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Crystal Structure of KSb_2F_7. On the Existence of the $Sb_2F_7^-$ Ion[1]

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The crystal structure of KSb_2F_7 has been determined by a three-dimensional single-crystal X-ray diffractometer study. The crystals are monoclinic, space group $P2_1/c$, with $a = 10.517$ (1) Å, $b = 7.596$ (1) Å, $c = 8.599$ (1) Å, and $\beta = 100.85$ (2)°. For $Z = 4$, $d_c = 4.09$ g/cm^3 compared with $d_m = 4.11(3)$ g/cm^3. The structure was refined by full-matrix least-squares techniques using 1856 observed reflections to an unweighted R value of 0.025. The structure contains trigonal-bipyramidal SbF_4^- ions and pyramidal SbF_3 molecules (counting the stereochemically active lone pair of electrons in each case). Axial fluorines of neighboring SbF_4^- ions complete a distorted octahedral coordination around the SbF_3 molecule, with "bridging" Sb–F distances of 2.409 (3) and 2.567 (3) Å. The Sb–F distances in SbF_4^- are 1.908 (3), 1.933 (3), 2.082 (3), and 2.051 (3) Å for the two equatorial and two axial fluorines, respectively. The Sb–F bond lengths in SbF_3 are 1.927 (4), 1.929 (3), and 1.964 (3) Å. The structure does not contain $Sb_2F_7^-$ ions, as has been reported for $CsSb_2F_7$.

Introduction

Antimony trifluoride forms a wide variety of complexes with alkali fluorides (including NH_4F and TlF), proportions of SbF_3 to MF ranging from 4:1 to 1:2 having been reported.[3-5] Some of these compounds have been investigated by Byström and coworkers, who have reported crystal structures for SbF_3 itself,[6] for MSb_4F_{13},[7] for M_2SbF_5[8] (each is isomorphous in the series M = K, Rb, Cs, NH_4, Tl), for $MSbF_4$ (M = K[9] and Na[10]), and for $CsSb_2F_7$.[11]

Byström and Wilhelmi described the structure of $CsSb_2F_7$ as containing pairs of tetrahedrally coordinated antimony atoms that share a fluorine to form $Sb_2F_7^-$ ions.[11] However, several recent reviewers have cited this compound as an example of a five-coordinate species containing a stereochemically active lone pair, the geometry around antimony being variously described as a trigonal bipyramid with the lone pair occupying an equatorial site,[12] a trigonal bipyramid with the lone pair occupying an apical site,[13,14] or a distorted square pyramid with the lone pair at a basal site.[14] (The compound in question was also incorrectly cited as the potassium salt in the latter two reviews.)

In connection with studies of other fluoride complexes, we have reexamined the structures of several antimony fluoride salts using the published data.[15] In all attempts to refine the published structure of $CsSb_2F_7$ using modern computational methods, two of the fluorines and, in particular, the "bridging" fluorine, failed to converge. Furthermore a difference Fourier phased on the atoms that did converge failed to show peaks that could be interpreted as fluorine atoms. Attempts to produce single crystals of $CsSb_2F_7$ invariably produced twins. Therefore, we have examined the structure of KSb_2F_7 in order to determine the coordination geometry around antimony and specifically to determine whether the $Sb_2F_7^-$ ion occurs in this structure.

Experimental Section

The compound KSb_2F_7 was prepared by heating a mixture of antimony trifluoride (9.4 g, 0.053 mol) and potassium bicarbonate (5.3 g, 0.053 mol) in 42% aqueous hydrofluoric acid in a Teflon beaker. Upon cooling to room temperature large colorless plates formed and were filtered off. Further evaporation at room temperature produced smaller plates of a thickness suitable for X-ray examination. *Anal.* Calcd for KSb_2F_7: Sb, 58.6; F, 32.00. Found: Sb, 57.8; F, 31.65. Antimony was determined by potentiometric titration; fluoride, by pyrohydrolysis followed by titration with La^{3+} using a fluoride-specific electrode.

