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The Crystal Structure of Chromium Hexacarbonyl

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Chromium hexacarbonyl crystallizes in the orthorhombic system, with cell dimensions $a=11{\cdot}769\pm0{\cdot}012$, $b=11{\cdot}092\pm0{\cdot}011$, $c=6{\cdot}332\pm0{\cdot}006$ Å. The space group is *Pnma* and there are four molecules per unit cell. Least-squares refinement has been completed on three-dimensional data (940 structure factors within the Cu $K\alpha$ sphere) for both Cr–C–O and Cr–O–C configurations. The former configuration has been shown to be correct and the final residual is 7·8 %. The structure consists of chromium hexacarbonyl molecules linked by van der Waals forces. The molecule is octahedral, the mean bonding distances (uncorrected for thermal vibration) are $1{\cdot}909\pm0{\cdot}003$ Å for chromium–carbon and $1{\cdot}137\pm0{\cdot}004$ Å for carbon–oxygen. The Cr–C–O bond is collinear within 1·8°. There are no abnormally short intermolecular distances. The thermal vibrations have been analysed and these suggest that probably the best values for the bond lengths are those corrected for riding motion. These mean bonding distances are 1·916 Å for chromium–carbon and 1·171 Å for the carbon–oxygen.

Introduction

The valence bond theory and the molecular orbital theory predict different results for the chromium–carbon bond in chromium hexacarbonyl. The former suggests that the bonding consists of six σ hybrid bonds alone, giving a bond order of unity, while the latter suggests that there may in addition be three π bonds which would increase the bond order to a maximum of 1·5.

Emeléus & Anderson (1960) suggested that the π bonding will increase progressively as carbonyl groups in chromium hexacarbonyl are successively replaced by σ bonding or weakly π bonding ligands, and it follows that one way of resolving the difference between the theories would be to compare the lengths of the chromium–carbon bonds in chromium hexacarbonyl and a series of its substitution products, several of which have already been prepared (Nigam, Nyholm & Stiddard, 1960; Nyholm, 1964).

There have been two attempts to evaluate the bond lengths of chromium hexacarbonyl; by X-ray diffraction (Rüdorff & Hofmann, 1935), and by electron diffraction from the vapour (Brockway, Ewens & Lister, 1938). The values obtained for the chromium–carbon bond length were 1·80 and 1·92 Å respectively. In view of the difference between these values the crystal structure was redetermined. Neither of these investigators was able to show that the atomic configuration was chromium–carbon–oxygen and not chromium–oxygen–carbon. This has also been examined.

Experimental

Chromium hexacarbonyl powder, obtained from E.I. Du Pont de Nemours & Co., by courtesy of Professor R.S. Nyholm, was recrystallized from methylcyclohexane. The crystals were generally needles of hexagonal cross section parallel to **c**, but platelets lying on (100) were also obtained. The prominent faces of the needles were indexed as of the forms {010} and {210}. The calculated angles are $\widehat{010\;210}$: 62·05° and $\widehat{210\;\bar{2}10}$: 55·9°. The crystal optics, morphology and Laue symmetry indicated that the crystals belong to the orthorhombic system.

The cell dimensions were determined by Farquhar & Lipson's (1946) method from oscillation photographs taken with copper radiation (Cu $K\alpha_1=1{\cdot}54050$ Å, Cu $K\alpha_2=1{\cdot}54434$ Å, Cu $K\beta=1{\cdot}39217$ Å) and are

$$a=11{\cdot}769\pm0{\cdot}012\text{ Å}$$
$$b=11{\cdot}092\pm0{\cdot}011$$
$$c=\ 6{\cdot}332\pm0{\cdot}006\,.$$

The measured density (by flotation) is $1{\cdot}769\pm0{\cdot}003$ g.cm^{-3}, and that calculated for $Z=4$ is $1{\cdot}768\pm0{\cdot}003$ g.cm^{-3}.

Systematic absences ($0kl$ absent when $k+l=2n+1$, $hk0$ when $h=2n+1$) were determined from Weissenberg photographs and indicate the space group to be either $Pn2_1a$ or *Pnma*. Structures based on both space groups were refined and for a variety of reasons, discussed in detail in the succeeding paper (Whitaker & Jeffery, 1967) it was concluded that the correct space group was *Pnma*. This space group requires that the chromium hexacarbonyl molecule should possess either $\bar{1}$ or m symmetry.

The $hk0$ reflexions had pseudo-hexagonal symmetry and were very strong when $h+2k=4n$ but very weak when $h+2k=4n+2$.

Cylindrical crystals parallel to **b** and **c** were obtained by allowing needle shaped crystals to sublime. The diameters were $0{\cdot}202\pm0{\cdot}015$ mm and $0{\cdot}168\pm0{\cdot}010$ mm respectively. The crystals were then coated with Bostik no. 1 to avoid further sublimation.

