Crystal and Molecular Structure of Tetracarbonyl-(7,7-dimethoxynorborn-2-ene)chromium(0)

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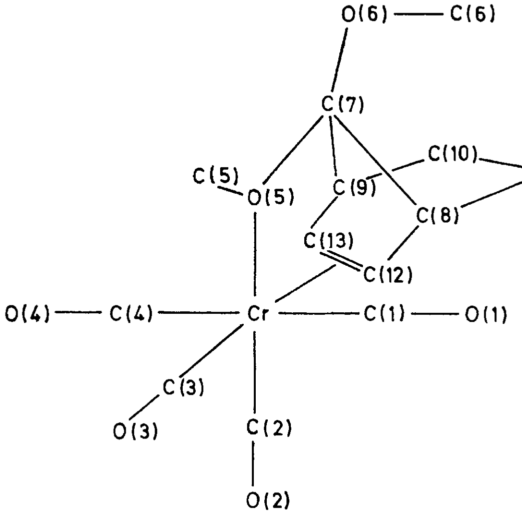
The crystal and molecular structure of the title compound has been determined from diffractometer data (840 reflections) and refined by full-matrix least-squares to R 0·047. Crystals are orthorhombic, space group $P2_12_12_1$, a = 14·786(2), b = 10·137(1), c = 9·440(1) Å, Z = 4.

The chromium atom is octahedrally co-ordinated by the organic ligand which is bidentate through the olefinic bond and one of the methoxy-groups [Cr–C 2·248 and 2·300(8), Cr–O 2·152(5) Å] and by the four carbonyl groups. Among the latter, an interesting comparison is found between the opposed pair of carbonyl groups with Cr–C 1·915 ± 0·015 and C–O 1·125 ± 0·015 Å and the pair opposite the ligand with Cr–C 1·83 ± 0·015 and C–O 1·165 ± 0·015 Å.

RECENTLY, the preparation of complexes of the type $LCr(CO)_4$ (L = *syn*-7-alkoxynorborn-2-ene) has been reported, in which the alkoxynorbornene acts as a bidentate ligand; the assignment of structure was based on spectroscopic evidence, particularly ^1H n.m.r.[1] Stable complexes in which oxygen atoms are co-ordinated to zerovalent chromium are quite rare[2] and it was considered to be of interest to establish the structure of one of these novel complexes (I) by single-crystal X-ray diffraction.



(I) showing the atom numbering system used in the analysis

EXPERIMENTAL

Preparation of Complex.—A solution of 7,7-dimethoxynorborn-2-ene (2·0 g) in di-n-butyl ether (50 ml) and cyclohexane (20 ml) was heated under reflux (bath temperature 140°) with chromium hexacarbonyl (4·0 g) under nitrogen for 10 h in the apparatus described previously.[3] Volatile material was removed under nitrogen at 80°/2 mmHg to leave an orange oil which crystallized from pentane to give the *complex* as orange prisms (0·34 g), m.p. 107—108 °C (Found: C, 49·4; H, 4·5. $C_{13}H_{14}CrO_6$ requires C, 49·1; H, 4·4%).

Crystallography.—A single compact polyhedral crystal fragment closely approximating to a sphere 0·25 mm in diameter was chosen. Cell dimensions were obtained by a least-squares fit of the angular parameters of 15 reflections centred in the counter aperture of a Syntex P$\bar{1}$ four-circle diffractometer. A unique data set in the range $2\theta < 100°$ was collected by use of a θ—2θ scan (840 independent reflections, all of which were used with unit weights in the structure determination and refinement). All data processing and computation was carried out on a CDC 6200 computer at the University of Western Australia, with a local adaption of the ' X-Ray '72 ' programme system.[4]

Crystal Data.—$C_{13}H_{14}CrO_6$, $M = 318{\cdot}3$. Orthorhombic, $a = 14{\cdot}786(2)$, $b = 10{\cdot}137(1)$, $c = 9{\cdot}440(1)$ Å, $U = 1414{\cdot}8(3)$ Å^3, $D_m = 1{\cdot}51$, $Z = 4$, $D_c = 1{\cdot}49$ g cm^{-3}, $F(000) = 656$. Space group $P2_12_12_1$ (D_2^4, No. 19).[5] Cu-K_α Radiation, Ni filtered, $\lambda = 1{\cdot}5418$ Å,[6] μ(Cu-K_α) = 144 cm^{-1}. Scattering factors for the neutral atoms were taken from ref. 7, those for chromium being corrected for the effects of anomalous dispersion ($\Delta f'$, $\Delta f''$).[8] Data were corrected for absorption (spherical approximation) but not extinction.