Precession photographs taken with Mo Kα radiation indicated monoclinic symmetry. The systematic extinctions observed were $h0l$ for l odd and $0k0$ for k odd, consistent with the space group $P2_1/c$ (C_{2h}^5).

No cleavage planes perpendicular to the large face of the plates could be found. Therefore, a small irregular fragment showing sharp extinction in polarized light was chosen from the bulk sample and used for data collection.

The cell constants and their standard deviations[16] were determined by a least-squares refinement of the setting angles of 12 reflections (with 2θ in the range 53–60°) that had been centered on a Picker four-circle automated X-ray diffractometer using the Mo Kα_1 component of the incident X-ray beam (graphite crystal (002) monochromator, takeoff angle 2°). The results were $a = 10.517$ (1) Å, $b = 7.596$ (1) Å, $c = 8.599$ (1) Å, and $\beta = 100.85$ (2)°. The calculated density is 4.09 g/cm^3 assuming $Z = 4$, compared with a measured density (by pycnometer) of 4.11 (3) g/cm^3.

The data crystal had well-formed faces (100), ($\bar{1}00$), (001), and ($\bar{1}\bar{1}0$); the remaining bounding faces were approximated by the planes ($00\bar{1}$), (110), and ($1\bar{1}0$). The crystal had dimensions 0.090 by *ca.* 0.20 mm along [100] and [001], respectively, while the thickness between (110) and ($\bar{1}\bar{1}0$) was *ca.* 0.10 mm. The crystal was mounted on ($1\bar{1}0$).

Intensity data were collected on the Picker diffractometer by the θ–2θ scan technique, using Mo Kα radiation (takeoff angle 4°). The count was taken over a 2θ range of 2° in 0.05° steps, for 2 sec at each step; stationary-counter, stationary-crystal background counts of 20 sec were taken at each end of the scan. Intensities were collected for all hkl and $hk\bar{l}$ reflections with $2\theta \leq 60°$. Of the 2073 reflections so measured, 1856 were observed according to the criterion $Im = f(t)[T - KB] \geq 2.5\sigma(Im)$ where $\sigma(Im) = [f^2(t)(T + KB) + \sigma_s^2(T - KB)^2]^{1/2}$, T is the total count, KB is the normalized background, and $f(t)$ is the time-dependent correction factor derived as outlined below. The quantity σ_s^2 is the percentage variance of the standard reflection

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[16] The least-squares standard deviation of the least significant digit is given by the figure in parentheses.

TABLE I

FINAL FRACTIONAL COORDINATES AND ANISOTROPIC TEMPERATURE FACTORS FOR KSb_2F_7[a,b]

	x	y	z	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	0.4269 (1)	0.6641 (2)	0.6690 (1)	65 (1)	90 (2)	73 (1)	18 (2)	26 (2)	−3 (2)
Sb(1)	0.25427 (3)	0.18160 (3)	0.51269 (3)	43.3 (3)	60.5 (5)	51.2 (4)	1.6 (5)	26.1 (5)	−5.2 (5)
Sb(2)	0.10205 (3)	0.67327 (3)	0.34674 (3)	41.8 (3)	62.5 (5)	64.3 (4)	6.0 (5)	6.9 (5)	−13.1 (5)
F(1)	0.3059 (3)	0.1174 (4)	0.3168 (3)	89 (3)	117 (5)	55 (3)	64 (7)	46 (5)	−22 (6)
F(2)	0.1512 (3)	0.4166 (3)	0.3137 (3)	93 (3)	62 (4)	110 (4)	32 (6)	41 (6)	4 (7)
F(3)	0.4049 (3)	0.3392 (3)	0.5388 (3)	57 (3)	91 (5)	100 (4)	−45 (6)	59 (4)	38 (7)
F(4)	0.3782 (3)	0.0135 (3)	0.6195 (3)	64 (3)	76 (4)	99 (4)	24 (6)	9 (5)	36 (7)
F(5)	0.2843 (3)	0.7028 (4)	0.3639 (3)	43 (3)	110 (5)	95 (4)	4 (5)	32 (5)	14 (7)
F(6)	0.1272 (3)	0.5992 (5)	0.5655 (3)	102 (4)	211 (3)	68 (4)	−1 (9)	57 (6)	10 (8)
F(7)	0.1243 (3)	0.9203 (4)	0.4532 (4)	80 (4)	127 (6)	239 (7)	−38 (8)	86 (8)	−217 (11)

