Crystal and Molecular Structure of μ-(Dichlorostannio)-bis(tricarbonyl-π-cyclopentadienylchromium)

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The crystal structure of the title compound has been determined by three-dimensional X-ray diffraction methods by use of counter data and refined to R 0·057 for 3458 unique reflections by least-squares methods. The monoclinic unit cell, space group $P2_1/n$, has dimensions $a = 10\cdot314 \pm 0\cdot012, b = 15\cdot646 \pm 0\cdot020, c = 12\cdot223 \pm 0\cdot012$ Å, $\beta = 93\cdot25 \pm 0\cdot1°$, for $Z = 4$. The molecular structure consists of $SnCl_2$ inserted into the metal–metal bond of the parent dimer $[\{(\pi\text{-}C_5H_5)Cr(CO)_3\}_2]$. The environment about the tin atom is distorted tetrahedral [Cr–Sn–Cr 130·2(1), Cl–Sn–Cl 95·0(1)°; mean Sn–Cr 2·697(3), Sn–Cl 2·417(4) Å]. The chromium atoms have distorted octahedral environments with the carbonyl groups lying along {100} directions and the cyclopentadienyl rings lying parallel to the ($\bar{1}\bar{1}\bar{1}$) faces. The Cr–Sn bonds are directed along the normals to the (11$\bar{1}$) faces of the octahedra.

RECENTLY a series of complexes of the type $[(\pi\text{-}C_5H_5)M(CO)_3][(\pi\text{-}C_5H_5)M'(CO)_3]SnX_2$ (M,M' = Cr, Mo, or W; X = Cl, Br, or I) have been prepared.[1] Those in which M = M' are obtained by the insertion on heating of tin(II) halides into the metal–metal bonds of the dimers $[\{(\pi\text{-}C_5H_5)M(CO)_3\}_2]$. The mixed-metal complexes are obtained from the reactions between $[(\pi\text{-}C_5H_5)M(CO)_3SnX_3]$ and $[\{(\pi\text{-}C_5H_5)M'(CO)_3\}_2]$.

The crystal structures of the complexes for a given halide would be of interest since it ought to be possible to correlate structural changes with the metal atoms present in the complexes. The series of complexes chosen for investigation have X = Cl. The crystal structure is reported of the complex for which M = M' = Cr.

EXPERIMENTAL

Crystal Data.—$C_{16}H_{10}Cl_2Cr_2O_6Sn$, $M = 591\cdot8$, $a = 10\cdot314 \pm 0\cdot012, b = 15\cdot646 \pm 0\cdot020, c = 12\cdot223 \pm 0\cdot012$ Å, $\beta = 93\cdot25 \pm 0\cdot1°$, $U = 1969\cdot3$ Å^3, $D_m = 1\cdot99$ (by flotation), $Z = 4$, $D_c = 1\cdot996$, $F(000) = 1144$. Mo-K_α radiation, $\lambda = 0\cdot71069$ Å, for cell dimensions and intensity measurements; μ(Mo-K_α) = 26·9 cm^{-1}. Space group $P2_1/n$ (C_{2h}^5, No. 14) [general positions: $\pm|x,y,z; \tfrac{1}{2} + x, \tfrac{1}{2} - y, \tfrac{1}{2} + z|$].

The complex crystallises as orange plates lying on the (001) face. Unit-cell parameters were obtained from single-crystal precession photographs by use of Mo-K_α radiation. The intensities were collected on a Philips PAILRED diffractometer by use of monochromatised Mo-K_α radiation. Each reflection in the 0—13kl layers, for sin θ $\leqslant$ 0·52, was recorded; 3458 unique reflections were considered observed[2] giving counts for which $\sigma(I)/I \leqslant 0\cdot5$, and were used for the structure analysis. The intensities were corrected for Lorentz and polarisation effects, but no correction for absorption or extinction was applied.

Scattering-factor curves for all atoms were taken from ref. 3, the values for tin, chromium, and chlorine atoms being corrected for the effects of anomalous dispersion. All calculations were carried out on a PDP 10 computer at the University of Essex, with programmes written by the author.