The intensity data were collected on double film equi-inclination integrating Weissenberg photographs taken about the *b* and *c* axes with filtered copper radiation. The precautions necessary to obtain highly accurate measurements (Jeffrey & Whitaker, 1965) were carried out. In this way the intensities of 798 independent reflexions were estimated. Those reflexions too weak to measure (another 142) were given half the intensity of the weakest measurable reflexions.

The observed intensities were corrected for absorption and Lorentz–polarization factors. The two sets of photographs were correlated by the method of Rollett & Sparks (1960), and the scale factor and average temperature factor were obtained by Wilson's (1942) method.

During the course of collecting the intensity data, powder diffraction lines began to appear on the Weissenberg photographs and the specimen appeared to turn brown. This was shown to be due to the effect of X-rays on the Bostik coating.

Structure determination and refinement

Initial attempts to solve the structure from the *b*- and *c*-axis projection failed. The positions of the chromium atoms were obtained successfully from Patterson projections, and possible positions of the other atoms were derived from Fourier syntheses phased only on the chromium atoms. However, the proposed structure would not refine although the octahedral symmetry of the molecule was apparent.

The three dimensional Patterson synthesis gave two possible sets of position parameters for the structure (Table 1), the configuration Cr–C–O again being assumed.

Table 1. *Coordinates for structures obtained from the Patterson syntheses*

	*P*1			*P*2		
	x	*y*	*z*	*x*	*y*	*z*
C	0·125	0·25	0·063	0·125	0·25	0·063
C(1)	0·21	0·25	0·31	0·03	0·25	0·31
C(2)	0·03	0·25	0·81	0·21	0·25	0·81
C(3)	0·02	0·37	0·18	0·22	0·37	0·18
C(4)	0·22	0·37	0·94	0·02	0·37	0·94
C(5)	0·02	0·13	0·18	0·22	0·13	0·18
C(6)	0·22	0·13	0·94	0·02	0·13	0·94
O(1)	0·27	0·25	0·46	0·97	0·25	0·46
O(2)	0·97	0·25	0·66	0·27	0·25	0·66
O(3)	0·97	0·45	0·24	0·27	0·45	0·24
O(4)	0·27	0·45	0·88	0·97	0·45	0·88
O(5)	0·97	0·05	0·24	0·27	0·05	0·24
O(6)	0·27	0·05	0·88	0·97	0·05	0·88

The residuals from (*a*) the initial data, and (*b*) after a single cycle of least-squares refinement using individual isotropic temperature factors, were:

	(*a*)	(*b*)
*P*1	23·2%	12·6%
*P*2	36·4%	37·1% .

In addition, the output for the second crystal structure gave negative temperature factors for two oxygen atoms. Because of this and the increased value of the residual the refinement of this structure was discontinued.

The atomic scattering factors used for chromium, oxygen and carbon were those from *International Tables for X-ray Crystallography* (1962, p. 201) but a correction for dispersion was applied to the chromium, the scattering factor used being the modulus of the complex scattering factor after the corrections for dispersion had been applied (*International Tables for X-ray Crystallography*, 1962, p. 213).

[In the following paper (Whitaker & Jeffery, 1967), corrections for anomalous dispersion of the chromium were not applied. This accounts for the very slight differences in bond lengths (0·0003 Å) and bond angles (0·01 °) between the results quoted there and here.]

The structure was then refined by diagonal matrix least-squares [Diamand (1964), based on Cruickshank's method (Pepinsky, Robertson & Speakman, 1961)] for both isotropic and anisotropic temperature factors, until the recommended shifts were less than one tenth of the appropriate standard deviations (Mason, 1964). The final parameters for the isotropic temperature refinement are given in Table 2 and those for the anisotropic temperature refinement in Table 3. The residuals for the isotropic and anisotropic temperature refinements were 10·1% and 7·8% respectively, while the standard deviations of the electron density were 0·194 and 0·167 e.Å^{-3} respectively. Standard deviations are derived from the least-squares matrix.

Table 2. *Parameters and standard deviations after isotropic refinement*

	x	*y*	*z*	*B*
Cr	0·1278 (1)	0·2500 (0)	0·0638 (2)	2·72 (2)
C(1)	0·2175 (7)	0·2500 (0)	0·3092 (14)	3·56 (14)
C(2)	0·0396 (7)	0·2500 (0)	0·8091 (15)	3·76 (14)
C(3)	0·0326 (5)	0·1296 (5)	0·1828 (9)	3·51 (9)
C(4)	0·2225 (4)	0·1287 (6)	0·9488 (9)	3·50 (9)
O(1)	0·2717 (6)	0·2500 (0)	0·4631 (12)	5·41 (15)
O(2)	0·9867 (6)	0·2500 (0)	0·6612 (12)	5·33 (15)
O(3)	0·9730 (4)	0·0571 (5)	0·2488 (7)	5·27 (10)
O(4)	0·2785 (5)	0·0540 (5)	0·8725 (8)	5·74 (11)

Comparison of the observed and calculated structure factors* indicates that for some intense reflexions, *e.g.* 020, 040, 060, 210, 230 and 231, the observed structure factors are smaller than the calculated ones. This is probably due to extinction. No corrections were applied to these reflexions and they were included in the refinement.