[a] Standard deviations occurring in the last significant figure are given in parentheses. [b] Extinction coefficient $g = 7.86 \pm 0.05 \times 10^{-6}$. [c] Anisotropic temperature factors are defined as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl]$; β_{ij} values are given $\times 10^4$.

after correction for counting statistics[17] and was 2.4×10^{-4} for this structure. The intensity of a standard reflection, measured after every 15 reflections, dropped by about 1% during data collection. Multiplicative correction factors for the data were determined by fitting these measurements as a function of time with a third-order polynomial. The order of the polynomial was determined from significance tests based on the sum of the squares of the residuals.[18] A standard correction was made for the Lorentz effect. The polarization correction was made assuming that the graphite crystal (002) monochromator was of perfect mosaicity. For the geometry used the polarization factor is $(\cos^2 2\alpha + \cos^2 2\theta)/(1 + \cos^2 2\alpha)$ where α is the diffraction angle the beam makes with the monochromator crystal. An absorption correction was made by the Busing and Levy method using Burnham's program as modified by Larson, Cromer, and Roof.[19] The linear absorption coefficient for Mo Kα radiation is 86.7 cm^{-1} and the calculated transmission factors varied from 0.269 to 0.448.

Structure factors were calculated using the scattering factors of Doyle and Turner[20] for the neutral atoms potassium, antimony, and fluorine with appropriate anomalous dispersion corrections[21] for potassium and antimony.

Refinement of the Structure

Approximate positions for the antimony and potassium atoms were determined from a three-dimensional Patterson function. Fluorine atom positions were determined from a difference-Fourier synthesis phased on this model. Refinement was carried out by full-matrix least-squares techniques.[22] Unobserved reflections were not included in the refinement. The function minimized was $\Sigma w_i(|F_o| - |F_c^*|)^2$, where w_i is the weight defined as $1/\sigma_i^2(F_o)$, $\sigma_i(F_o) = \sigma(I)/2F_o$, and $F_c^* = kF_c/\{1 + gLp[2(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)^2]F_c^2\}^{1/2}$, in which k is a scale constant, Lp is the Lorentz–polarization factor, g is the extinction coefficient,[23] and F_c is the structure factor calculated in the usual way.

The structure refined to a Hamilton's R' factor, $R' = [\Sigma w_i(F_o - F_c^*)^2/\Sigma w_i F_o^2]^{1/2}$, of 0.052 with anisotropic temperature factors for the heavy atoms only. With anisotropic temperature factors for all atoms R' was 0.045. Inclusion of a secondary extinction correction further reduced R' to 0.037. Hamilton's significance tests[18] on R' reject the hypotheses, at better than the 0.005 confidence level, that extinction is not present and that the light atoms do not vibrate anisotropically. Parameter shifts in the last refinement cycle were less than 0.001σ for all parameters. The final unweighted R $(\Sigma||F_o| - |F_c^*||/\Sigma|F_o|)$ was 0.025.[24] The goodness of fit of an observation of unit weight was 1.7. A final difference-Fourier map showed residuals near the antimony positions ranging in value from −1.2 to 3.9 and residuals of ±0.6 e$^-$/Å^3 centered around the potassium positions; the largest residuals elsewhere were *ca.* ±0.4 e$^-$/Å^3 with $\sigma(\rho)$ = 0.2 e$^-$/Å^3. The positional and thermal parameters, with their estimated standard deviations, are given in Table I.

