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.

Acknowledgments.—We wish to thank I. K. Kressin for performing the elemental analyses, A. C. Larson for use of his unpublished computer programs, and D. T. Cromer for helpful discussions.

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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/cm³, 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/cm³, 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/cm³ 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 $W_2Cl_6(C_5H_5N)_4 \cdot {}^2/_3(CH_3)_2CO$.

from 0 to 1. Therefore, we do not consider the measured density sufficiently reliable to determine accurately the number of acetone molecules present. In any event, there are three $W_2Cl_6(C_5H_5N)_4$ molecules in the unit cell. The only condition for nonextinction ($l = 3n$ for $000l$, as observed on the $h0il$ precession photograph with Mo Kα radiation and later confirmed by counter methods), the Laue symmetry ($\bar{3}m$), and the setting of symmetry elements (321) limited the possible space groups to $P3_121$ or its enantiomorph $P3_221$. These space groups require that the molecule lie on a twofold axis of symmetry.

Intensity Data Collection.—The crystal mounted along the c axis was used for intensity measurements. Three-dimensional intensity data were collected using Mo Kα radiation (λ 0.7107 Å) on a Datex automated General Electric spectrogoniometer equipped with a single-crystal orienter, scintillation counter, and pulse height analyzer with the window set to admit 90% of the characteristic radiation. The standard crystal to source distance of 5.73 in., crystal to counter distance of 7.0 in., and 2° aperture receiving collimator for this instrument were used. The takeoff angle was 2°. One unique enantiomorphic set of intensities was collected using the θ–2θ scan technique. Later, half of the second enantiomorphic set was collected. The full second set was not collected due to instrumental failure. Reflections were scanned through a range of 2.4° in 2θ at a speed of 2°/min. Stationary-counter, stationary-crystal background counts of 20 sec were taken before and after each scan. A 0.03-mm Zr β filter was used for all measurements. No attenuating filters were used. No intensity exceeded 5000 counts/sec. All reflection scans were followed on a chart recorder. This check gave no indication of overlapping peaks.

Integrated intensities, I, and standard errors, $\sigma(I)$, were calculated as $I = C - 0.5(t_c/t_b)(B_1 + B_2)$ and $\sigma(I) = (C + 0.25(t_c/t_b)^2(B_1 + B_2) + (0.03I)^2)^{1/2}$, where C is the total integrated peak count obtained in a scan of time t_c; B_1 and B_2 are the background counts, each obtained in time t_b. Out of a calculated total of 1043 unique reflections in the range $2\theta = 0$–45°, 1017 were observed (integrated intensity >0). Lorentz and polarization corrections were made in the usual manner. No corrections for absorption ($\mu_{Mo} = 96.0$ cm^{-1}) or extinction were included. Calculated transmission factors, assuming cylindrical crystal shape, were in the range 0.515–0.435. Two reflections, 042 and 402, monitored during the data collection, revealed no systematic trends. The former had a maximum of 2703 counts above background, a minimum of 2583, and an average deviation from the mean of 26 or about 1%. The latter had a maximum of 1007 counts above background, a minimum of 845, and an average deviation from the mean of 30 or a little over 3%. Although this gave us no indication of crystal decomposition during the data collection, 2 weeks later while equipment repairs were being made diffraction photographs indicated that the crystal under study now had a polycrystalline composition and that our entire sample had in some way decomposed. Consequently the collection of the second enantiomorphic set of data was not completed.

Structure Determination.—All nonzero intensities of one unique enantiomorphic set of data were used for the structure determination. By means of a Patterson synthesis, the two nonequivalent tungsten atoms were unambiguously located on the twofold axes in the special positions[5] b (x, 0, $^5/_6$; 0, x, $^1/_6$; $\bar{x}$, $\bar{x}$, $^1/_2$). A Fourier synthesis, calculated with the phases due to the tungsten atoms, revealed the chlorine and nitrogen atoms. A subsequent difference map showed all of the pyridine carbon atoms. The residual, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, for the initial trial structure was 0.15 ($R_w = (\Sigma w(F_o^2 - F_o^2)^2/\Sigma w(F_o^2)^2)^{1/2} = 0.23$). Three cycles of least-squares refinement varying atomic positions and isotropic temperature factors for all atoms led to a residual of $R = 0.052$ ($R_w = 0.092$). The function minimized was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/(\sigma(|F_o|^2))^2$. Two further cycles, similar but refining the tungsten and chlorine atoms anisotropically, reduced R to 0.045 ($R_w = 0.085$). By employing a significance test on the decrease in R,[6] it was shown that the anisotropic correction is significant at the 0.5% significance level. Although anisotropic motion, especially of the cis and trans chlorine atoms, is reasonable, the shapes and orientations of the thermal ellipsoids are to be interpreted with caution, particularly as absorption corrections were not carried out.

