Crystal and Molecular Structure of Pentacarbonyl(trimethylphosphine sulphide)chromium(0)

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The crystal structure of the title compound has been determined, by Patterson and Fourier methods, from diffractometer data. Crystals are monoclinic, $a = 6{\cdot}445(1)$, $b = 18{\cdot}752(3)$, $c = 10{\cdot}897(2)$ Å, and $\beta = 90{\cdot}12(2)°$, space-group $P2_1/n$. The structure was refined, by least-squares methods, to R 0·065 for 2002 independent reflections. Co-ordination around the chromium atom is distorted octahedral. Metal–ligand bond distances [Cr–S 2·510(2), Cr–C(*trans*) 1·815(8), and Cr–C(*cis*) 1·900(4) Å (mean)] are consistent with simple σ donation from sulphur to chromium, with little or no π interaction. There is no evidence for significant interaction between the $SPMe_3$ ligand and any of the *cis*-carbonyl groups.

COMPLEXES of the type $ML(CO)_5$ provide a convenient means for examining the nature of the bond between the metal M and ligand L. This is because the M–L bond influences the bond order of the M–CO bonds, particularly that in the *trans*-position. The regular octahedral co-ordination geometry usually adopted by the Group VI metals, Cr, Mo, and W, makes them particularly useful for this purpose.

There has been considerable interest in ligands such as carbenes,[1-3] and in phosphorus-containing ligands such as triphenylphosphine and triphenyl phosphite[4] in complexes of this type, but no structural data is available for ligands in which a chalcogen atom, S or Se, is bonded to the metal. The crystal structure of pentacarbonyl-(triphenylphosphine sulphide)chromium(0), first prepared and characterised by Ainscough *et al.*,[5] has therefore been determined in order to investigate the nature of the Cr–S bond and obtain accurate structural data for the whole molecule. It was also noted[5] that the i.r. spectrum of $Cr(CO)_5SPMe_3$ does not show the C_{4v} symmetry usually characteristic of $ML(CO)_5$ complexes. It was therefore of interest to see whether this could be accounted for by interaction between the $SPMe_3$ ligand and one or more of the *cis*-carbonyl groups.

EXPERIMENTAL

$Cr(CO)_5SPMe_3$ was crystallised from a benzene–hexane solution as clear yellow blocklike crystals, sometimes elongated to thin needles. The space-group and approximate cell dimensions were obtained from oscillation and Weissenberg photographs. More accurate cell parameters were obtained from a least-squares treatment of the positions of 12 general reflections on a four-circle X-ray diffractometer.

Crystal Data.—$C_8H_9CrO_5PS$, $M = 300$, Monoclinic, $a = 6{\cdot}445(1)$, $b = 18{\cdot}752(3)$, $c = 10{\cdot}897(2)$ Å, $\beta = 90{\cdot}12(2)°$, $U = 1316$ Å^3, $D_m = 1{\cdot}51(1)$ gm cm^{-3} (by flotation), $Z = 4$, $D_c = 1{\cdot}514$ g cm^{-3}. Mo-K_α Radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 12·1 cm^{-1}. Space-group $P2_1/n$ from systematic absences.

Data Collection and Reduction.—Intensity measurements were made with a computer-controlled Hilger and Watts four-circle X-ray diffractometer, by use of Mo-K_α radiation and a crystal of dimensions 0·03 × 0·015 × 0·015 cm. A θ—2θ scan, of 60 steps of 0·01°, was made through each reflection, with a count of 1 s at each step and a background count of 10 s at the beginning and end of the scan. Standard reflections were monitored at frequent intervals to check for possible crystal deterioration or misalignment. All hkl and $\bar{h}kl$ reflections were measured up to θ 27°, giving a total of 2900 reflections. Those for which the intensity $I_{hkl} < 1{\cdot}5\sigma(I_{hkl})$ were considered unobserved and omitted from the refinement, and after taking the weighted mean for equivalent reflections which had been measured more than once, a total of 2002 independent reflections remained. The usual Lorentz and polarisation corrections were applied, but no correction was made for absorption.