Discussion

If one considers the two distant fluorines (see Figure 1) as part of the coordination sphere of Sb_1, then the structure can be viewed as containing infinite chains of alternate octahedral and trigonal-bipyramidal coordination polyhedra (including the lone pairs of electrons). The geometries of these polyhedra are shown in Figures 1 and 2, respectively. A listing of selected

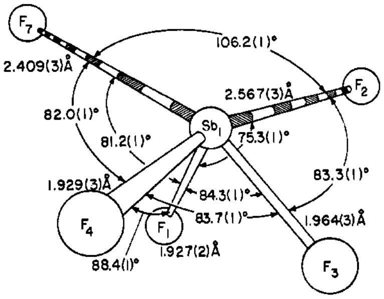

Figure 1.—Coordination sphere of Sb_1.

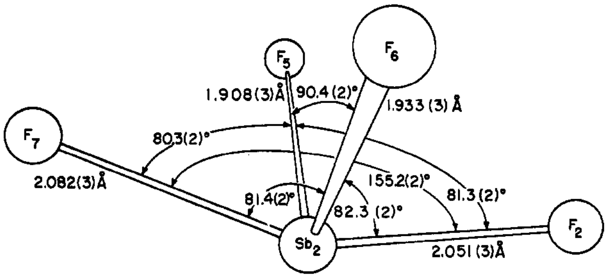

Figure 2.—Coordination sphere of Sb_2.

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(24) A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

TABLE II
INTERATOMIC DISTANCES (Å) AND ANGLES (DEG) IN KSb_2F_7[a,b]

Atoms	Distance	Atoms	Angle
(a) In the Sb_1 Coordination Sphere			
Sb_1–F_1	1.927 (4)	F_1–Sb_1–F_2	75.3 (1)
Sb_1–F_2	2.567 (3)	F_1–Sb_1–F_3	84.3 (1)
Sb_1–F_3	1.964 (3)	F_1–Sb_1–F_4	88.4 (1)
Sb_1–F_4	1.929 (3)	F_1–Sb_1–F_7(I)	81.2 (1)
Sb_1–F_7(I)	2.409 (3)	F_2–Sb_1–F_3	83.3 (1)
F_1–F_2	2.792 (4)	F_2–Sb_1–F_4	160.1 (1)
F_1–F_3	2.611 (4)	F_2–Sb_1–F_7(I)	106.2 (1)
F_1–F_4	2.689 (4)	F_3–Sb_1–F_4	83.7 (1)
F_1–F_7(I)	2.847 (4)	F_3–Sb_1–F_7(I)	159.9 (1)
F_2–F_3	3.044 (4)	F_4–Sb_1–F_7(I)	82.0 (1)
F_2–F_7(I)	>3.9		
F_3–F_4	2.598 (4)	Sb_1'''–F_2–Sb_2	130.9 (1)
F_4–F_7(I)	2.870 (4)	Sb_1(III)–F_7–Sb_2	148.0 (2)
(b) In the Sb_2 Coordination Sphere			
Sb_2–F_2	2.051 (3)	F_2–Sb_2–F_5	81.3 (2)
Sb_2–F_5	1.908 (3)	F_2–Sb_2–F_6	82.3 (2)
Sb_2–F_6	1.933 (3)	F_2–Sb_2–F_7	155.2 (2)
Sb_2–F_7	2.082 (3)	F_5–Sb_2–F_6	90.4 (2)
F_2–F_5	2.578 (4)	F_5–Sb_2–F_7	80.3 (2)
F_2–F_6	2.623 (4)	F_6–Sb_2–F_7	81.4 (2)
F_5–F_6	2.726 (4)		
F_5–F_7	2.576 (4)		
F_6–F_7	2.622 (5)		
(c) In the K Coordination Sphere			
K–F_1'''	2.901 (3)	K–F_4''	2.723 (3)
K–F_1	3.246 (3)	K–F_4(III)	2.722 (3)
K–F_3	2.702 (3)	K–F_5	2.781 (3)
K–F_3'	2.741 (3)	K–F_5'''	2.651 (3)
K–F_3''	3.089 (3)	K–F_6	3.148 (3)