Solution of the structure was by conventional heavy-atom methods, the final stages of refinement being carried out by full-matrix least-squares; anisotropic thermal parameters for non-hydrogen atoms were refined according to the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Hydrogen atoms were located geometrically and their positional parameters refined, the isotropic thermal parameter U being constrained to 0·10 Å^2. In the final least-squares cycle, no non-hydrogen parameter

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[1] D. Wege and S. P. Wilkinson, *J.C.S. Chem. Comm.*, 1972, 1335.

[2] Gmelins, ' Handbuch der Anorganischen Chemie,' Band 3 Chrom–Organische Verbindungen, Verlag Chemie, Weinheim, 1971.

[3] D. Wege and S. P. Wilkinson, *Austral. J. Chem.*, 1973, **26**, 1751.

[4] X-Ray program system, version of June 1972. Technical Report TR-192 of the Computer Science Centre, University of Maryland, U.S.A.

[5] ' International Tables for X-Ray Crystallography,' vol. 1, Kynoch Press, Birmingham, 2nd edn., 1965, p. 105.

[6] Ref. 5, vol. III, p. 59.

[7] Ref. 6, pp. 202 ff.

[8] Ref. 6, pp. 215.

TABLE 1

Atomic fractional cell (a decimal point precedes x, y, and z) and anisotropic thermal parameters (10^3U_{ij} Å^2), with estimated standard deviations in parentheses, for non-hydrogen atoms

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	13147(9)	8126(1)	6132(1)	45(1)	44(1)	56(1)	1(1)	0(1)	−3(1)
C(1)	0022(7)	8263(8)	6230(9)	58(7)	48(5)	74(6)	5(4)	0(5)	−7(6)
O(1)	−0729(5)	8375(8)	6329(8)	51(5)	99(5)	99(5)	17(4)	4(4)	−9(5)
C(2)	1366(6)	8420(9)	803(1)	49(5)	77(6)	70(6)	58(5)	−13(5)	−10(5)
O(2)	1400(6)	8636(9)	9240(7)	86(5)	134(7)	64(4)	11(5)	2(4)	−19(4)
C(3)	1299(7)	991(1)	584(1)	72(6)	63(7)	82(6)	2(5)	4(6)	−2(5)
O(3)	1285(7)	1063(7) *	569(1)	131(7)	44(5)	162(8)	−6(4)	−27(6)	3(5)
C(4)	2603(8)	8239(9)	6246(9)	65(7)	63(5)	58(5)	−4(5)	8(5)	−1(7)
O(4)	3351(5)	8347(9)	6439(9)	44(4)	120(6)	125(6)	−16(4)	−6(4)	−9(6)
C(5)	1955(8)	813(1)	299(1)	101(8)	52(5)	71(6)	−7(6)	14(6)	22(5)
O(5)	1297(4)	7523(5)	3946(6)	59(3)	37(3)	50(3)	1(3)	4(4)	9(2)
C(6)	0581(9)	585(1)	163(1)	88(7)	93(8)	68(6)	−4(7)	−31(6)	−10(6)
O(6)	1362(4)	5658(5)	2496(6)	68(3)	57(3)	55(3)	9(3)	−3(3)	−8(3)
C(7)	1309(6)	6082(7)	3877(8)	57(5)	38(4)	51(5)	12(4)	−6(6)	3(4)
C(8)	0537(5)	5557(8)	4772(9)	41(4)	46(5)	70(5)	0(4)	7(4)	−1(4)
C(9)	2056(5)	5506(8)	4796(8)	39(4)	45(5)	49(4)	3(4)	6(4)	2(4)
C(10)	1798(6)	4041(8)	477(1)	63(5)	45(5)	84(6)	3(4)	4(5)	−11(5)
C(11)	0741(6)	4077(9)	473(1)	62(5)	46(5)	91(7)	−7(4)	2(5)	2(5)
C(12)	0851(6)	6016(8)	622(1)	62(6)	45(5)	59(5)	−2(4)	−5(5)	−2(5)
C(13)	1781(5)	5963(7)	6230(9)	47(5)	38(4)	65(5)	12(4)	−5(4)	10(5)

* Add 1.

shift was $>0·2\sigma$ and a difference Fourier showed no significant features; R was 0·047 and R' 0·070 $\{R' = [\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}\}$, for the preferred hand, values for the alternative parity being 0·067 and 0·092. Positional and thermal parameters are listed in Table 1 and bond distances and angles in Table 2, for non-hydrogen atoms.