Fourier syntheses were calculated on sections perpendicular to **b** passing through the centers of the atoms. A composite diagram of these sections is given in Fig. 1. The signs of the structure factors in these syntheses were obtained from the anisotropic refinement.

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* Copies of the table (Whitaker, 1965) may be obtained from the authors.

Table 3. *Parameters and standard deviations after anisotropic refinement*

Positions

	x	y	z
Cr	0·1278 (1)	0·2500 (0)	0·0638 (1)
C(1)	0·2173 (5)	0·2500 (0)	0·3117 (11)
C(2)	0·0392 (5)	0·2500 (0)	0·8077 (11)
C(3)	0·0320 (4)	0·1288 (4)	0·1830 (7)
C(4)	0·2227 (3)	0·1275 (4)	0·9466 (7)
O(1)	0·2712 (5)	0·2500 (0)	0·4634 (8)
O(2)	0·9865 (4)	0·2500 (0)	0·6625 (9)
O(3)	0·9734 (3)	0·0567 (3)	0·2494 (5)
O(4)	0·2781 (3)	0·0540 (3)	0·8726 (6)

Vibrations ($\times 10^5$)

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
Cr	51 (1)	50 (1)	175 (2)	0	−2 (2)	0
C(1)	67 (4)	79 (6)	216 (16)	0	9 (15)	0
C(2)	74 (4)	80 (6)	210 (15)	0	16 (16)	0
C(3)	69 (3)	66 (4)	226 (10)	−24 (12)	−11 (10)	2 (6)
C(4)	64 (3)	74 (4)	243 (11)	−34 (13)	12 (10)	−3 (6)
O(1)	98 (4)	142 (7)	245 (14)	0	−104 (13)	0
O(2)	98 (4)	149 (7)	258 (14)	0	−87 (14)	0
O(3)	96 (3)	95 (4)	359 (12)	55 (11)	56 (9)	−68 (6)
O(4)	95 (3)	101 (4)	436 (14)	−105 (13)	33 (10)	58 (6)

The temperature factor is defined by $\exp\left[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+klB_{23}+lhB_{31}+hkB_{12})\right]$.

Test of atomic configuration Cr–O–C

Starting with the atomic coordinates of Table 2, the structure was again refined with the use of isotropic temperature factors but assuming the atomic configuration Cr–O–C.

The final parameters and standard deviations obtained are given in Table 4.

Table 4. *Parameters and standard deviations after isotropic refinement assuming atomic configuration* Cr–O–C

	x	y	z	B
Cr	0·1279 (2)	0·2500 (0)	0·0646 (4)	2·48 (3)
O(1)	0·2160 (14)	0·2500 (0)	0·3135 (28)	5·73 (32)
O(2)	0·0420 (14)	0·2500 (0)	0·8085 (28)	5·82 (33)
O(3)	0·0304 (10)	0·1278 (10)	0·1846 (18)	5·93 (23)
O(4)	0·2239 (9)	0·1272 (11)	0·9498 (17)	5·58 (22)
C(1)	0·2729 (14)	0·2500 (0)	0·4630 (28)	3·34 (28)
C(2)	0·9888 (13)	0·2500 (0)	0·6584 (27)	3·12 (26)
C(3)	0·9731 (10)	0·0582 (11)	0·2490 (16)	3·11 (19)
C(4)	0·2783 (10)	0·0537 (11)	0·8760 (18)	3·48 (21)

Comparison of the temperature factors in Table 4 with those in Table 2 shows little difference. In Table 2 the temperature factors for the carbon atoms are in the range 3·5 to 3·8 and for the oxygen atoms 5·3 to 5·7. With the Cr–O–C configuration the temperature factors are in the range 3·1 to 3·5 for carbon and 5·6 to 5·9 for oxygen. However, it is reasonable to expect that the amplitude of vibration will increase as one proceeds outward along each Cr–C–O chain of atoms. This is found if the atomic configuration is Cr–C–O (Table 2), but if the configuration is Cr–O–C the central atom vibrates more than the outermost one even though the latter is less constrained by neighbouring atoms.

Further comparison of Table 2 and Table 4 shows that for the sequence Cr–O–C the standard deviation of position parameters is considerably worse, generally by a factor of about two, while the differences of the parameters in the two Tables are not significant compared with the larger standard deviation of each pair of parameters (the maximum difference is 2·3 times the appropriate standard deviation). The standard deviations for the temperature factors are also worse by a factor of 1½ to 3, depending on the atom.

In addition it is found that both the residual and the standard deviation of electron density for the configuration Cr–O–C are worse than for the configuration Cr–C–O, the residual being 16·3% compared with 10·1% and the standard deviation of electron density 0·343 e.Å^{-3} compared with 0·194 e.Å^{-3}.