Structure Determination.—The positions of the tin, chromium, and chlorine atoms were obtained from a three-dimensional Patterson synthesis. A Fourier synthesis, phased by these atoms, yielded the positions for all non-hydrogen atoms.

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Refinement of the structure was carried out by a least-squares procedure in which the function minimised was $\Sigma w\Delta^2$. The weight for each reflection, w, was initially unity and in the final refinement was calculated from the expression $w = (10\cdot0 - 0\cdot12|F_o| + 0\cdot0007|F_o|^2)^{-1}$. For this latter weighting scheme the average values of $w\Delta^2$ for ranges of increasing $|F_o|$ were almost constant. Reflections for which $|F_o| < \tfrac{1}{3}|F_o|$ were omitted from the least-squares analysis.

TABLE 1

Atomic co-ordinates (fractional), with estimated standard deviations in parentheses

	x/a	y/b	z/c	σ_{rms}/Å
Sn	−0·08082(7)	0·17340(5)	0·15081(7)	0·0008
Cr(1)	0·1431(2)	0·2512(1)	0·2172(2)	0·002
Cr(2)	−0·2289(2)	0·0651(1)	0·2567(2)	0·002
Cl(1)	−0·0356(3)	0·1158(2)	−0·0267(3)	0·004
Cl(2)	−0·2386(3)	0·2764(2)	0·0799(3)	0·004
O(T11)	−0·0121(11)	0·2514(11)	0·4166(10)	0·013
O(T12)	0·0429(11)	0·3581(8)	0·0270(11)	0·012
O(T13)	0·1950(12)	0·4277(7)	0·3017(11)	0·014
O(T21)	−0·2955(11)	0·2322(7)	0·3482(10)	0·012
O(T22)	0·0376(10)	−0·0125(8)	0·2906(11)	0·012
O(T23)	−0·2227(16)	0·0182(11)	0·4942(11)	0·016
C(T11)	0·0419(13)	0·2499(11)	0·3370(13)	0·016
C(T12)	0·0737(12)	0·3135(8)	0·0982(13)	0·014
C(T13)	0·1748(13)	0·3602(10)	0·2698(13)	0·015
C(T21)	−0·2626(13)	0·1679(10)	0·3131(13)	0·015
C(T22)	−0·0628(14)	0·0194(9)	0·2760(12)	0·014
C(T23)	−0·2233(16)	0·0351(11)	0·4046(14)	0·017
C(11)	0·2720(13)	0·1866(9)	0·1069(10)	0·013
C(12)	0·3469(14)	0·2439(10)	0·1796(17)	0·017
C(13)	0·3333(13)	0·2151(10)	0·2858(15)	0·016
C(14)	0·2570(14)	0·1433(10)	0·2813(14)	0·015
C(15)	0·2185(12)	0·1224(8)	0·1727(11)	0·013
C(21)	−0·4263(18)	0·0223(24)	0·2321(20)	0·028
C(22)	−0·4053(26)	0·0673(15)	0·1500(24)	0·027
C(23)	−0·3138(28)	0·0392(24)	0·0930(16)	0·029
C(24)	−0·2739(19)	−0·0375(22)	0·1384(31)	0·032
C(25)	−0·3484(32)	−0·0485(17)	0·2276(28)	0·031
H(11)	0·259	0·191	0·025	
H(12)	0·399	0·295	0·160	
H(13)	0·372	0·242	0·355	
H(14)	0·233	0·111	0·345	
H(15)	0·164	0·072	0·148	
H(21)	−0·489	0·038	0·288	
H(22)	−0·458	0·120	0·133	
H(23)	−0·277	0·052	0·021	
H(24)	−0·205	−0·075	0·110	
H(25)	−0·345	−0·099	0·279	

The initial refinement used a full-matrix procedure in which the positional and invidual isotropic thermal parameters for each atom were varied. When the maximum

[1] P. Hackett and A. R. Manning, *J.C.S. Dalton*, 1972, 2434.
[2] M. Mack, *Norelco Reporter*, 1965, **12**, 40.
[3] ' International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

shift in any parameter was of the order of its σ a difference synthesis was calculated. This map showed no unusual features and indicated the approximate positions for the hydrogen atoms. The positions of the hydrogen atoms were optimised, assuming C–H 1·0 Å, and in subsequent refinement the hydrogen atoms were included with an isotropic thermal parameter of B 6·0 Å², but not refined.

Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Owing to the large number of parameters (245) being refined four block-matrices were used, containing the parameters for the following: (1) overall scale and temperature factor; (2) the tin, chromium, chlorine atoms, and the six carbonyl groups; and (3) and (4) each cyclopentadienyl ligand. The refinement was terminated when the maximum shift in any parameter was $<0·1\sigma$. 3438 Reflections were included in the final cycle of refinement. The final value for R, based on 3458 reflections, was 0·057 and for R' [$= (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$] was 0·086.

Final atomic co-ordinates and thermal parameters together with their estimated standard deviations are given in Tables 1 and 2. Observed and calculated structure

TABLE 2

Thermal parameters ($\times 10^4$),* with estimated standard deviations in parentheses

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Sn	41·9(5)	19·7(2)	35·5(5)	0·1(4)	1·9(4)	−1·0(4)
Cr(1)	39(2)	21(1)	47(1)	−1(1)	6(1)	−3(1)
Cr(2)	46(2)	21(1)	51(2)	−2(1)	10(1)	3(1)
Cl(1)	77(3)	37(2)	42(2)	6(2)	4(2)	−8(2)
Cl(2)	62(3)	31(1)	76(3)	14(2)	−10(2)	8(2)
O(T11)	74(11)	116(11)	58(9)	−4(9)	11(8)	−38(8)
O(T12)	95(12)	43(6)	106(12)	5(7)	8(10)	34(7)
O(T13)	95(13)	32(5)	189(18)	1(7)	−45(12)	−30(8)
O(T21)	115(13)	41(6)	77(9)	0(7)	32(9)	−15(6)
O(T22)	75(11)	57(7)	109(12)	22(7)	−1(9)	31(7)
O(T23)	206(22)	98(11)	63(11)	28(13)	39(12)	37(9)
C(T11)	62(12)	48(8)	62(12)	1(8)	11(10)	−14(8)
C(T12)	49(11)	24(6)	83(13)	8(6)	17(9)	−8(7)
C(T13)	54(12)	34(6)	75(13)	3(7)	−16(10)	−11(7)
C(T21)	66(12)	28(6)	85(13)	−12(8)	27(10)	−5(8)
C(T22)	75(13)	28(6)	61(11)	−2(7)	18(10)	5(7)
C(T23)	105(18)	46(8)	62(13)	8(10)	25(12)	11(8)
C(11)	75(12)	38(7)	31(8)	17(7)	6(8)	−10(6)
C(12)	61(13)	34(7)	127(18)	−1(8)	50(12)	−3(9)
C(13)	48(12)	39(7)	98(15)	22(8)	9(11)	−4(8)
C(14)	60(12)	37(7)	82(14)	8(8)	20(11)	−1(8)
C(15)	59(12)	29(5)	40(9)	8(6)	12(8)	−3(6)
C(21)	60(17)	160(26)	101(21)	−40(18)	−31(15)	18(20)
C(22)	177(32)	60(12)	124(25)	4(16)	−115(24)	−8(14)
C(23)	175(32)	135(22)	46(13)	−122(24)	−6(17)	−4(14)
C(24)	65(17)	98(18)	221(38)	21(15)	−34(20)	−113(23)
C(25)	224(40)	60(12)	217(38)	−101(20)	−159(34)	72(18)

For all hydrogen atoms $B = 6·0$ Å.