[a] Standard deviations in the last significant figure are given in parentheses. [b] Unlabeled atoms are at x, y, z; singly primed atoms at $\bar{x}, \bar{y}, \bar{z}$; doubly primed atoms at $\bar{x}, {}^1/_2 + y, {}^1/_2 - z$; triply primed atoms at $\bar{x}, {}^1/_2 - y, {}^1/_2 + z$; the Roman numeral I refers to atoms in the 0, −1, 0 unit cell, II to atoms in the 0, 0, −1 unit cell, and III to atoms in the 0, 1, 0 unit cell.

bond distances and angles is given in Table II. In the following discussion, however, we have adopted the view that the structure is more consistently described in terms of isolated antimony coordination polyhedra, namely, trigonal-bipyramidal SbF_4^- ions and SbF_3 molecules.

The geometry of the SbF_4^- ion is consistent with the model predicted for an MX_nE_{5-n} molecule from the electron pair repulsion theory of Gillespie and Nyholm.[25] The angle between axial fluorines in SbF_4^- is $F_{ax}MF_{ax}$ = 155.2 (2)° compared with 174° in ClF_3[26] and 176.8 (2.5)° in SF_4,[27] and $F_{eq}MF_{eq}$ = 90.4 (2)° compared with 103.8 (6)° in SF_4. However such distortion is more favorable energetically in SbF_4^- due to the longer M–F bonds, as seen from the very short F–F contact distances of 2.30 Å and 2.23–2.43 Å in ClF_3 and SF_4, respectively, compared with the F–F contacts of 2.58–2.72 Å in SbF_4^-. The longer axial M–F bonds (0.1–0.2 Å) in SbF_4^- are also consistent with what has been found in other trigonal-bipyramidal molecules.[14,25b] However the inverse correlation between the Sb–F_{ax} bond distances and the corresponding bridging distances to adjacent SbF_3 molecules, 2.051 (3) *vs.* 2.567 (3) Å and 2.082 (3) *vs.* 2.409 (3) Å for F_2 and F_7, respectively, indicates that the axial bond length is influenced by this interaction as well so that a more quantitative discussion of these effects is not warranted.

The SbF_3 molecule is slightly but significantly distorted from the expected C_{3v} symmetry, the most significant distortion probably being due to an extra F–K contact for F_3 which lengthens the Sb–F_3 bond by *ca.* 0.04 Å. Distortions of SbF_3 attributable to the "bridging" F_2 and F_7 atoms are not readily apparent. Although interactions in the solid do influence the geometry of the molecule, the F–Sb–F angles in SbF_3 are consistent with the trend established for the other halides in the series, 96 (4)° for $SbCl_3$,[13] 96 (2)° for $SbBr_3$,[13] and 99 (1)° for SbI_3.[28] This trend can be satisfactorily explained in terms of a diminishing lone pair–halogen repulsion relative to halogen–halogen repulsion as the halogen increases in size and the Sb–X bond length increases.

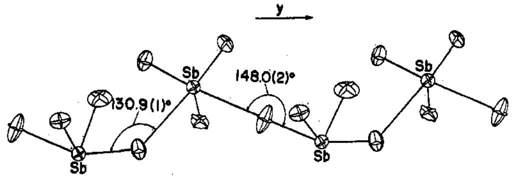

Figure 3.—A section of the pseudochain in KSb_2F_7. Thermal ellipsoids are drawn at 3 times the rms amplitudes.