A correction for tungsten anomalous scattering was made as described by Ibers and Hamilton.[7] In carrying out the correction for noncentrosymmetric crystals, it is assumed that the absolute configuration is known. A first attempt to determine the handedness by comparing intensities of Friedel pairs belonging, respectively, to the previously refined enantiomorphic set of data and the (partially obtained) second enantiomorphic set gave inconclusive results. This was probably due to the relatively small differences in Friedel pair intensities, particularly between intense, statistically reliable reflections. It was believed that a less ambiguous result might be obtained by carrying out independent least-squares refinements with one enantiomorphic set of data on the right- and left-handed configurations (corresponding to the two space groups $P3_121$ or $P3_221$). As has been pointed out,[6,7] the best refinement should correspond to the correct configuration. The refinements in $P3_121$ and $P3_221$ yielded R's of 0.041 and 0.055, respectively ($R_w = 0.079$ and 0.103). The decrease of R from 0.045 (no correction) to 0.041 (correction in $P3_121$) was estimated to be significant at the 0.5% significance level.[6] Therefore we assume that $P3_121$ is the correct space group for the particular crystal we studied. As a further check on the handedness, refinements in both space groups were carried out using what was available of the $\bar{h}\bar{k}\bar{l}$ intensities. Again the $P3_121$ configuration refined significantly better than the $P3_221$ configuration ($R = 0.041$ *vs.* 0.055).

The atomic parameters from the best refinement with anomalous dispersion correction were used to calculate the structure factor amplitudes given in Table I[8] and all calculated structure parameters. All parameter shifts for this cycle were less than 30% of their respective standard deviations. Unobserved intensities were not included in the refinements or in the calculation of residuals. The final standard deviation of an observation of unit weight was 0.84. Scattering factors used for tungsten are those calculated by Cromer and Waber;[9] those given by Ibers[10] were used for all lighter atoms. Anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ for tungsten were obtained from the tables due to Cromer.[11] A final difference map showed 24 peaks on the order of 1 e$^-$/Å^3. All but seven of these were either in the close vicinity of heavy atoms or in reasonable positions for hydrogen atoms. The final seven were unexplained.

Computations.—All computations were performed on a CDC 3600 computer. Patterson and electron density maps were computed using the Gvildys Fourier summation program.[12] The Busing and Levy full-matrix least-squares program[13] was used for the structure refinement, and their function and error program[14] was used for calculation of bond distances, angles, and their respective standard deviations. Figures 1 and 2 were drawn with the aid of the Johnson thermal ellipsoid plot program.[15]

Description of the Structure

Atomic coordinates and isotropic temperature factors are given in Table II. Anisotropic temperature parameters calculated for the tungsten and chlorine atoms are compiled in Table III. Figure 1 shows the molecular packing as viewed parallel to the c axis. The complex molecules lie on twofold axes which pass through the two tungsten atoms. The basal planes of the molecules (which are defined by the tungsten,

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(5) "International Tables for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1962, p 257.

(6) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(7) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

(8) Table I, a listing of observed and calculated 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.

(9) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(10) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, pp 202–207.

(11) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(12) J. Gvildys, "B-149, Two- and Three-Dimensional Crystallographic Fourier Summation Program," Argonne National Laboratory, Argonne, Ill., 1965.

(13) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(14) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(15) C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

TABLE II

ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

Atom	x/a_1	y/a_2	z/c	B, Å^2
W_1[a]	0.5752 (1)[b]	0.5752 (1)	$^1/_2$	. . .[c]
W_2	0.4204 (1)	0.4204 (1)	$^1/_2$	. . .
Cl_c[d]	0.7110 (4)	0.6443 (5)	0.3407 (8)	. . .
Cl_t	0.3463 (5)	0.4653 (4)	0.3053 (8)	. . .
Cl_b	0.5385 (4)	0.4571 (4)	0.3078 (7)	. . .
N_c	0.361 (1)	0.295 (1)	0.354 (2)	2.8 (4)
N_t	0.528 (1)	0.640 (1)	0.331 (2)	2.3 (4)
C_{1t}	0.535 (2)	0.636 (1)	0.163 (3)	3.1 (5)
C_{2t}	0.508 (2)	0.678 (2)	0.047 (3)	3.7 (5)
C_{3t}	0.468 (2)	0.732 (2)	0.108 (3)	4.1 (6)
C_{4t}	0.459 (2)	0.729 (2)	0.283 (3)	4.3 (5)
C_{5t}	0.488 (2)	0.684 (2)	0.391 (3)	2.9 (5)
C_{1c}	0.367 (2)	0.297 (2)	0.175 (3)	3.5 (5)
C_{2c}	0.326 (2)	0.215 (2)	0.087 (3)	4.1 (6)
C_{3c}	0.283 (2)	0.136 (2)	0.167 (3)	4.5 (5)
C_{4c}	0.276 (2)	0.137 (2)	0.343 (3)	4.3 (5)
C_{5c}	0.317 (2)	0.215 (1)	0.434 (3)	3.6 (5)