* Anisotropic thermal parameters in the form:
$\exp -(h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + 2hk b_{12} + 2hl b_{13} + 2kl b_{23})$.

factors are listed in Supplementary Publication No. SUP 21189 (20 pp., 1 microfiche).†

DISCUSSION

The Figure shows the molecular geometry of the complex [4] and the labelling of the atoms. Bond distances and angles, together with their estimated

† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[4] C. K. Johnson, ORTEP: A Fortran Thermal-ellipsoid Plot Programme for Crystal Structure Illustrations, Report ORNL 3794, 1965, Revised 1971, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
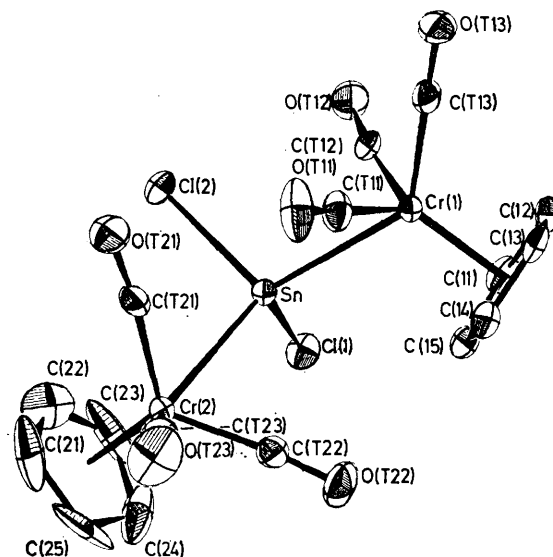
A perspective drawing of the molecule and the labelling of the atoms. Thermal ellipsoids are scaled to include 35% probability

TABLE 3

Bond lengths and angles, with estimated standard deviations in parentheses

(a) Distances (Å)

Sn–Cr(1)	2·694(2)	Sn–Cl(1)	2·419(3)
Sn–Cr(2)	2·701(2)	Sn–Cl(2)	2·416(3)
Cr(1)–C(T11)	1·846(15)	Cr(2)–C(T21)	1·843(15)
Cr(1)–C(T12)	1·861(16)	Cr(2)–C(T22)	1·838(14)
Cr(1)–C(T13)	1·846(15)	Cr(2)–C(T23)	1·852(17)
Cr(1)–Cp(1) *	1·838(13)	Cr(2)–Cp(2) *	1·831(18)
Cr(1)–C(11)	2·193(12)	Cr(2)–C(21)	1·131(17)
Cr(1)–C(12)	2·181(13)	Cr(2)–C(22)	2·180(17)
Cr(1)–C(13)	2·165(14)	Cr(2)–C(23)	2·167(18)
Cr(1)–C(14)	2·175(15)	Cr(2)–C(24)	2·152(19)
Cr(1)–C(15)	2·238(13)	Cr(2)–C(25)	2·136(17)
C(T11)–O(T11)	1·149(17)	C(T21)–O(T21)	1·151(17)
C(T12)–O(T12)	1·146(17)	C(T22)–O(T22)	1·154(17)
C(T13)–O(T13)	1·141(17)	C(T23)–O(T23)	1·127(19)
C(11)–C(12)	1·454(22)	C(21)–C(22)	1·255(35)
C(12)–C(13)	1·389(24)	C(22)–C(23)	1·282(35)
C(13)–C(14)	1·370(21)	C(23)–C(24)	1·376(39)
C(14)–C(15)	1·403(20)	C(24)–C(25)	1·380(41)
C(15)–C(11)	1·418(19)	C(25)–C(21)	1·370(42)

(b) Angles (°)

