = CeOCe^{6+} + H_2O \tag{2}$$
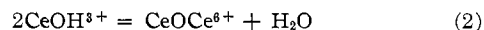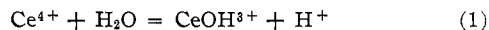
Here, $K_1 = 5.2$ and $K_2 = 16.2$ at 25°. Migration experiments confirmed the presence of only positively charged ceric species in solution.

More recently, Baker, Newton, and Kahn determined equilibrium constants for the hydrolysis of cerium(IV) in perchloric acid solution in connection with a kinetic study of the U(IV)–Ce(IV) reaction.[8] The constants obtained for the equilibria

$$Ce^{4+} + H_2O = CeOH^{3+} + H^+ \tag{1}$$
$$CeOH^{3+} + H_2O = Ce(OH)_2^{2+} + H^+ \tag{3}$$
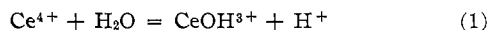
were $K_1 > 15$ and $K_3 = 0.15$ at 25°. They concluded that $CeOH^{3+}$ is the predominant species at 2.0 M

(1) This investigation was supported by the National Science Foundation. Taken from part of the Ph.D. thesis of P. C. Ford, 1967.

(2) NIH predoctoral fellow, 1963–1966.

(3) G. F. Smith and C. A. Goetz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191 (1938).

(4) M. S. Sherrill, C. B. King, and R. C. Spooner, *J. Am. Chem. Soc.*, **65**, 170 (1943).

(5) L. J. Heidt and M. E. Smith, *ibid.*, **70**, 2476 (1948).

(6) E. L. King and M. L. Pandow, *ibid.*, **74**, 1966 (1952).

(7) T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 818 (1951).

(8) F. B. Baker, T. W. Newton, and M. Kahn, *J. Phys. Chem.*, **64**, 109 (1960).