A Fourier synthesis (Fig. 2) was calculated based on structure factors obtained from the parameters in (Table 4). In this the higher peaks are at the original oxygen positions, which certainly suggests the linkage Cr–C–O. There is very little difference between this Fourier synthesis and the one calculated for the linkage Cr–C–O with anisotropic temperature factors (Fig. 1). The reason for this was seen when the signs of the individual structure factors were examined. Of the 940 structure factors only 31 exhibit a change of sign between these two Fourier syntheses, and of these 31 only 5 have a structure factor greater than 4·0, the largest being 16·8 (421).

It would appear that the signs of structure factors less than 4 are more sensitive to small changes in parameters than those of greater amplitude, as there are 15 changes of sign when the configuration Cr–C–O is refined with anisotropic temperature factors compared with isotropic temperature factors and the largest of these structure factors is 3·9.

The structure Cr–O–C was also refined with anisotropic temperature factors to give the parameters in Table 5. Comparison of Table 5 with Table 3 again shows that the standard deviations of the coordinates are worse by a factor of two or three, but in this case some of the parameters are significantly different in the two cases (four are greater than 3σ and the largest is $4\cdot4\sigma$, where σ is the larger standard deviation of each pair). The standard deviations of the temperature parameters are also worse by a factor of two or three.

The residual and standard deviation of electron density are also worse for the configuration Cr–O–C, the residual being 14·6% compared with 7·8% and the standard deviation of electron density 0·294 e.Å^{-3} compared with 0·167 e.Å^{-3}.

In view of this evidence there seems no doubt that the correct configuration in chromium hexacarbonyl is Cr–C–O. This compares with the results of Ladell, Post & Fankuchen (1952) who found the configuration in nickel tetracarbonyl to be Ni–C–O, and with Donohue & Caron (1964) who found a similar configuration in iron pentacarbonyl. The published electron-density diagrams of dicyclopentadienyldi-iron tetracarbonyl (Mills, 1958) also imply that it is the carbon that is bonded to the metal atom.

Discussion of the structure

Effect on intensities

It can be seen from Table 3 that the coordinates of the chromium atom are approximately $(\frac{1}{8}, \frac{1}{4}, \frac{1}{16})$. Inserting these values into the structure-factor formula shows that the chromium atoms only contribute to the $hk0$ reflexions when $h+2k=4n$. This explains the ob-

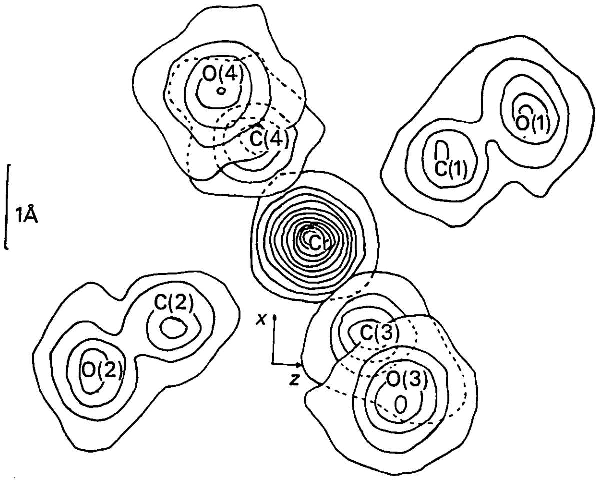

Fig. 1. Composite Fourier synthesis of sections through atomic peaks of the molecules assuming Cr–C–O bonding. The contouring is at intervals of 5 e.Å^{-3} about the chromium atom and 2 e.A^{-3} about the carbon and oxygen atoms. First contour zero.

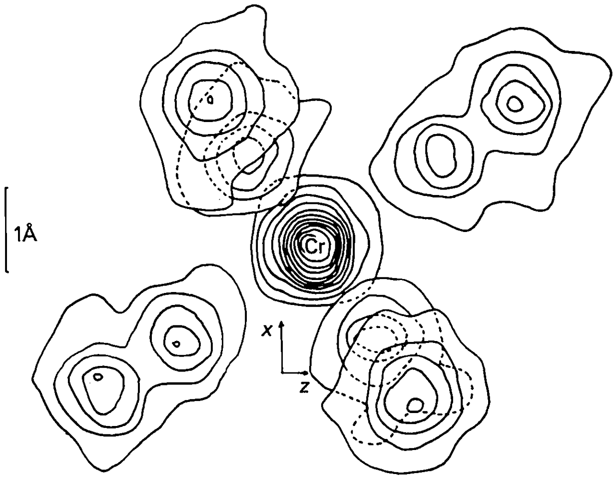

Fig. 2. Composite Fourier synthesis of sections through atomic peaks of the molecule assuming Cr–O–C bonding. The intervals of contouring are the same as in Fig. 1.