[a] The coordinates of the third tungsten of the equivalent set (x, 0, $^5/_6$; 0, x, $^1/_6$; $\bar{x}$, $\bar{x}$, $^1/_2$) were those actually refined. W_1, for example, occurs at the three symmetry-equivalent positions: 0.4248, 0, $^5/_6$; 0, 0.4248, $^1/_6$; 0.5752, 0.5752, $^1/_2$. [b] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the last significant digits. [c] Anisotropic temperature factors for W_1, W_2, Cl_c, Cl_t, and Cl_b are given in Table III. [d] The subscripts c, t, and b refer to cis, trans, and bridge, respectively.

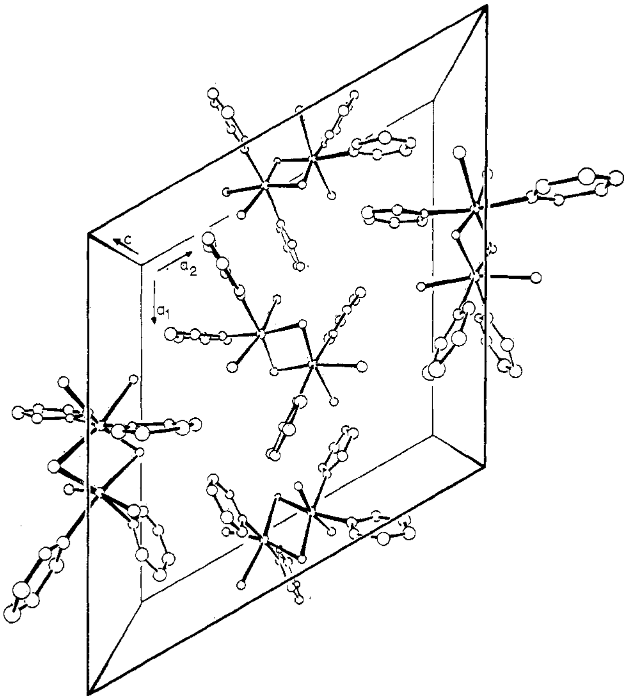

Figure 1.—Perspective packing diagram for $W_2Cl_6(C_5H_5N)_4$, in the orientation corresponding to space group $P3_121$, viewed in the direction of negative c. Each molecule lies on a twofold axis which passes through the tungsten atoms. 3_1 screw axes are parallel to the c axis at the origin and at the positions ($^2/_3$, $^1/_3$, z) and ($^1/_3$, $^2/_3$, z).

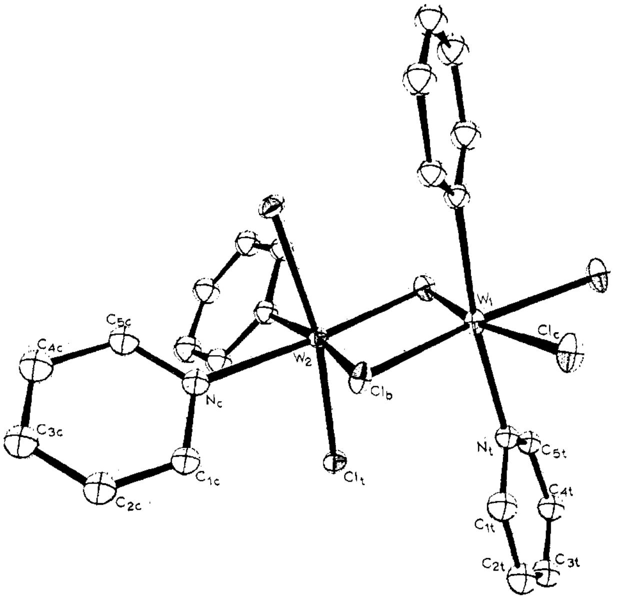

Figure 2.—The $W_2Cl_6(C_5H_5N)_4$ molecule. Thermal ellipsoids are drawn at 25% probability.