Cr(1)–Sn–Cr(2)	130·2(1)	Cl(1)–Sn–Cl(2)	95·0(1)
Cr(1)–Sn–Cl(1)	103·5(1)	Cr(2)–Sn–Cl(1)	109·3(1)
Cr(1)–Sn–Cl(2)	110·8(1)	Cr(2)–Sn–Cl(2)	102·5(1)
C(T11)–Cr(1)–C(T12)	114·6(6)	C(T21)–Cr(2)–C(T22)	118·0(6)
C(T11)–Cr(1)–C(T13)	80·3(7)	C(T21)–Cr(2)–C(T23)	80·3(5)
C(T12)–Cr(1)–C(T13)	80·8(6)	C(T22)–Cr(2)–C(T23)	79·5(6)
C(T11)–Cr(1)–Sn	73·8(5)	C(T21)–Cr(2)–Sn	73·6(4)
C(T12)–Cr(1)–Sn	73·5(4)	C(T22)–Cr(2)–Sn	75·3(4)
C(T13)–Cr(1)–Sn	130·9(4)	C(T23)–Cr(2)–Sn	128·7(5)
Sn–Cr(1)–Cp(1) *	112·8(7)	Sn–Cr(2)–Cp(2) *	114·1(7)
C(T11)–Cr(1)–Cp(1) *	123·2(7)	C(T21)–Cr(2)–Cp(2) *	119·3(7)
C(T12)–Cr(1)–Cp(1) *	121·4(7)	C(T22)–Cr(2)–Cp(2) *	122·2(7)
C(T13)–Cr(1)–Cp(1) *	116·4(7)	C(T23)–Cr(2)–Cp(2) *	117·2(7)
Cr(1)–C(T11)–O(T11)	174·2(13)	Cr(2)–C(T21)–O(T21)	173·7(12)
Cr(1)–C(T12)–O(T12)	172·1(12)	Cr(2)–C(T22)–O(T22)	175·0(13)
Cr(1)–C(T13)–O(T13)	179·5(16)	Cr(2)–C(T23)–O(T23)	178·4(17)
C(15)–C(11)–C(12)	107·6(12)	C(25)–C(21)–C(22)	107·1(26)
C(11)–C(12)–C(13)	107·0(13)	C(21)–C(22)–C(23)	114·0(26)
C(12)–C(13)–C(14)	108·4(15)	C(22)–C(23)–C(24)	107·0(22)
C(13)–C(14)–C(15)	111·2(14)	C(23)–C(24)–C(25)	105·1(20)
C(14)–C(15)–C(11)	105·8(12)	C(24)–C(25)–C(21)	106·6(21)

* Cp is the centroid of a cyclopentadienyl ring.

standard deviations derived directly from the least-squares inverse matrices, are given in Table 3, and details of planes in Table 4. The molecules are held in the crystal by van der Waals forces. The closest approach of two atoms involving carbonyl groups is

TABLE 4

Least-squares planes and their equations given by $lX' + mY' + nZ' - p = 0$ where the orthogonalised co-ordinates X', Y', and Z' are derived from the atomic co-ordinates, X, Y, and Z by $X' = X \sin \beta$, $Y' = Y$, and $Z' = Z + X \cos \beta$. Deviations (Å) of the most relevant atoms from the planes are given in square brackets

	l	m	n	p
Plane (1): Sn, Cr(1), Cr(2)	−0·5171	0·7603	0·3931	3·2363
Plane (2): Sn, Cl(1), Cl(2)	0·7280	0·6746	−0·1225	0·9926
Plane (3): C(11)—(15)	0·8151	−0·5673	−0·1173	0·0041

[C(11) −0·012, C(12) 0·009, C(13) −0·003, C(14) −0·005, C(15) 0·011]

Plane (4): C(21)—(25)	−0·6932	−0·4859	−0·5323	1·2542

[C(21) −0·023, C(22) 0·025, C(23) −0·015, C(24) 0·001, C(25) 0·013]

3·14 Å $[O(T12) \cdots O(T23)$ at $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}]$ and involving a chlorine atom is 3·39 Å $[Cl(2) \cdots O(T11)$ at $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}]$.