Table 5. *Parameters and standard deviations after anisotropic refinement assuming atomic configuration* Cr–O–C

Positions

	x	y	z
Cr	0·1279 (2)	0·2500 (0)	0·0645 (4)
O(1)	0·2163 (12)	0·2500 (0)	0·3122 (27)
O(2)	0·0422 (12)	0·2500 (0)	0·8012 (25)
O(3)	0·0292 (9)	0·1247 (10)	0·1880 (15)
O(4)	0·2257 (9)	0·1240 (10)	0·9464 (17)
C(1)	0·2719 (12)	0·2500 (0)	0·4624 (19)
C(2)	0·9874 (11)	0·2500 (0)	0·6619 (22)
C(3)	0·9735 (8)	0·0572 (9)	0·2502 (15)
C(4)	0·2776 (9)	0·0534 (9)	0·8716 (17)

Vibrations ($\times 10^5$)

	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
Cr	48 (1)	45 (1)	162 (4)	0	−1 (5)	0
O(1)	94 (10)	118 (15)	510 (56)	0	143 (46)	0
O(2)	94 (10)	152 (18)	368 (43)	0	78 (40)	0
O(3)	140 (9)	153 (12)	276 (24)	−149 (33)	98 (29)	51 (20)
O(4)	109 (8)	150 (13)	400 (32)	49 (38)	94 (30)	−74 (18)
C(1)	73 (10)	110 (17)	97 (29)	0	−137 (30)	0
C(2)	60 (9)	99 (16)	143 (31)	0	−101 (29)	0
C(3)	60 (6)	47 (8)	271 (29)	72 (23)	73 (21)	−81 (13)
C(4)	64 (7)	59 (10)	319 (32)	−120 (29)	63 (24)	74 (14)

servation that *hk*0 reflexions were very strong when $h+2k=4n$ and very weak when $h+2k=4n+2$.

Examination of the (001) projection shows that the chromium atoms lie on a distorted hexagonal array. Each chromium atom in projection has three pairs of chromium neighbours at distances of 5·885, 6·247 and 6·310 Å and adjacent pairs of these neighbours subtend angles of 62·6 (twice), 55·9 (twice) and 61·5° (twice) at the central atom. This explains the pseudo-hexagonal symmetry of the *hk*0 reflexions and the morphology of the needle-shaped crystals.

Molecular configuration

The molecule is octahedral and there is little or no deviation from the values expected for a regular octahedron (Table 6). The half height of the octahedron is constant within experimental error but there are small but statistically significant differences $(>3\sigma)$ from the angles expected for a regular octahedron. However, thermal displacements of the atoms will have some effect on these angles (Busing & Levy, 1964) and because of this it is thought that the small discrepancies (maximum 0·82°) are not physically significant.

Table 6. *Molecular configuration*

Interatomic distances	
Cr–O(1)	3·042 (5) Å
Cr–O(2)	3·037 (5)
Cr–O(3)	3·046 (4)
Cr–O(4)	3·053 (4)
Mean	3·046 (2)
Angles	
O(1)–Cr–O(3)	90·6 (1)°
O(1)–Cr–O(4)	90·5 (1)
O(2)–Cr–O(3)	89·8 (1)
O(2)–Cr–O(4)	89·2 (1)
O(3)–Cr–O(3*a*)	89·5 (1)
O(4)–Cr–O(4*a*)	90·8 (1)

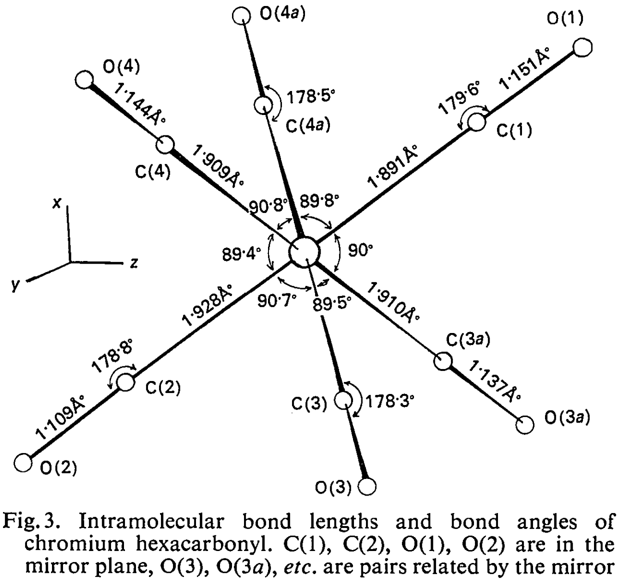

Fig. 3. Intramolecular bond lengths and bond angles of chromium hexacarbonyl. C(1), C(2), O(1), O(2) are in the mirror plane, O(3), O(3*a*), *etc.* are pairs related by the mirror plane.

The intramolecular bond lengths (uncorrected for thermal vibration) and bond angles are given in Table 7 and shown diagrammatically in Fig. 3.