TABLE 2

Interatomic distances (Å) and angles (°), with least-squares estimated standard deviations in parentheses

(*a*) The Cr environment			
Cr–C(1)	1·92(1)	Cr–C(12)	2·248(8)
Cr–C(2)	1·82(1)	Cr–C(13)	2·300(8)
Cr–C(3)	1·84(1)		
Cr–C(4)	1·91(1)	Cr–O(5)	2·152(5)
C(1)–Cr–C(2)	89·0(4)	C(3)–Cr–C(4)	87·8(4)
C(1)–Cr–C(3)	85·6(4)	C(3)–Cr–O(5)	97·7(3)
C(1)–Cr–C(4)	170·3(4)	C(3)–Cr–C(12)	160·4(4)
C(1)–Cr–O(5)	93·1(3)	C(3)–Cr–C(13)	162·2(4)
C(1)–Cr–C(12)	76·3(3)	C(4)–Cr–O(5)	94·8(3)
C(1)–Cr–C(13)	111·5(3)	C(4)–Cr–C(12)	111·1(4)
C(2)–Cr–C(3)	89·2(4)	C(4)–Cr–C(13)	75·9(3)
C(2)–Cr–C(4)	83·9(4)	O(5)–Cr–C(12)	76·2(3)
C(2)–Cr–O(5)	172·8(3)	O(5)–Cr–C(13)	76·8(3)
C(2)–Cr–C(12)	97·6(4)	C(12)–Cr–C(13)	35·2(3)
C(2)–Cr–C(13)	96·0(4)		
(*b*) Carbonyl groups			
C(1)–O(1)	1·12(1)	Cr–C(1)–O(1)	177·4(8)
C(2)–O(2)	1·16(1)	Cr–C(2)–O(2)	178·6(9)
C(3)–O(3)	1·17(1)	Cr–C(3)–O(3)	177·6(9)
C(4)–O(4)	1·13(1)	Cr–C(4)–O(4)	173·5(8)
(*c*) The ligand			
C(12)–C(13)	1·38(1)		
C(13)–C(9)	1·49(1)	C(12)–C(13)–C(9)	106·3(8)
C(9)–C(10)	1·53(1)	C(13)–C(9)–C(10)	104·3(7)
C(10)–C(11)	1·56(1)	C(13)–C(9)–C(7)	101·6(6)
C(11)–C(8)	1·53(1)	C(7)–C(9)–C(10)	100·5(6)
C(8)–C(12)	1·52(1)	C(9)–C(10)–C(11)	103·1(7)
C(7)–C(8)	1·52(1)	C(10)–C(11)–C(8)	102·6(7)
C(7)–C(9)	1·52(1)	C(11)–C(8)–C(7)	100·4(7)
C(7)–O(5)	1·46(1)	C(11)–C(8)–C(12)	105·3(7)
C(7)–O(6)	1·38(1)	C(12)–C(8)–C(7)	99·5(6)
O(5)–C(5)	1·46(1)	C(8)–C(12)–C(13)	107·4(8)
O(6)–C(6)	1·43(1)	C(8)–C(7)–C(9)	95·4(6)
C(8)–C(7)–O(5)	108·5(6)	C(9)–C(7)–O(5)	111·5(6)
C(8)–C(7)–O(6)	117·5(7)	C(9)–C(7)–O(6)	112·3(6)
C(7)–O(5)–C(5)	112·7(6)	C(7)–O(6)–C(6)	116·8(7)
Cr–O(5)–C(7)	109·0(4)	Cr–O(5)–C(5)	117·6(5)
C(4) · · · C(13)	2·61(1)	C(1) · · · C(12)	2·59(1)

Structure-factor tables and hydrogen-atom parameters are given in Supplementary Publication No. SUP 21047 (11 pp., 1 microfiche).*

DISCUSSION

The chromium atom is pseudo-octahedrally co-ordinated by the four carbonyl groups and the methoxy and olefinic groups of the ligand (Figure). With the exception of the terminal methyl substituents of the ligand, the molecule has an approximate point-symmetry of *m*, the mirror plane passing through the metal atom, the methoxy-oxygen and carbonyls (2) and (3) (Table 3).

TABLE 3

Equation of least-squares plane, with atomic deviations (Å). Orthogonal co-ordinates (Å) are derived for the fractional cell co-ordinates by the transformation: $X = ax$, $Y = by$, $Z = cz$

Plane: Cr,O(2),O(3),O(6),C(2),C(3),C(7)

Equation: $0·999X + 0·027Y - 0·026Z = 2·055$ (σ 0·33Å)

Deviations: Cr −0·03, C(2) 0·00, C(3) 0·00, C(7) −0·05, O(2) 0·03, O(3) 0·01, O(6) 0·05, O(5) −0·03, C(5) 0·98, C(12) −0·78, C(13) 0·59, C(10) 0·60, C(11) −0·96, C(8) −1·22, C(9) 1·02