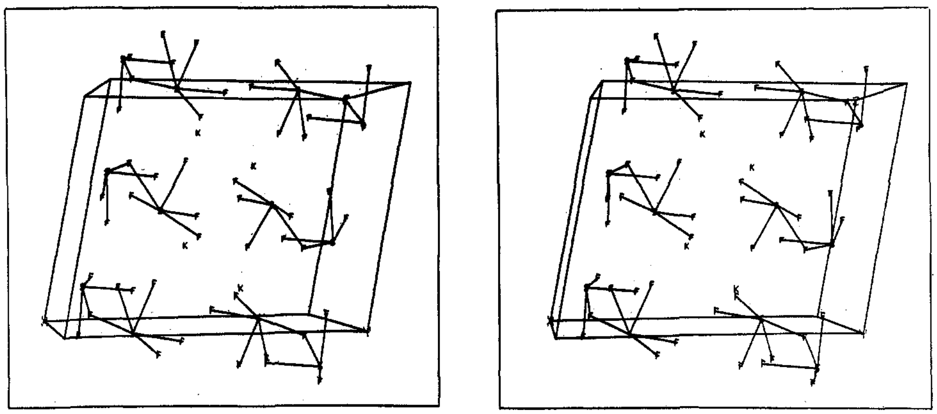

Figure 4.—Stereoview of the pseudochains in the unit cell, viewed from 10° off the y axis.

A section of the pseudochain formed by linking alternate SbF_4^- and SbF_3 species through the apical fluorines of the SbF_4^- ion is shown in Figure 3, together with the thermal ellipsoids for all atoms. It is interesting to note that the atoms with the largest thermal motions are the bridging fluorines, which are

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not in the coordination sphere of the potassium atom.[29] Figure 4 is a stereoview of the pseudochains in the unit cell.

The absence of $Sb_2F_7^-$ ions in the structure of KSb_2F_7 and the inability to reproduce the reported structure of $CsSb_2F_7$ from the data of Byström and Wilhelmi[11] make a reexamination of the $CsSb_2F_7$ structure desirable.

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[29] The closest F_2–K and F_7–K contacts are 3.592 (6) and 3.902 (6) Å, respectively.

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The Crystal and Molecular Structure of the Di-μ-chloro-ditungsten(III) Complex $W_2Cl_6(C_5H_5N)_4 \cdot x(CH_3)_2CO$

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The crystal and molecular structure of *trans*-dichloro-*cis*-dipyridinetungsten(III)di-μ-chloro-*cis*-dichloro-*trans*-dipyridinetungsten(III), $W_2Cl_6(C_5H_5N)_4 \cdot x(CH_3)_2CO$, has been determined from three-dimensional single-crystal X-ray diffraction data. From acetone, the material crystallizes in the trigonal space group $P3_121$-$D_3{}^4$ with three complex molecules in the unit cell of dimensions $a = 17.68$ (2) and $c = 7.89$ (1) Å. The calculated and observed densities are 2.23 and 2.20 g/cm^3, respectively (assuming three acetone molecules in the unit cell); 1017 intensities above background were collected by counter techniques. The structure was refined by least-squares methods to a residual, R, of 0.041. The symmetry of the molecule is 2-C_2; a twofold axis passes through the bridged tungsten atoms. The geometry of the complex is that of two octahedra sharing a common edge with the tungsten atoms distorted significantly from the octahedral centers toward each other. The tungsten–tungsten separation is 2.737 ± 0.003 Å. The acetone molecules of crystallization were not located.