Structure Determination.—A three-dimensional Patterson synthesis, with coefficients sharpened to describe point atoms, revealed the positions of the chromium, sulphur, and phosphorus atoms. A Fourier synthesis, phased by these three atoms, then revealed the remaining light atom positions. Least-squares refinement, by use of the block-diagonal approximation, was then undertaken.[6] The weighting scheme applied weights $w = 1/[1 + (F_o - b)^2/a^2]$, with a and b chosen to give approximately constant values of $\Sigma w(|F_o| - |F_c|)^2$ over ranges of $|F_o|$. With individual isotropic temperature factors for all atoms, R was reduced to 0·110. The assumption of anisotropic temperature factors for all atoms further reduced R to 0·081 before refinement again converged. At this stage a difference-Fourier synthesis clearly revealed 5 of the 9 hydrogen atom positions. The remaining 4 were less obvious, but were included in positions compatible both with the difference map and with normal tetrahedral geometry. Further least-squares refinement, in which the hydrogen atoms were not refined but were included in the structure-factor calculation, with isotropic temperature factors B 7·5 Å^2, reduced R to 0·069. A further difference-Fourier, following a structure-factor calculation from which hydrogen atoms were omitted, gave improved positions for the 9 hydrogen atoms and was otherwise relatively featureless. A final three cycles of least-squares refinement of the non-hydrogen atoms, with hydrogen atoms included in their new positions, yielded R 0·065.

The final atomic co-ordinates and temperature parameters are listed in Table 1, and calculated bond lengths and angles in Table 2. The atomic numbering system for non-hydrogen atoms is shown in the Figure; the

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[6] G. A. Mair, SFLS program for IBM 1620.

TABLE 1

Final atomic co-ordinates, with standard deviations in parentheses, and anisotropic thermal parameters * ($\times 10^4$)

Atom	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Cr	0·0446(2)	0·0896(1)	0·2427(1)	231	27	90	−4	17	−6
S	0·2008(2)	0·2116(1)	0·2465(1)	263	28	148	−6	−3	−3
P	−0·0124(2)	0·2884(1)	0·2479(1)	294	28	97	−4	−20	5
C(1)	0·0511(7)	−0·0013(2)	0·2357(4)	296	37	123	−14	22	−14
C(2)	0·2932(6)	0·0613(2)	0·1637(4)	327	35	118	−4	23	1
C(3)	0·1706(7)	0·0674(2)	0·3974(4)	317	41	110	7	2	−32
C(4)	−0·0792(7)	0·1067(2)	0·0870(4)	324	38	102	−6	8	3
C(5)	−0·2019(6)	0·1140(2)	0·3262(4)	291	37	105	−2	20	−29
O(1)	−0·1153(5)	0·0586(2)	0·2301(3)	468	35	201	−13	59	−58
O(2)	0·4405(5)	0·0420(2)	0·1168(3)	375	61	196	−42	150	45
O(3)	0·2381(6)	0·0497(2)	0·4872(4)	518	74	129	50	−101	−37
O(4)	−0·1520(5)	0·1132(2)	−0·0052(3)	535	68	116	−7	−115	10
O(5)	−0·3545(5)	0·1250(2)	0·3777(3)	342	64	179	−7	140	10
C(6)	0·1111(8)	0·3709(3)	0·2106(5)	377	34	149	15	−36	−25
C(7)	−0·1321(8)	0·3005(3)	0·3950(5)	470	55	108	−10	40	72
C(8)	−0·2203(7)	0·2778(3)	0·1394(4)	356	59	137	−4	−128	9
H(61)	0·182	0·355	0·122						
H(62)	0·250	0·370	0·277						
H(63)	−0·030	0·410	0·200						
H(71)	−0·010	0·312	0·431						
H(72)	−0·130	0·249	0·455						
H(73)	−0·265	0·340	0·396						
H(81)	−0·166	0·278	0·043						
H(82)	−0·300	0·325	0·150						
H(83)	−0·292	0·239	0·183						