Table 7. *Intramolecular bond lengths and bond angles*

Bond lengths			
Cr–C(1)	1·891 (7) Å	C(1)–O(1)	1·151 (8) Å
Cr–C(2)	1·928 (7)	C(2)–O(2)	1·109 (8)
Cr–C(3)	1·910 (4)	C(3)–O(3)	1·137 (6)
Cr–C(4)	1·909 (4)	C(4)–O(4)	1·143 (6)
Mean	1·909 (3)	Mean	1·137 (4)
Bond angles			
		C(1)–Cr–C(3)	90·0 (2)°
Cr–C(1)–O(1)	179·6 (6)°	C(1)–Cr–C(4)	89·8 (2)
Cr–C(2)–O(2)	178·8 (6)	C(2)–Cr–C(3)	90·7 (2)
Cr–C(3)–O(3)	178·3 (4)	C(2)–Cr–C(4)	89·4 (2)
Cr–C(4)–O(4)	178·5 (4)	C(3)–Cr–C(3a)	89·5 (3)
		C(4)–Cr–C(4a)	90·8 (3)

The mean bonding distances are

Cr–C 1·909 ± 0·003 Å
C–O 1·137 ± 0·004

and although one distance, C(2)–O(2), differs from the mean by $3{\cdot}4\sigma$ it is thought that the difference is not significant in view of the correction that may be required for thermal vibrations.

The minimum intramolecular non-bonding distances are

C–C 2·68 Å
C–O 3·58
O–O 4·27 .

The mean value of the chromium–carbon bond length is in good agreement with that of 1·92 ± 0·04 Å obtained by Brockway, Ewens & Lister (1938) but not in very good agreement with the X-ray results of Rüdorff & Hofmann (1935) who gave a value of 1·80 ± 0·05 Å. Part of the difference between the latter result and the present one may be accounted for by the consistently lower cell dimensions found by Rüdorff & Hofmann (1935).

The mean value of the carbon–oxygen bond length is in agreement with the value of 1·16 ± 0·05 Å found by Brockway, Ewens & Lister (1938). It is also in agreement with the values found by other investigators in similar substances, namely 1·15 ± 0·03 Å in nickel carbonyl (Ladell, Post & Fankuchen, 1952); 1·12 ± 0·04 Å in dicyclopentadienyldi-iron tetracarbonyl (Mills, 1958); 1·14 Å in MeC ⋮ CMe . $H_2Fe_2(CO)_8$ (Hock & Mills, 1961); 1·13 ± 0·02 Å in tetracarbonyl (acrylonitrile) iron (Luxmoore & Truter, 1962); 1·16 ± 0·01 Å in dimanganese decacarbonyl (Dahl & Rundle, 1963); 1·20 ± 0·02 Å in $[BrMn(CO)_4]_2$ (Dahl & Chin-Hsuan Wei, 1963); 1·12 ± 0·02 Å in iron pentacarbonyl (Donohue & Caron, 1964), and 1·17 Å in dicobalt octacarbonyl (Sumner, Klug & Alexander, 1964).

The bonding Cr–C–O is collinear within 1·8°. Although this non-linearity is 4·5σ, it is thought to be not significant in view of the lack of knowledge of the effect of the thermal vibrations on the angles (Busing & Levy, 1964).

Intermolecular relationship

Fig. 4 shows a *b*-axis projection of the atomic configuration with respect to the unit cell. The atoms are associated with two levels within the cell (the mirror planes at $y=\frac{1}{4}$ and $\frac{3}{4}$) and the molecules associated with the plane at $y=\frac{1}{4}$ are drawn bolder than the others. It can be seen from Fig. 4 that chromium hexacarbonyl consists of octahedral $Cr(CO)_6$ molecules linked together by van der Waals forces. All independent intermolecular distances below 3·4 Å, associated with one molecule, are given in Fig. 4.

The shortest intermolecular distances obtained were:

oxygen–oxygen 3·27 Å
carbon–oxygen 3·25 .

In spite of the fact that Rüdorff & Hofmann (1935) were able to determine only the positions of the chromium atoms, they were able to suggest the orientation of the molecule (assuming that it was octahedral) from a consideration of packing and the change of intensities on passing through the isomorphous series, chromium hexacarbonyl, molybdenum hexacarbonyl, tungsten hexacarbonyl.

The orientation suggested had the (111) face of the octahedron parallel to the (100) face of the unit cell and the [110] direction of the octahedron parallel to the *b* axis of the unit cell. Calculations show that the angle between the appropriate (111) faces of the octahedron and the (100) face of the unit cell is 5°, while the [110] direction of the octahedron must be parallel to the *b* axis because of the mirror plane in the cell. The orientation suggested was therefore substantially correct.

It is interesting to note that the model they suggested fits a centrosymmetric structure. Though they found only the chromium atom positions, they acknowledge that these could fit either a centrosymmetric or a non-centrosymmetric structure. It is thought, although there is no evidence for this, that they may have used the latter structure to allow greater tolerance in packing the molecules but did not consider whether their final model could fit the centrosymmetric space group.

