TABLE V

LEAST-SQUARES PLANES FOR THE 2,2′-BIPYRIDYL GROUP[a]

Plane[b]	Atoms	Equation	χ^2 values
1	$N_1C_1C_2C_3C_4C_5$	$0.5071X + 0.3126Y - 0.8032Z + 5.1542 = 0$	$\chi^2 = 2.2$
			$[\chi^2_{3,0.50} = 2.4]$
2	$N_2C_6C_7C_8C_9C_{10}$	$0.5359X + 0.3749Y - 0.7565Z + 4.3055 = 0$	$\chi^2 = 2.1$
3	$N_1C_1C_2C_3C_4C_5$	$0.5151X + 0.3434Y - 0.7858Z + 4.7524 = 0$	$\chi^2 = 93.8$
	$N_2C_6C_7C_8C_9C_{10}$		$\chi^2_{9,0.01} = 21.7$

Deviation from Plane 3

Atom	Dev, Å	Esd, Å	Atom	Dev, Å	Esd, Å
N_1	−0.031	0.011	N_2	0.008	0.010
C_1	−0.025	0.016	C_6	−0.038	0.014
C_2	0.026	0.017	C_7	−0.069	0.016
C_3	0.056	0.016	C_8	−0.036	0.017
C_4	0.046	0.017	C_9	0.051	0.016
C_5	−0.021	0.014	C_{10}	0.064	0.016
Mo	−0.120	0.002	(Not included in plane calculation)		

[a] The equations are given in ångström units. The coordinate system used refers to three orthogonal axes such that *X* lies along the *a* axis, *Y* along *b*, and *Z* along *c**. [b] Interplanar angle is 4.7° for planes 1 and 2.

We believe that the angle between the two rings is significant in view of the physically feasible nature of the distortions from coplanarity.

This structural determination reveals the coordination geometry of "isomer II" in the series of compounds, discussed by Kummer and Graham.[1] The unexpected stereochemistry of the tin atom suggests that the difference between the two structural isomers may be related to the tin coordination number. However, we leave further discussion of this point until the results of related structures are available.

Acknowledgments.—We are deeply indebted to Dr. W. A. G. Graham for several helpful discussions and to Dr. R. Kummer for supplying the samples for this work. We gratefully acknowledge the financial support of the National Research Council of Canada.

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The Crystal and Molecular Structure of μ-Chloro-(dichloromethyltin)-2,5-dithiahexanetricarbonyltungsten, $(C_4H_{10}S_2)(CO)_3ClWSnCH_3Cl_2$

BY M. ELDER AND D. HALL

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The crystal structure determination of $DTH(CO)_3ClWSnCH_3Cl_2$ (DTH = $CH_3SCH_2CH_2SCH_3$, 2,5-dithiahexane) is reported. The compound crystallizes in space group C_{2h}^5-$P2_1/c$ with four molecules per unit cell of dimensions $a = 7.458 \pm 0.003$ Å, $b = 15.044 \pm 0.009$ Å, $c = 16.228 \pm 0.012$ Å, and $\beta = 110.75 \pm 0.02°$. The observed and calculated densities are, respectively, 2.4 and 2.46 g cm^{-3}. The structure was refined by a full-matrix least-squares method to a conventional *R* factor of 7.7% using 1743 observations above background collected on a PAILRED diffractometer. The dithiahexane ligand occupies two of seven coordination positions around the tungsten atom which has capped octahedral symmetry. The tungsten–tin distance is 2.759 ± 0.003 Å. The tin atom is effectively five-coordinate since there is a long Sn–Cl bond of 2.958 ± 0.010 Å between the tin atom and the chlorine atom which is attached to the tungsten.

Introduction

The crystal structure determination of μ-chloro-(dichloromethyltin)dithiahexanetricarbonyltungsten, $DTH(CO)_3ClWSnCH_3Cl_2$ (DTH = $CH_3SCH_2CH_2SCH_3$, 2,5-dithiahexane) has been undertaken as part of a group of crystallographic studies of molybdenum- and tungsten-substituted carbonyls with germanium and tin tetrahalides and alkyl halides. The structure of a closely related compound, $bipy(CO)_3ClMoSnCH_3Cl_2$, has been recently reported[1] (bipy = 2,2′-bipyridyl). That structure revealed seven- and five-coordinate molybdenum and tin, respectively, with a chlorine atom bridging the short molybdenum–tin bond. The present compound was undertaken in order to determine the effect of replacing the molybdenum with the third-row element tungsten. It was expected that any differences resulting from this replacement would be

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(1) M. Elder and D. Hall, *Inorg. Chem.*, **8**, 1268 (1969).

revealed in the transition metal–tin–bridging chlorine system. Such differences would aid the interpretation of the bonding and, in particular, the nature of the tin five-coordination.