* In the form: $f = f_0 \exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{23}hl + 2b_{13}hl + 2b_{12}hk)$.

numbering of the hydrogen atoms is consistent with that of the carbon atoms to which they are attached. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20778 (5 pp.).*

TABLE 2

(*a*) Bond lengths (Å), with standard deviations in parentheses

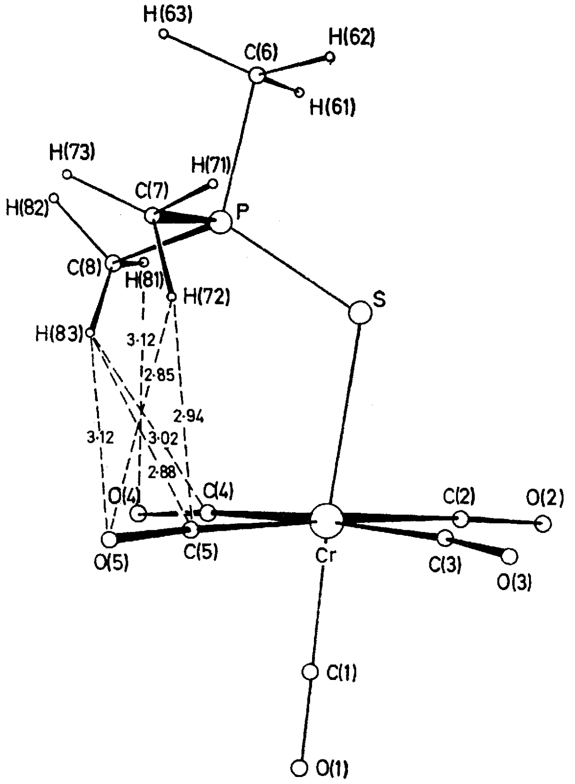
Cr–S	2·510(2)	C(3)–O(3)	1·121(10)
Cr–C(1)	1·815(8)	C(4)–O(4)	1·115(10)
Cr–C(2)	1·896(8)	C(5)–O(5)	1·152(9)
Cr–C(3)	1·916(8)	C(6)–H(61)	1·11
Cr–C(4)	1·900(7)	C(6)–H(62)	1·15
Cr–C(5)	1·889(7)	C(6)–H(63)	1·17
S–P	1·990(3)	C(7)–H(71)	0·90
P–C(6)	1·787(8)	C(7)–H(72)	1·17
P–C(7)	1·794(9)	C(7)–H(73)	1·13
P–C(8)	1·796(9)	C(8)–H(81)	1·11
C(1)–O(1)	1·152(10)	C(8)–H(82)	1·03
C(2)–O(2)	1·138(10)	C(8)–H(83)	0·99

(*b*) Bond angles (deg.), with standard deviations in parentheses

C(1)–Cr–S	173·4(2)	C(5)–Cr–S	96·3(2)
C(1)–Cr–C(2)	90·3(3)	Cr–S–P	112·5(1)
C(1)–Cr–C(3)	88·6(3)	Cr–C(1)–O(1)	178·5(6)
C(1)–Cr–C(4)	88·8(3)	Cr–C(2)–O(2)	177·7(7)
C(1)–Cr–C(5)	87·8(3)	Cr–C(3)–O(3)	175·0(8)
C(2)–Cr–S	85·6(2)	Cr–C(4)–O(4)	176·5(7)
C(2)–Cr–C(3)	88·9(3)	Cr–C(5)–O(5)	176·3(7)
C(2)–Cr–C(4)	89·7(3)	S–P–C(6)	108·5(3)
C(2)–Cr–C(5)	177·3(3)	S–P–C(7)	113·3(3)
C(3)–Cr–S	90·8(2)	S–P–C(8)	115·4(3)
C(3)–Cr–C(4)	176·9(3)	C(6)–P–C(7)	106·7(4)
C(3)–Cr–C(5)	89·1(3)	C(6)–P–C(8)	106·1(4)
C(4)–Cr–S	91·7(2)	C(7)–P–C(8)	106·3(4)
C(4)–Cr–C(5)	92·1(3)		
P–C(6)–H(61)	99	H(71)–C(7)–H(72)	87
P–C(6)–H(62)	101	H(71)–C(7)–H(73)	120
P–C(6)–H(63)	103	H(72)–C(7)–H(73)	122
H(61)–C(6)–H(62)	103	P–C(8)–H(81)	113
H(61)–C(6)–H(63)	114	P–C(8)–H(82)	102
H(62)–C(6)–H(63)	132	P–C(8)–H(83)	97
P–C(7)–H(71)	93	H(81)–C(8)–H(82)	105
P–C(7)–H(72)	113	H(81)–C(8)–H(83)	127
P–C(7)–H(73)	115	H(82)–C(8)–H(83)	110