Analysis of thermal vibrations

The r.m.s. thermal displacements along the vibration ellipsoid axes and the direction cosines of these axes are given in Table 8 together with the estimated errors of the thermal displacements. From this Table it can be seen that the vibration ellipsoids for the chromium and carbon atoms are approximately spherical. Although there is a small but significant variation from a sphere for the chromium atom there is no obvious

Table 8. *R.M.S. thermal displacements and orientation with respect to crystallographic axes*

	R.M.S. displacement	Direction cosines with respect to **a**	**b**	**c**
Cr	0·190 ± 1 Å	−0·809	0·000	0·588
	0·188 ± 1	0·588	0·000	0·809
	0·177 ± 1	0·000	1·000	0·000
C(1)	0·222 ± 8	0·000	1·000	0·000
	0·218 ± 8	0·905	0·000	0·425
	0·207 ± 8	−0·425	0·000	0·905
C(2)	0·229 ± 8	0·957	0·000	0·290
	0·223 ± 8	0·000	1·000	0·000
	0·204 ± 8	−0·290	0·000	0·957
C(3)	0·225 ± 8	−0·709	−0·339	0·618
	0·215 ± 8	0·702	−0·412	0·580
	0·197 ± 8	−0·058	−0·846	−0·530
C(4)	0·234 ± 8	0·248	−0·577	0·778
	0·211 ± 8	0·951	0·298	−0·082
	0·203 ± 8	0·185	−0·760	−0·623
O(1)	0·298 ± 8	0·000	1·000	0·000
	0·285 ± 8	−0·847	0·000	0·531
	0·194 ± 8	0·531	0·000	0·847
O(2)	0·305 ± 8	0·000	1·000	0·000
	0·281 ± 8	−0·851	0·000	0·526
	0·206 ± 8	−0·526	0·000	−0·851
O(3)	0·294 ± 8	−0·788	0·583	−0·195
	0·279 ± 8	0·069	0·399	0·914
	0·188 ± 8	0·611	0·707	−0·355
O(4)	0·315 ± 8	−0·145	−0·516	0·844
	0·284 ± 8	0·799	0·442	0·407
	0·197 ± 8	0·583	−0·734	−0·348

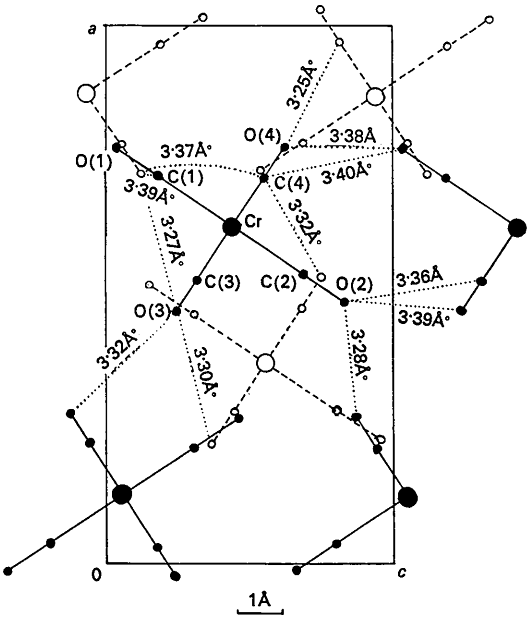

Fig. 4. The packing of chromium hexacarbonyl molecules in the unit cell, showing the independent intermolecular distances up to 3·4 Å.

reason for this. Also there appears to be no obvious relationship between the orientations of the vibration ellipsoids of the chromium and carbon atoms and the directions of neighbouring atoms.

In order to estimate the effect of the errors in the anisotropic temperature parameters on the magnitudes and orientations of the thermal ellipsoids, the latter were calculated not only for the anisotropic temperature parameters from the least-squares refinement but also for these values plus and minus the respective standard deviations. The effects of these errors on the direction cosines of the vibration ellipsoids of the chromium and carbon atoms are considerable; axial movements of up to 40° for the carbon atoms and 30° for the chromium were found; this is no doubt due to the vibration ellipsoids being so nearly spherical and this effect would complicate efforts to determine any relationship between the orientation of the vibration ellipsoids and the directions of neighbouring atoms. On the other hand, for the oxygen atoms the vibration ellipsoids approximate to an oblate ellipsoid of rotation and the angles between the unique axis of the ellipsoid and the appropriate carbon–oxygen bond are 1·4, 2·3, 1·0 and 3·8° for O(1), O(2), O(3) and O(4) respectively, showing that the amplitudes of the oxygen atom vibrations are considerably greater in the directions perpendicular to the carbon–oxygen bond than along it. The shapes and directions of the unique axes of the oxygen vibration ellipsoids were hardly affected by errors in the anisotropic temperature factors; the greatest effect of the errors was to cause the angle between the unique axis and the appropriate bond to increase only to 5°.