Experimental Section

Crystals of DTH(CO$_3$)ClWSnCH$_3$Cl$_2$ prepared according to the method of Kummer and Graham[2] were kindly supplied by Dr. R. Kummer. They were small orange-yellow prisms and a number of single crystals of regular dimensions were easily found. These were mounted on thin glass fibers and showed no signs of decomposition though exposed to the air for a number of weeks. Preliminary photographs showed monoclinic symmetry and systematic absences consistent with the space group C_{2h}^5-$P2_1/c$. Two accurately aligned crystals were used for measurement of the unit cell parameters on a PAILRED automatic X-ray diffractometer. Final values and their standard deviations are $a = 7.458 \pm 0.003$ Å, $b = 15.044 \pm 0.009$ Å, $c = 16.228 \pm 0.012$ Å, and $\beta = 110.75 \pm 0.02°$ (temperature 27°, λ 0.70926 Å for Mo Kα_1 radiation). The experimental method involved precise measurement of ω differences, with the detector set manually at the appropriate angle $\Upsilon = 2\theta$ for the six or seven zero-level axial reflections on each axis. A least-squares fit of the resultant measurements for each axis yielded the appropriate lattice constant and a value ω_0, the ω value at $\Upsilon = 2\theta = 0°$, together with standard error measurements. With a^* and c^* measured from the same zero level the difference between the two ω_0 values gave β^*. With four molecules per unit cell and formula weight 630.3 the calculated density is 2.46 g cm^{-3}. This figure is in agreement with the experimental density of 2.4 g cm^{-3} obtained with a density bottle using water as the displacing liquid and under conditions of limited accuracy owing to the small sample mass.

A third crystal also mounted on a glass fiber was used for data collection. It was irregular with a number of faces slightly developed, roughly spherical in shape with a radius in the range 0.07–0.08 mm. The linear absorption coefficient for the material is 98 cm^{-1} for Mo Kα radiation. Absorption corrections were not applied in view of the difficulty of measuring the crystal accurately and since μR was small enough to make any but a very accurate calculation of transmission factors not worthwhile. The methods for data collection and processing have been previously described.[1] Only differences will be outlined here. Crystal monochromatized Mo Kα radiation was used, with the pulse-height analyzer centered on the Kα peak to include approximately 95% of the transmitted beam. Levels $0kl$–$6kl$ were scanned with a scan speed of 1°/min. The scan range varied from 1.6° for the zero layer to 4.0° for the sixth. Background was counted for 0.4 min at the beginning and end of each scan. A counter aperture of 1.5° was employed. A number of standard reflections were checked after each layer; they indicated no crystal or electronic instability. Data were rejected[1] for $\Delta I/I > 0.35$ giving 1743 unique reflections above background within a volume limited by $\sin\theta > 0.46$, a resolution limit of 0.77 Å. There is a considerable degree of anisotropy in the data since resolution in the a direction, that about which data were collected, is limited to 1.20 Å. The 1743 unique measurements contain the average of the two equivalent forms of the $0kl$ data obtained in the course of data collection.

Structure Solution and Refinement

Inspection of the sharpened Patterson function computed using all of the above-background data revealed the positions of the two heavy atoms. An electron density map phased with the two heavy atoms revealed a plausible set of positions for the remaining nonhydrogen atoms. Least-squares refinement of this model using isotropic temperature parameters for each atom and an over-all scale factor converged at values of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o{}^2|)^{1/2}$ of 9.8 and 13.1%, respectively.[3] Atomic scattering factors for neutral W, Sn,[4a] Cl, S, O, and C[4b] were used with the real dispersion corrections for molybdenum radiation applied to the W, Sn, Cl, and S[4c] curves. Use of a weighting scheme of the form $w = a^2/(a^2 + (F_o - b)^2)$, where $a = 52.3$ and $b = 85.5$ on the absolute scale, minimized the variation of $\Sigma w \cdot ||F_o| - |F_c||^2$ calculated for ranges of F_o. The full-matrix refinement was based upon F.