DISCUSSION

The compound has the expected octahedral co-ordination about the central chromium atom. The octahedron is slightly distorted, the principal axes deviating from linearity as follows: C(1)–Cr–S 173·4(2), C(2)–Cr–C(5) 177·3(2), and C(3)–Cr–C(4) 176·9(3)°.



A view of the molecule, showing closest intramolecular contacts (Å) between the methyl groups and the equatorial carbonyl groups

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-size copies.)

Such deviations are commonly observed in substituted hexacarbonylchromium compounds.[1-3,7-9] The chromium atom lies 0·04 Å above a least-squares plane through the four equatorial carbon atoms C(2)—(5) (see Table 3), in the direction of the $SPMe_3$ ligand, while the four equatorial carbonyl oxygen atoms, O(2)—(5), all lie 0·06—0·13 Å below this plane. Such an 'umbrella-like' configuration is also seen in the structures of [diethylamino(methyl)carbene]-[2] and (phenylmethoxycarbene)-pentacarbonylchromium(0).[1]

TABLE 3

Equations of * least-squares planes through atomic positions, with, in square brackets, distances (Å) of relevant atoms from the planes

Plane (i): C(2)—(5)

$$0{\cdot}3220X + 0{\cdot}9452Y + 0{\cdot}0531Z - 1{\cdot}791 = 0$$

[C(2) 0·006, C(3) −0·006, C(4) −0·006, C(5) 0·006, Cr 0·037, O(2) −0·056, O(3) −0·128, O(4) −0·093, O(5) −0·087]

Plane (ii): S, C(1), C(2), C(5)

$$-0{\cdot}4276X + 0{\cdot}1990Y - 0{\cdot}8818Z + 2{\cdot}148 = 0$$

[S 0·009, C(1) 0·013, C(2) −0·011, C(5) −0·010, Cr 0·021, O(1) 0·030, O(2) −0·039, O(5) −0·043]

Plane (iii): S, C(1), C(3), C(4)

$$-0{\cdot}8255X + 0{\cdot}3242Y + 0{\cdot}4620Z - 1{\cdot}489 = 0$$

[S −0·021, C(1) −0·030, C(3) 0·025, C(4) 0·025, Cr 0·049, O(1) −0·065, O(3) 0·013, O(4) 0·014]

* In the equations, X, Y, and Z refer to orthogonal coordinates obtained by the transformation:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix}$$

The length of the Cr–S bond is 2·510(2) Å. Because of the paucity of structural data for similar complexes, no direct comparison can be made with other Cr^0–S bonds. Distances of 2·42—2·46 and 2·42—2·43 Å have been reported for Cr^{III}–S bonds in the chromium sulphides[10] and tris(diethyl dithiophosphate) chromium(III)[11] respectively. These would, however, be expected to be shorter than the corresponding bonds in compounds of Cr^0 because of the smaller covalent radius of Cr^{III}. The calculated length of a single Cr^0–S bond is 2·52 Å, taking the covalent radius of Cr^0 as 1·48 (ref. 8) and the covalent radius of sulphur as 1·04 Å.[12] It seems probable, therefore, that the Cr–S distance of 2·510(2) Å in $Cr(CO)_5SPMe_3$ represents an essentially single bond, and that the sulphur ligand is co-ordinated to the chromium atom by simple σ donation, with little or no π interaction.