Bond lengths corrected for thermal vibrations

Busing & Levy (1964) have pointed out that one of the effect of thermal vibration is to alter the apparent bond lengths and they showed how to correct for the effect. Values of the bond lenghts are included in Table 9, corrected for three of the cases they discuss; (*A*) the atoms are vibrating in phase, (*B*) the outer atoms are 'riding' on the inner ones and (*C*) the atoms are moving independently of each other. The carbon atoms are tightly packed around the chromium atom (the average non-bonded carbon–carbon distance is only 2·7 Å), and the r.m.s. amplitude of thermal vibration is 0·2 Å. This suggests that the carbon shell is oscillating as a whole about the chromium atom. Thus it appears that the riding values are likely to be the nearest to the true ones. There is clearly much less steric hindrance to the motion of the oxygen atoms (4·3 Å apart), and their vibration ellipsoids indicate a riding motion on the carbons (or about the chromium). A certain amount of independent vibration, especially along the bonds, would account for the significantly larger amplitudes of the carbon and oxygen in these directions compared with the chromium atom.

Thus the observations may be qualitatively explained by a model in which the chromium is vibrating almost spherically. The six carbon atoms surround the chromium and vibrate as a shell but with some independence of the chromium, while the oxygen atoms are riding on the neighbouring carbon (or about the chromium).

Until further evidence is obtained on the types of interaction that occur in chromium hexacarbonyl, it is probably best to use the riding values for the bond lengths, but to regard the standard deviations given as minimum values which might well be too low.

Bond lengths, double-bond character

There appears to be no measured value of the octahedral covalent radius of chromium, but an estimate may be obtained from the isoelectronic series: Ni(IV), Co(III) and Fe(II) (where the roman numerals indicate the number of electrons removed from the atom). The octahedral covalent radii for these atoms are 1·21, 1·22 and 1·23 Å respectively (Pauling, 1960) and extrapolation from these figures suggests a covalent radius of 1·25 Å for neutral chromium.

Combining this figure with that for the tetrahedral covalent radius of carbon (0·77 Å) suggests a chromium–carbon bond length of 2·02 Å. This distance is uncorrected for thermal vibration and so must be compared with the uncorrected observed value, 1·909 Å. The difference between these cannot be accounted for by the experimental error in the present results and must presumably be due to partial double-bonding between the atoms.

This suggests a qualitative agreement with the molecular orbital theory, but extent of π bonding cannot be assessed accurately until a reliable covalent

Table 9. *Bond lengths* (Å) *corrected for thermal vibrations*

	Uncorrected bond length	Corrected bond length			Standard deviation
		A (in-phase)	*B* (riding)	*C* (independent)	
Cr–C(1)	1·891	1·891	1·897	1·933	0·007
Cr–C(2)	1·928	1·928	1·935	1·970	0·007
Cr–C(3)	1·910	1·910	1·915	1·951	0·004
Cr–C(4)	1·909	1·910	1·917	1·953	0·004
Mean	1·909	1·910	1·916	1·952	0·003
C(1)–O(1)	1·151	1·156	1·185	1·266	0·008
C(2)–O(2)	1·109	1·114	1·143	1·230	0·008
C(3)–O(3)	1·137	1·142	1·171	1·247	0·006
C(4)–O(4)	1·143	1·149	1·179	1·265	0·006
Mean	1·137	1·143	1·171	1·253	0·004

radius for octahedral chromium has been measured, rather than relying on the extrapolation of the covalent radii of the isoelectronic series.

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Significance Tests on the Crystallographic *R* Factor The Space Group of Chromium Hexacarbonyl

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The Laue symmetry and systematic absences of chromium hexacarbonyl indicated that the space group is either $Pn2_1a$ or $Pnma$. The former had already been reported by other investigators. Structures based on both groups were refined by least squares. The crystallographic evidence of consistency between the results of isotropic and anisotropic refinement – of consistency of equivalent bond lengths, bond angles, parameter standard deviation and isotropic temperature factors – suggests the centrosymmetric structure to be correct. This is reinforced by the morphology, the statistical tests for a centre of symmetry and the relative ease in refining the centrosymmetric structure compared with the non-centrosymmetric one. On the other hand, the weighted residual test strongly suggests a non-centrosymmetric structure. It is thought that this is most likely to originate from an ill-conditioned least-squares matrix which arises from the pseudo-symmetry of the non-centrosymmetric structure. In such cases it would appear unwise to depend on the weighted residual test alone.

Introduction

Hamilton (1965) has defined a function R'' as

$$R''=\left[\frac{\Sigma w(|F_o|-|F_c|)^2}{\Sigma w|F_o|^2}\right]^{\frac{1}{2}}$$

where $w=1/\sigma^2$ (σ^2 is the variance of F_o). F_o and F_c are the observed and calculated structure factors.

This function Hamilton (1965) terms the weighted residual. He shows that $\mathcal{R}=R''_Q/R''_0$ (where R''_0 is the weighted residual from an unrestrained least-squares refinement and R''_Q that from a refinement with constraints on some parameters) may be statistically significant. Tables are given to obtain the level of significance.

The test was applied during the crystal structure determination of chromium hexacarbonyl.

CHROMIUM HEXACARBONYL

1. Possible space groups

The Laue symmetry and systematic absences of chromium hexacarbonyl indicate that the space group is either $Pn2_1a$ or $Pnma$. The former had already been