Introduction

The structure of the $W_2Cl_9{}^{3-}$ ion has been determined.[1] Each of the tungsten atoms was found to be coordinated to six chlorine atoms. Three of the chlorines are shared, forming a tri-μ-chloro bridge between the metal atoms, and the complex geometry can be described as two octahedra sharing a common face. Saillant, Hayden, and Wentworth[2] have determined that the products from the reactions of $K_3W_2Cl_9$ with R (R = pyridine, 4-picoline, or 4-isopropylpyridine) are of the type $W_2Cl_6R_4$. These authors have proposed that one tungsten–chlorine–tungsten bridge is broken in the reaction and that the geometry of the product corresponds to two octahedra sharing an edge. This product appears reasonable as its formation would presumably require little molecular rearrangement and would seem likely to have a minimum of nonbonded repulsions between ligands. However two observations appear to be inconsistent with this conclusion. (a) The visible and infrared spectra of the $W_2Cl_6R_4$ compounds have remarkable similarities with those of $K_3W_2Cl_9$. This implies that the bridging arrangement of the $W_2Cl_9{}^{3-}$ ion is not radically altered by the reaction. (b) If, in $W_2Cl_6R_4$, an octahedral edge is shared, the two tungsten atoms, being at octahedral centers, would be expected to be separated by a greater distance than in $W_2Cl_9{}^{3-}$, in which faces are shared. Nevertheless the $W_2Cl_6R_4$ products were found to be diamagnetic, indicating that there is still effective tungsten–tungsten interaction. It is also of interest that Jonassen, Cantor, and Tarsey[3] have reported that the reaction of $K_3W_2Cl_9$ with pyridine, carried out under the same conditions as that above, yielded a substance analyzing as $W_2Cl_6(C_5H_5N)_3$. These authors proposed that the tri-μ-chloro bridge remains intact during the reaction.

Since the configurations of the product molecules as well as the empirical formulas were in doubt, we undertook the X-ray crystallographic determination of $W_2Cl_6(C_5H_5N)_4 \cdot x(CH_3)_2CO$.

Experimental Section

Crystal Data.—In an attempt to find a suitable crystal of $W_2Cl_6(C_5H_5N)_4$ for the X-ray investigation, the products from recrystallization from both acetone and methylene chloride were studied. These products have previously been analyzed and reported.[2] Crystals from acetone (analyzed as $W_2Cl_6(C_5H_5N)_4 \cdot {}^1/_3(CH_3)_2CO$)[4] and from methylene chloride (analyzed as $W_2Cl_6(C_5H_5N)_4$) gave qualitatively identical *hki*0, *hkil*, *h*0*il*, and *h*1*il* precession photographs (Mo Kα radiation). As those from acetone were of a more nearly optimum size, they were chosen for the present investigation.

$W_2Cl_6(C_5H_5N)_4 \cdot x(CH_3)_2CO$ crystallizes in long red well-formed prismatic needles approximately 0.08 mm in diameter with roughly hexagonal-shaped faces perpendicular to the direction of elongation. Two single crystals approximately 0.3 mm in length were obtained by cleaving the needle perpendicular to the prism faces and were mounted, respectively, along and perpendicular to the needle direction. Precession photographs using Mo Kα radiation (λ 0.7107 Å) showed that the complex crystallizes in the trigonal system with $a = 17.68 \pm 0.02$ and $c = 7.89 \pm 0.01$ Å at 20°, where c corresponds to the needle direction. Standard deviations in cell dimensions were obtained from successive readings on various films. The photographs indicated that the crystals had a normal mosaicity. The observed density of 2.20 ± 0.05 g/cm^3, as determined by flotation, corresponds most closely to a unit cell containing $3W_2Cl_6(C_5H_5N)_4$ and ${}^5/_2(CH_3)_2CO$. Calculated densities for a unit cell content of three $W_2Cl_6(C_5H_5N)_4 \cdot x(CH_3)_2CO$ vary only from 2.09 to 2.23 g/cm^3 for x varying

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[1] W. H. Watson, Jr., and J. Waser, *Acta Crystallogr.*, **11**, 689 (1958).

[2] R. Saillant, J. L. Hayden, and R. A. D. Wentworth, *Inorg. Chem.*, **6**, 1497 (1967).

[3] H. B. Jonassen, S. Cantor, and A. R. Tarsey, *J. Amer. Chem. Soc.*, **78**, 271 (1956).

[4] Due to an error in ref 2, the result of the analysis was incorrectly reported as $W_2Cl_6(C_5H_5N)_4 \cdot {}^2/_3(CH_3)_2CO$.