Further support for this conclusion can be found in the Cr–C bond lengths in the molecule. It is generally accepted that in compounds of the type $ML(CO)_5$ a lack of multiple bonding in the M–L bond allows greater π interaction in the M–C bonds, particularly that in the *trans*-position. The *cis*- and *trans*-Cr–C bond lengths observed in a variety of substituted derivatives of $Cr(CO)_6$ are shown in Table 4, and compared with the value in $Cr(CO)_6$ itself. Where appreciable Cr–L π bonding occurs, as in carbene derivatives,[1-3] the *cis*- and *trans*-Cr–C distances are very similar, only very slight shortening of the *trans*-bond being observed. For ligands of lesser π bonding ability, such as triphenylphosphine and triphenyl phosphite,[4] the *trans*- is significantly shorter than the *cis*-Cr–C bonds, which in turn are shorter than those in $Cr(CO)_6$. Where the ligand has no π bonding ability, as with diethylenetriamine, with co-ordinated nitrogen atoms. the shortening of the *trans*-Cr–C bonds is considerably more marked.

TABLE 4

Cr–C bond lengths (Å)

Compound	*cis*-Cr–C (mean)	*trans*-Cr–C
$Cr(CO)_6$ [a]	1·909(3)	
$Cr(CO)_5[C(SPh)Me]$ [b]	1·910(2)	1·899(3)
$Cr(CO)_5[C(Ph)OMe]$ [c]	1·89(1)	1·87(3)
$Cr(CO)_5(PPh_3)$ [d]	1·880(4)	1·844(4)
$Cr(CO)_5[P(OPh)_3]$ [d]	1·896(4)	1·861(4)
$Cr(CO)_4$(diphos) [e,f]	1·884(7)	1·831(7) (mean)
$Cr(CO)_3$(dien) [g,h]		1·816(5) (mean)
$Cr(CO)_5(SPMe_3)$ [i]	1·900(4)	1·815(8)

[a] Ref. 13. [b] Ref. 3. [c] Ref. 1. [d] Ref. 4. [e] diphos = 1,2-Bis-(diphenylphosphino)ethane. [f] Ref. 9. [g] dien = Diethylenetriamine. [h] Ref. 8. [i] This work.

In $Cr(CO)_5SPM_3$, the four *cis*-Cr–C bonds have lengths of 1·889—1·916(8), mean 1·900(4) Å, slightly, but not significantly, shorter than the Cr–C distance of 1·909(3) Å found in $Cr(CO)_6$.[13] The Cr–C bond *trans* to the $SPMe_3$ ligand, however, has a length of 1·815(8) Å, considerably shorter than the *cis*-Cr–C bonds and the Cr–C bonds in $Cr(CO)_6$. Moreover, the extent of this shortening is almost identical with that in $Cr(CO)_3$(diethylenetriamine)[8] [where the mean *trans*-Cr–C distance is 1·816(5) Å], and is therefore consistent with a single Cr–S bond.

The C–O distances in the co-ordinated carbonyl groups are not expected to reflect changes in bond order so clearly.[14] Nevertheless, although the four *cis*-C–O bonds range from 1·115(10) to 1·152(9) Å, their mean [1·131(5) Å] is slightly less than that of the *trans*-C–O bond [1·152(10) Å]. This is the predicted behaviour, since an increase in the bond order of the *trans*-Cr–C bond should be accompanied by a decrease in the bond order (and hence increase in bond length) of the associated C–O bond. Thus, as in similar compounds,[4,9] the lengthening of the *trans*-C–O bond, although not statistically significant, is in the expected

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direction. The carbonyl groups are co-ordinated in the usual angular fashion, the angles Cr–C–O ranging from 175·0(8) to 178·5(6)°.