A difference Fourier map calculated at this point confirmed that the chosen model was correct, but the areas of residual electron density around the heavier atoms suggested the use of anisotropic temperature parameters for these atoms. Further cycles of refinement with anisotropic parameters for W, Sn, Cl, and S atoms reduced the agreement factors to $R_1 = 7.7\%$ and $R_2 = 10.2\%$. When the remaining atoms were refined with anisotropic thermal parameters, a number of nonpositive-definite temperature factors resulted. Furthermore, the decreases in R factor were not significant at the 95% level, judged by Hamilton's criteria.[5] Thus the model with only the W, Sn, Cl, and S atoms anisotropic was accepted as final. A difference map revealed areas of residual electron density in the range -3.4 to 2.7 e$^-$/Å^3 around the tungsten atom position. Remote from heavy-atom positions, the background was ± 1.4 e$^-$/Å^3, about one-fifth the height of a carbon atom on the same scale. Positional and thermal parameters together with the estimated standard deviations obtained from the inverse least-squares matrix are listed in Table I. An indication of the magnitudes and orientations of the thermal ellipsoids for the anisotropic atoms can be seen in Figure 1. Table II lists the final values of the observed and calculated structure factors. No extinction correction was applied, the data of Table II indicating that one was unnecessary. The nature of the anisotropy of the heavier atoms seems essentially reasonable, but we doubt that the variation in the isotropic thermal parameters of the carbon and oxygen atoms has physical significance. Together with the relatively large positional errors of the light atoms, this variation is presumably one of the visible aspects of the problem of locating light atoms accurately in the presence of much heavier ones. The problem has undoubtedly been accentuated by the lack of resolution in one direction and possibly by the neglect of absorption corrections.

Discussion

The structure consists of molecular units of DTH(CO)$_3$ClWSnCH$_3$Cl$_2$ occupying a set of fourfold general positions. The molecular structure is shown in Figure

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(2) R. Kummer and W. A. G. Graham, to be submitted for publication.

(3) Programs of local origin for the IBM 360/67 computer were used throughout this work together with programs from F. R. Ahmed, a modified version of Busing and Levy's ORFLS full-matrix least-squares, ORFFE, and Johnson's ORTEP plotting program.

(4) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962: (a) pp 211,212; (b) p 202; (c) pp 215, 216.

(5) W. C. Hamilton, "Statistics in Physical Science," The Ronald Press Co., New York, N. Y., 1964.

TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR $DTH(CO)_3ClWSnCH_3Cl_2$

Atom	x	y	z	B, Å^2
W	0.16203 (20)[a]	0.62147 (7)	0.34420 (7)	
Sn	0.04819 (37)	0.56818 (13)	0.17049 (13)	
Cl_1	−0.2832 (17)	0.5327 (6)	0.1050 (7)	
Cl_2	0.0484 (17)	0.6911 (6)	0.0775 (6)	
Cl_3	0.4415 (14)	0.6069 (6)	0.2925 (6)	
S_1	0.4498 (14)	0.6151 (6)	0.4865 (5)	
S_2	0.2420 (15)	0.7887 (5)	0.3650 (6)	
C_1	0.114 (5)	0.491 (2)	0.339 (2)	3.9 (7)
O_1	0.079 (4)	0.416 (2)	0.337 (2)	5.0 (6)
C_2	0.006 (4)	0.611 (2)	0.416 (2)	1.9 (4)
O_2	−0.087 (5)	0.601 (2)	0.459 (2)	6.0 (7)
C_3	−0.086 (5)	0.677 (2)	0.275 (2)	2.5 (5)
O_3	−0.220 (5)	0.721 (2)	0.241 (2)	5.6 (6)
C_4	0.389 (6)	0.610 (2)	0.586 (2)	4.1 (7)
C_5	0.572 (7)	0.725 (3)	0.494 (3)	5.0 (8)
C_6	0.416 (6)	0.798 (3)	0.475 (2)	4.5 (8)
C_7	0.360 (6)	0.826 (3)	0.292 (3)	5.2 (8)
C_8	0.175 (7)	0.461 (3)	0.126 (3)	5.6 (9)

Atom	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	0.0136 (3)	0.00191 (4)	0.00219 (4)	−0.00023 (12)	0.00157 (8)	−0.00021 (5)
Sn	0.0212 (7)	0.00248 (9)	0.00244 (8)	−0.00010 (18)	0.00106 (18)	−0.00020 (7)
Cl_1	0.028 (3)	0.0032 (4)	0.0058 (5)	−0.0007 (8)	0.0006 (9)	0.0005 (3)
Cl_2	0.034 (3)	0.0036 (4)	0.0039 (4)	−0.0016 (8)	0.0030 (9)	0.0010 (3)
Cl_3	0.015 (3)	0.0048 (5)	0.0051 (4)	0.0000 (7)	0.0043 (7)	−0.0011 (3)
S_1	0.021 (3)	0.0037 (4)	0.0030 (3)	0.0009 (8)	0.0006 (7)	0.0000 (3)
S_2	0.021 (3)	0.023 (3)	0.0050 (4)	−0.0018 (6)	0.0028 (8)	−0.0008 (3)

[a] Parenthetical values are the estimated standard deviations in the least significant figures. [b] The anisotropic ellipsoid has the form: $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$.