cis chlorine, μ chlorine, and cis nitrogen atoms) are inclined 50° to the a_1,a_2 plane. The apparent absence of acetone molecules in the crystal is difficult to explain. It is certain, as shown by the chemical analysis, by the infrared spectrum,[2] and by the density measurement, that some acetone originally crystallized along with the complex molecules. From a map showing van der Waals radii for all atoms including estimated hydrogens, a roughly cylindrical channel 3.1 Å in radius was found which is coaxial with the c axis. It is likely that the acetone molecules were originally packed in these holes. We can consider several degrees of acetone occupation at the time of data collection: (a) three acetones per unit cell in an ordered arrangement (true $P3_121$ symmetry), (b) three acetones per unit cell—disordered, (c) less than three acetones per unit cell—ordered, (d) less than three acetones per unit cell—disordered, and (e) no acetones. (a) and (c) can be ruled out on the basis of the final difference map. The six small residual peaks appearing in the large crystal hole could not be meaningfully interpreted. Even when large temperature factors were assumed for the acetone atoms, restrictions due to van der Waals interactions and bond distances for acetone frustrated all attempts to fit these peaks to ordered acetone molecules. If the acetones were ordered, we expect that they would have appeared at this stage, particularly considering the rather satisfactory refinement of the rest of the structure. (b) (and also (a)) can probably be ruled out on the basis of the chemical analysis, which indicates approximately one molecule of acetone in the unit cell. It is unlikely that the hole is vacant as in (e) since a crystal with a hole of this size would not be expected to be stable. It may be, of course, that acetone was gradually being lost and that at some point of low occupancy the crystal decomposed as we observed. These considerations lead us to postulate (d) as a reasonable explanation for the acetone probelm. It has been suggested to us that this conclusion is faulty and that even in the event of one acetone in the unit cell the crystal would be unstable. It is interesting to note, however, that the product recrystallized from methylene chloride contained no methylene chloride as determined by chemical analysis (a conclusion substantiated by the molecular weight determination),[2] and yet these crystals give excellent diffraction photographs which indicate a structure identical with that of the acetone product. We do not imply that the holes are completely vacant

TABLE III

ANISOTROPIC THERMAL MOTION PARAMETERS[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{max}	B_{med}	B_{min}
W_1[b]	20 (1)	20 (1)	107 (3)	11 (1)	7 (1)	−7 (1)	3.0	1.9	1.4
W_2	19 (1)	19 (1)	92 (2)	10 (1)	−1 (1)	1 (1)	2.3	1.9	1.7
Cl_c	27 (3)	31 (4)	190 (14)	13 (3)	26 (5)	6 (6)	5.4	3.1	2.0
Cl_t	32 (3)	30 (4)	163 (12)	18 (3)	−20 (5)	5 (6)	4.9	3.0	1.8
Cl_b	31 (4)	23 (3)	125 (11)	14 (2)	10 (5)	−3 (5)	3.6	2.5	2.1

[a] Anisotropic temperature factors were calculated and refined in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. β's are × 10^4. B's (in $Å^2$) are the isotropic thermal parameters corresponding to the three principal axes of the vibration ellipsoid. They are related to the equivalent root-mean-square amplitudes, $(\bar{u}^2)^{1/2}$, by $(B/8\pi^2)^{1/2} = (\bar{u}^2)^{1/2}$. [b] The special positions of the tungsten atoms require $\beta_{22} = \beta_{11}$ and $\beta_{23} = -\beta_{13}$.

in either crystal but that there is evidence that only a small number of solvent molecules may be required to prevent crystal decomposition. In any case, we think it only possible to report the crystal composition as $W_2Cl_6(C_5H_5N)_4 \cdot x(CH_3)_2CO$.

Intramolecular distances and angles and their respective standard deviations are given in Table IV.