Bond lengths and angles within the $SPMe_3$ ligand show that its geometry changes little on co-ordination. The S–P distance is 1·990(3) Å, compared with that of 1·959(2) Å in the free ligand.[15] As has also been observed in the structure of $Cu(SPMe_3)_3ClO_4$,[15] where the S–P bond length is 1·994(17) Å, the bond order of the S–P bond therefore changes little on co-ordination. This is again consistent with a lack of π interaction between the metal atom and the $SPMe_3$ ligand. The Cr–S–P bond angle of 112·5(1)° is slightly higher than the values in $Cu(SPMe_3)_3ClO_4$, *viz.* 104·4(3)—110·3(3)°. P–C distances are as expected, 1·787(8)—1·796(9) Å [*cf.* free $SPMe_3$ 1·798(2), $Cu(SPMe_3)_3ClO_4$ 1·793(8) Å]. The angles about the phosphorus atom are approximately tetrahedral [106·1(4)—115·4(3)°].

The relative dispositions of the methyl groups of the $SPMe_3$ ligand and the equatorial carbonyl groups are shown in the Figure. The closest approaches involve hydrogen atoms H(72) and H(83) and the atoms C(5) and O(5). The bond C(5)–O(5) is slightly longer [1·152(9) Å)] than the mean value for the other three equatorial C–O bonds [1·125(6) Å] but the distances of *ca.* 2·9 Å between the hydrogen atoms and this carbonyl group are too long to imply any significant interaction such as a C–H · · · O hydrogen bond. Thus no explanation in terms of an attractive interaction can be offered for the departure from C_{4v} symmetry seen in the i.r. spectrum. Indeed, some minor distortions in the molecule could be attributed to slight steric repulsion between the methyl groups and carbonyl groups (4) and (5). Thus the angles C(5)–Cr–S [96·5(2)°], Cr–S–P [112·5(1)°], S–P–C(8) [115·4(3)°], and S–P–C(7) [113·3(3)°] are all slightly larger than usual so as to increase the separation between the $SPMe_3$ ligand and the equatorial carbonyl groups. Any such steric repulsion must be very slight, however, in view of the interatomic distances (Figure), and can not be said significantly to affect the length of the Cr–S bond.

The molecules are separated, in the crystal, by normal van der Waals distances, the shortest of these being listed in Table 5.

TABLE 5

Closest intermolecular approaches (Å)

$C(1) \cdots H(62^{I})$	3·10	$O(2) \cdots O(4^{III})$	3·23
$C(1) \cdots H(63^{II})$	3·25	$O(2) \cdots H(63^{I})$	3·23
$C(3) \cdots O(5^{III})$	3·25	$O(3) \cdots O(5^{III})$	3·21
$C(4) \cdots H(73^{IV})$	3·07	$O(3) \cdots H(63^{VIII})$	2·86
$O(1) \cdots O(3^{V})$	3·19	$O(3) \cdots H(82^{VIII})$	2·95
$O(1) \cdots O(4^{VI})$	3·17	$O(4) \cdots H(62^{IX})$	2·47
$O(1) \cdots H(62^{I})$	2·71	$O(4) \cdots H(71^{IX})$	2·79
$O(1) \cdots H(63^{II})$	2·48	$O(4) \cdots H(73^{IV})$	2·86
$O(1) \cdots H(73^{II})$	2·47	$O(5) \cdots H(61^{X})$	2·70
$O(1) \cdots H(82^{II})$	2·60	$O(5) \cdots H(81^{X})$	3·26
$O(2) \cdots O(2^{VII})$	3·09		

Roman numerals as superscripts refer to the following equivalent positions, relative to the reference molecule at x, y, z:

I $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
II $-\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
III $1 + x, y, z$
IV $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$
V $-x, -y, 1 - z$
VI $-x \ -y, -z$
VII $1 - x, -y, -z$
VIII $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
IX $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$
X $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$

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