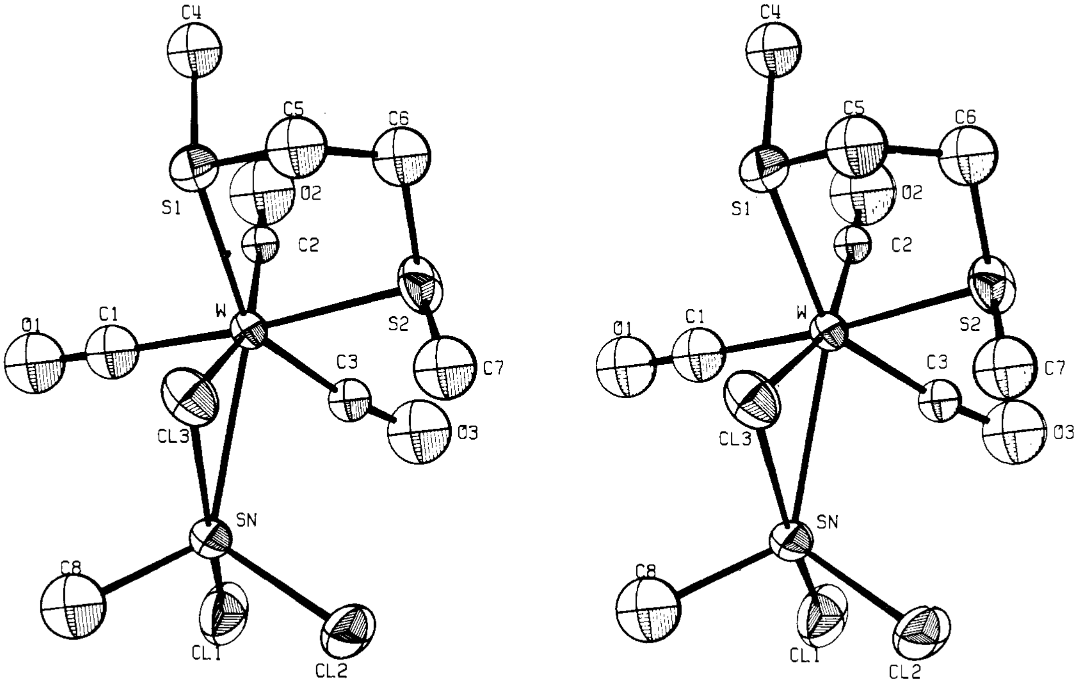

Figure 1.—A molecule of μ-chloro-(dichloromethyltin)dithiahexanetricarbonyltungsten. The thermal ellipsoids are scaled to include 50% probability.

1, with intramolecular bond lengths and angles listed in Table III. Selected intermolecular contacts, the shortest of their type, are also listed in this table; none is unusually short. There is a tungsten–tin bond making the tungsten seven-coordinate, and the weak bond between the chlorine bonded to the tungsten and the tin makes the tin five-coordinate. The structure is very similar to the previously described $bipy(CO)_3ClMoSnCH_3Cl_2$.[1] The major difference lies in the geometry of the tungsten–bridging chlorine–tin system. The W–Sn bond length of 2.759 (3) Å agrees closely with the Mo–Sn bond length of 2.753 (3) Å. This implies that the tungsten and molybdenum covalent radii are very close, since the degree of π bonding in this particular

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DTH(CO)$_3$ClWSnCH$_3$Cl$_2$ (×10)