TABLE IV

DISTANCES (Å) AND ANGLES (DEG) FOR $W_2Cl_6(C_5H_5N)_4$[a]

W_1–W_2	2.737 (3)	W_1–W_2–Cl_b	55.0 (2)
W_1–Cl_b	2.392 (7)	W_2–W_1–Cl_b	55.1 (2)
W_2–Cl_b	2.392 (8)	W_1–Cl_b–W_2	69.8 (2)
W_1–Cl_c	2.430 (8)	W_1–W_2–Cl_t	96.2 (2)
W_2–Cl_t	2.397 (8)	Cl_b–W_2–N_c	81.9 (7)
W_1–N_t	2.18 (2)	N_c–W_2–N_c'	86.1 (14)
W_2–N_c	2.24 (2)	W_2–W_1–N_t	94.1 (7)
$Cl_b \cdots Cl_b'$	3.92 (1)	Cl_c–W_1–Cl_c'	83.6 (4)
N_t–C_{1t}	1.33 (3)	Cl_b–W_1–Cl_c	83.1 (3)
C_{1t}–C_{2t}	1.41 (4)	W_1–N_t–C_{1t}	120.5 (20)
C_{2t}–C_{3t}	1.39 (4)	W_1–N_t–C_{5t}	121.6 (17)
C_{3t}–C_{4t}	1.40 (3)	N_t–C_{1t}–C_{2t}	123.4 (27)
C_{4t}–C_{5t}	1.43 (4)	C_{1t}–C_{2t}–C_{3t}	119.1 (26)
C_{5t}–N_t	1.36 (3)	C_{2t}–C_{3t}–C_{4t}	119.2 (28)
		C_{3t}–C_{4t}–C_{5t}	117.6 (28)
N_c–C_{1c}	1.42 (3)	C_{4t}–C_{5t}–N_t	122.6 (24)
C_{1c}–C_{2c}	1.43 (3)	C_{1t}–N_t–C_{5t}	117.9 (24)
C_{2c}–C_{3c}	1.37 (4)	W_2–N_c–C_{1c}	119.8 (17)
C_{3c}–C_{4c}	1.40 (3)	W_2–N_c–C_{5c}	121.6 (16)
C_{4c}–C_{5c}	1.40 (4)	N_c–C_{1c}–C_{2c}	117.9 (25)
C_{5c}–N_c	1.37 (3)	C_{1c}–C_{2c}–C_{3c}	123.3 (25)
		C_{2c}–C_{3c}–C_{4c}	117.2 (28)
		C_{3c}–C_{4c}–C_{5c}	120.9 (29)
		C_{4c}–C_{5c}–N_c	122.0 (23)
		C_{1c}–N_c–C_{5c}	118.6 (22)

[a] Primed labels here and in the text refer to atoms in the molecule related to the respective unprimed atoms by the twofold axis.

The molecule consists of two somewhat distorted octahedra sharing a common edge (Figure 2). The W_1–Cl_c and W_2–Cl_t bond lengths of 2.430 (8) and 2.397 (8) Å, respectively, agree well with that of 2.40 Å found for the tungsten to terminal chlorine distance in $K_3W_2Cl_9$.[1] The W_1–Cl_b and W_2–Cl_b bond lengths are identical (2.392 (8) and 2.392 (7) Å) but are significantly shorter than the 2.48 Å determined for the distance from a tungsten atom to a bridging chlorine atom in $K_3W_2Cl_9$. If an undistorted octahedral arrangement of chlorine and nitrogen atoms around the tungstens were assumed, the calculated W_1–W_2 separation would be 3.4 Å. The observed distance of 2.737 Å indicates considerable octahedral distortion, the effect of which is to bring the tungsten atoms closer together with an accompanying increase of the Cl_b–W–Cl_b angles to an average value of 110°. This result and the observed diamagnetism strongly suggest that there is appreciable tungsten–tungsten interaction. A similar distortion was observed for $K_3W_2Cl_9$ in which the tungsten–tungsten separation of 2.409 Å is approximately 0.3 Å shorter than that calculated for ideal octahedra sharing a face.

It is noteworthy that the trans chlorine atoms and the trans pyridine rings are bent slightly away from each other. The perpendicular distance from Cl_t to the plane of the trans pyridine is 3.20 Å, indicating these trans ligands assume positions close to those expected for the undistorted octahedra. That they are not drawn closer together along with the tungsten atoms is probably due to repulsions between them. The minimum distance allowed between Cl_t and the trans pyridine ring, assuming van der Waals radii, is calculated as approximately 3.4 Å. Clearly, if the W_2–Cl_t and W_1–N_t bonds were perpendicular to the basal plane, the resultant distance of 2.74 Å between Cl_t and N_t would imply significant interaction.

The pyridine rings are planar within error and the bond lengths and angles are normal. Also, the eight atoms describing the basal plane of the complex are coplanar. Planes through each of the trans pyridines intersect the basal plane along the same line. The inclination of approximately 45° of the cis pyridine rings to the basal plane is an expected configuration which tends to maximize interatomic distances between ring carbons and chlorine atoms and also between the two cis pyridine rings themselves.

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