The molecules have the predicted structure [1] with tin(II) chloride inserted into the metal–metal bond of $[\{(\pi\text{-}C_5H_5)Cr(CO)_3\}_2]$. The corresponding distances and angles within each $[(\pi\text{-}C_5H_5)Cr(CO)_3]$ fragment are, within experimental error, the same and show no significant variations from those in the parent dimer.[5] The environment about the tin atom is distorted tetrahedral, with Cr–Sn–Cr 130·2 and Cl–Sn–Cl 95·0°. This environment has been observed in similar complexes, e.g. $[\{(\pi\text{-}C_7H_8)Co(CO)_2\}_2]SnCl_2$ (ref. 6) and $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2]SnCl_2$ (ref. 7), in which the corresponding angles are respectively 128·3 and 98·1°, and 128·6 and 94·1°. The Sn–Cl distance (mean 2·417 Å) is in good agreement with those in the aforementioned cobalt [6] and iron [7] complexes but is significantly longer than that (2·31 Å) in $SnCl_4$.[8] It is also in good agreement with the sum of the single-bond covalent radii (1·40 + 0·99 Å).[9]

[5] R. D. Adams, D. E. Collins, and F. A. Cotton, *J. Amer. Chem. Soc.*, 1974, **96**, 749.

[6] F. P. Boer and J. J. Flyn, *J. Amer. Chem. Soc.*, 1971, **93**, 6495.

[7] J. E. O'Connor and E. R. Corey, *Inorg. Chem.*, 1967, **6**, 968.

From the Sn–Cr distance (mean 2·697 Å) and assuming the tetrahedral radius of 1·40 Å for tin(IV) the radius of the chromium atom is estimated to be 1·30 Å. This value is considerably shorter than that (1·48 Å) for the estimated single-bond covalent radius of chromium in $[Cr(dien)(CO)_3]$ (dien = diethylenetriamine).[10]

The environment about a chromium atom is best described as octahedral in which the carbonyl groups lie approximately along {100} directions and the cyclopentadienyl ring lies parallel to the $(\bar{1}\bar{1}1)$ face. The Cr–Sn bond is then directed along the normal to the $(11\bar{1})$ face. As shown in Table 5 a distortion from a

TABLE 5

Comparison of the angles about the chromium atoms in the present structure (I) and in the parent dimer (II) with those calculated for a regular octahedral environment

	(I)	(II)	Calc.	Directions †
Cp–Cr–M *	113·5°	116·7°	109·5°	$(\bar{1}\bar{1}\bar{1}) : (11\bar{1})$
C(T1)–Cr–M	74·0	71·3	54·7	$\frac{(100)}{(010)} : (11\bar{1})$
C(T2)–Cr–M				
C(T3)–Cr–M	129·8	127·8	125.3	$(001) : (11\bar{1})$
Cp–Cr–C(T1)	121·5	124·5	125·3	$(\bar{1}\bar{1}\bar{1}) : \frac{(100)}{(010)}$
Cp–Cr–C(T2)				
Cp–Cr–C(T3)	116·8	114·8	125·3	$(\bar{1}\bar{1}\bar{1}) : (001)$
C(T1)–Cr–C(T2)	116·3	114·4	90·0	$(100) : (010)$
C(T1)–Cr–C(T3)	80·2	80·0	90·0	$\frac{(100)}{(001)} : (001)$
C(T2)–Cr–C(T3)				
Cr–C(T1)–O(T1)	173·8	172·0		
Cr–C(T2)–O(T2)				
Cr–C(T3)–O(T3)	179·0	178·7		

* Cp is the centroid of the cyclopentadienyl ring; M = Sn for (I) and M = Cr for (II). Values for (II) were calculated from co-ordinates given in ref. 5. † Directions in the octahedron.

regular geometry is evident and is similar to that found in the parent dimer $[\{(\pi\text{-}C_5H_5)Cr(CO)_3\}_2]$.[5] It involves a shift of the carbonyl groups away from the other metal atom with the two carbonyl groups nearest it bending slightly away. The distortion most likely arises from intra-atomic repulsions.

[8] R. L. Livingston and C. N. R. Rao, *J. Chem. Phys.*, 1959, **30**, 339.

[9] L. Pauling, ' The Nature of the Chemical Bond,' 2nd edn., Cornell University Press, Ithaca, New York, 1948, p. 179.

[10] F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, 1966, **5**, 1851.