K	L	FO	FC	K	L	FO	FC
H = 0				14	1	1165	1136
				14	5	1082	-1042
0	4	2513	-2615	14	6	534	491
0	6	3052	3295	14	7	676	694
0	8	448	-424	14	8	378	-255
0	10	1554	-1406	14	11	766	-841
0	12	1755	1853	14	13	423	276
0	16	1084	-1068	14	14	465	-390
0	18	604	538	14	15	650	487
1	4	1231	1210	15	2	928	871
1	5	713	772	15	4	797	-806
1	6	350	326	15	6	370	-152
1	7	857	833	15	8	785	824
1	8	1367	-1331	15	11	411	-286
1	9	315	-187	15	14	642	628
1	10	703	-739	16	0	1221	1244
1	11	810	-777	16	2	553	-494
1	12	700	674	16	4	575	-575
1	13	952	909	16	6	1040	1111
1	14	471	-453	16	8	460	-382
1	16	427	-394	16	10	635	-709
1	17	740	-764	16	12	763	781
1	18	523	526	17	1	635	635
1	19	442	458	17	3	474	-587
2	3	510	-583	17	7	553	619
2	4	1248	-1147	18	1	928	-1014
2	5	2068	2076	18	5	862	976
2	6	1227	1183	18	6	453	397
2	7	2031	-2069	18	7	489	-671
2	8	558	-626	19	2	460	-451
2	9	638	-596	20	0	698	-788
2	11	1611	1645	20	2	440	319

bond is unlikely to differ by an amount sufficient to alter the bond length in two such similar systems. The agreement between the metal–carbonyl lengths confirms this point: W–CO$_{\text{mean}}$ = 1.96 (2) Å; Mo–CO$_{\text{mean}}$ = 1.98 (1) Å. A value of 1.96 Å has previously been observed for the tungsten–carbonyl length in (π-C$_5$H$_5$)C$_6$H$_5$(CO)$_3$W by Semion, *et al.*,[6] who use it to estimate a covalent radius for tungsten of 1.58 Å.

The Sn–Cl$_3$ distance is long (2.96 Å) and sufficiently less than the sum of the van der Waals distances, 4.0

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[6] V. A. Semion, Y. A. Chapovskii, Yu. T. Struchkov, and A. N. Nesmeyanov, *Chem. Commun.*, 666 (1968).

TABLE III

Selected Distances, Å

Intramolecular (bonded)		Intramolecular (nonbonded)	
W-Sn	2.759 (3)	Sn-C$_1$	2.84 (3)
W-Cl$_3$	2.517 (10)	Sn-C$_3$	2.79 (3)
W-S$_1$	2.537 (8)		
W-S$_2$	2.580 (8)	Cl$_1$-Cl$_2$	3.57 (2)
W-C$_1$	1.99 (4)	Cl$_2$-Cl$_3$	3.89 (2)
W-C$_2$	1.92 (3)		
W-C$_3$	1.98 (3)	Cl$_1$-C$_8$	3.49 (5)
		Cl$_2$-C$_8$	3.60 (5)
Sn-Cl$_1$	2.379 (12)	Cl$_3$-C$_8$	3.50 (5)
Sn-Cl$_2$	2.387 (9)	Cl$_3$-S$_1$	3.13 (1)
Sn-Cl$_3$	2.958 (10)	Cl$_3$-S$_2$	3.51 (1)
Sn-C$_8$	2.12 (5)	Cl$_3$-C$_1$	3.30 (4)
		Cl$_3$-C$_3$	3.99 (3)
C$_1$-O$_1$	1.15 (4)		
C$_2$-O$_2$	1.16 (4)	S$_1$-S$_2$	3.31 (1)
C$_3$-O$_3$	1.16 (4)	S$_1$-C$_2$	3.10 (3)
		S$_1$-C$_1$	3.35 (4)
S$_1$-C$_4$	1.83 (4)	S$_2$-C$_2$	3.46 (3)
S$_1$-C$_5$	1.87 (4)	S$_2$-C$_3$	2.90 (3)
S$_2$-C$_6$	1.80 (4)		
S$_2$-C$_7$	1.80 (4)	C$_1$-C$_2$	2.49 (4)
		C$_1$-C$_3$	3.17 (5)
C$_5$-C$_6$	1.55 (6)	C$_2$-C$_3$	2.37 (4)
Intermolecular		Intermolecular	
O-O	3.30	O-CH$_3$	3.47
Cl-O	3.40	Cl-CH$_2$	3.55

Selected Angles, deg

W-Sn-Cl$_1$	114.6 (3)	S$_1$-W-S$_2$	80.6 (3)
W-Sn-Cl$_2$	110.6 (2)	S$_1$-W-C$_1$	94.8 (10)
W-Sn-Cl$_3$	52.1 (2)	S$_1$-W-C$_2$	86.9 (8)
W-Sn-C$_8$	123.8 (12)	S$_1$-W-C$_3$	148.5 (8)
Cl$_1$-Sn-Cl$_2$	97.2 (4)	S$_2$-W-C$_1$	175.2 (10)
Cl$_1$-Sn-Cl$_3$	165.9 (3)	S$_2$-W-C$_2$	99.3 (8)
Cl$_1$-Sn-C$_8$	101.3 (13)	S$_2$-W-C$_3$	77.7 (9)
Cl$_2$-Sn-Cl$_3$	92.7 (3)	C$_1$-W-C$_2$	79.0 (13)
Cl$_2$-Sn-C$_8$	105.7 (13)	C$_1$-W-C$_3$	106.0 (13)
Cl$_3$-Sn-C$_8$	85.5 (13)	C$_2$-W-C$_3$	74.6 (12)
W-Cl$_3$-Sn	59.9 (2)	W-C$_1$-O$_1$	176.7 (35)
		W-C$_2$-O$_2$	177.3 (25)
Sn-W-Cl$_3$	68.0 (2)	W-C$_3$-O$_3$	170.2 (27)
Sn-W-S$_1$	140.7 (2)		
Sn-W-S$_2$	113.0 (2)	C$_4$-S$_1$-C$_5$	104.6 (18)
Sn-W-C$_1$	71.5 (10)	W-S$_1$-C$_5$	105.1 (13)
Sn-W-C$_2$	124.2 (7)	W-S$_1$-C$_4$	114.4 (13)
Sn-W-C$_3$	69.8 (8)	C$_6$-S$_2$-C$_7$	106.4 (20)
Cl$_3$-W-S$_1$	76.5 (3)	W-S$_2$-C$_6$	104.8 (13)
Cl$_3$-W-S$_2$	87.0 (3)	W-S$_2$-C$_7$	111.4 (14)
Cl$_3$-W-C$_1$	93.2 (11)		
Cl$_3$-W-C$_2$	161.0 (8)	S$_1$-C$_5$-C$_6$	107.3 (30)
Cl$_3$-W-C$_3$	124.3 (9)	S$_2$-C$_6$-C$_5$	111.4 (26)

Å,[7] to imply the existence of a weak bond, but significantly longer than the equivalent Sn–Cl length of 2.805 Å in the molybdenum compound. Accompanying this change is a decrease in the length of the other bond formed by the bridging chlorine, from 2.557 Å for Mo–Cl to 2.517 Å for W–Cl. In view of the standard error estimates, the difference is only just significant but is reinforced by the Sn–W–Cl angle of 68.0° which is significantly greater than the corresponding angle in the molybdenum compound. Both differences indicate that in the present compound the bridging chlorine forms a stronger bond with the tungsten while the Sn–Cl bond is weakened. The effect of this difference upon the geometry around the tin atom is not very great. Comparison of the angles subtended at the tin atom in the two compounds reveals no significant differences. While there is definitely a marked distortion of the tetrahedral face defined by W, Cl$_2$, and C$_8$ to accommodate the bridging chlorine, the resulting bond is weak and minor differences in its length apparently have little effect upon the geometry of the other atoms bonded to the tin. However, the Sn–Cl distances involving the two nonbridging chlorine atoms are equivalent in the present compound and close to the mean of the two (significantly different) values for the molybdenum complex. Apparently the electronic differences accompanying the weakening of the Sn–Cl$_{\text{bridge}}$ bond have removed the distinction between axial and equatorial chlorine atoms, with respect to a trigonal bipyramid, which existed in the molybdenum compound.

The tungsten atom exhibits a capped octahedral structure. The octahedral face that is capped by the $SnCH_3Cl_2$ group is distorted to allow a close approach of the tin atom. This face has ligand–metal–ligand angles in the range 99–124° compared with the opposite face, determined by S$_1$, S$_2$, and C$_2$, where the range is 78–87°. The tungsten–tin bond makes angles of 68–72° with the three nearest bonds. The dithiahexane ligand subtends 80.6° at the molybdenum; both sulfur atoms have a tetrahedral arrangement of bonds with a lone pair presumably occupying the vacant position. The difference between the two W–S bonds is barely significant and is certainly hard to account for chemically.

Acknowledgment.—We are deeply indebted to Dr. W. A. G. Graham for his continued interest in this work and to Dr. R. Kummer for supplying the crystalline samples used. We acknowledge gratefully the financial support of the National Research Council of Canada.

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(7) F. P. Boer, J. J. Flynn, H. H. Freedman, S. V. McKinley, and V. R. Sandel, *J. Am. Chem. Soc.*, **89**, 5068 (1967), gave 2.2 Å for Sn.