With respect to this plane, the carbonyl groups fall into two classes: two are mutually *trans* and normal to the plane [C(1),O(1); C(4),O(4)], while the other two in the plane are mutually *cis* [C(2),O(2); C(3),O(3)]. Significant differences are found in the bonding of these two sets of carbonyl groups, probably too large to be accounted for by thermal motion for which no correction has been applied. In the *cis*-pair, the chromium–carbonyl distances are short [1·83(1) Å] with correspondingly long carbon–oxygen bonds [1·165(15) Å], whereas

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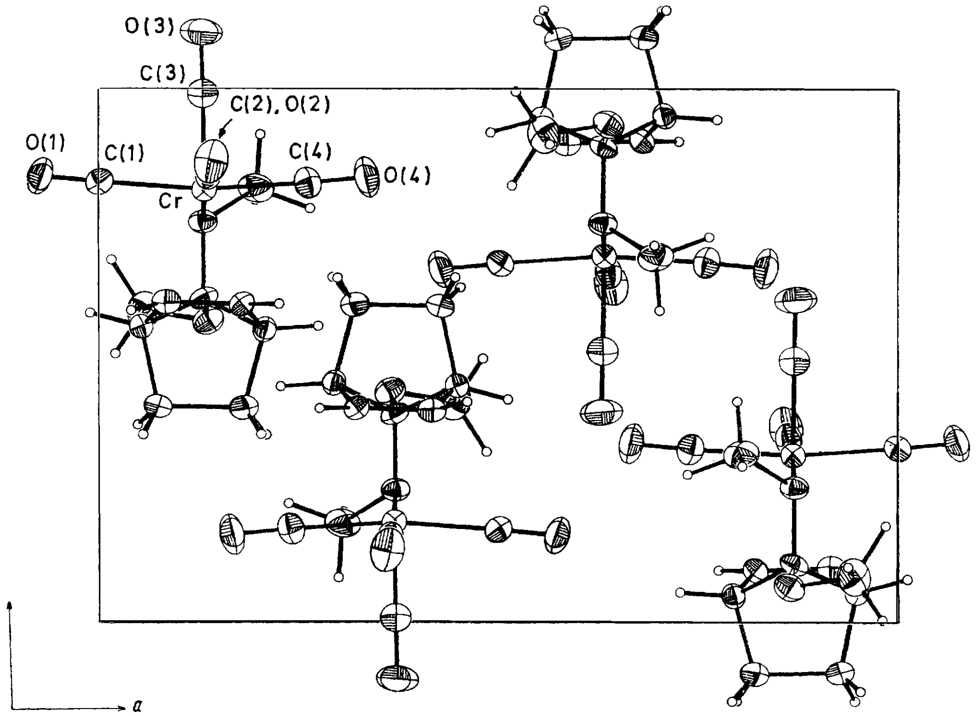
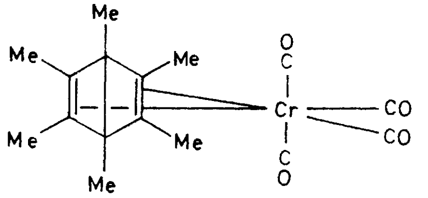
* For details, see Notice to Authors, No. 7, in *J.C.S. Dalton*, 1973, Index issue.

in the *trans*-pair the chromium–carbonyl distances are long [1·91(1) Å] with short carbon–oxygen distances [1·125(15) Å]. These differences can be rationalised in terms of metal–ligand π back-bonding from the filled metal t_{2g}^{6} orbital set (O_h description) to the empty ligand π^* orbitals. In the case of the opposed or *trans*-carbonyl pair, (1) and (4), the available electrons must be equally shared between both acceptor groups. With the *cis*-pair, however, it appears in each case that the π-acceptor properties of the opposing methoxy or olefinic ligand groups must be very small, these being primarily σ-donors, so that the distribution of the metal π-donation within each of these opposing pairs is asymmetric in favour of the two carbonyl groups. Their metal–carbon distances are therefore shorter than those of the opposed carbonyl pair, and the carbon–oxygen distances correspondingly longer. Although a large number of structure determinations have been carried out on chromium–carbonyl derivatives,[2] there are no similarly symmetrical structures of comparable accuracy. The closest approximation, perhaps, is the structure of (II), tetracarbonyl-(hexamethylbicyclo[2.2.0]hexa-2,5-diene)chromium(0),[9] which is analogous to the present complex but having the methoxy-group replaced by an olefinic bond. In (II), the opposed chromium–carbonyl distances were found to be 1·86(2) Å, while the adjacent pair are both 1·83(1) Å. Although the authors did not consider the differences significant, their refinement was carried out by full-matrix methods and the difference parallels that found in (I). In (I) the olefinic carbon–chromium distances [2·248(8) and 2·300(8) Å] are somewhat shorter than in (II) [2·33(1) and 2·34(1) Å]. The asymmetry of the methoxy-groups is the probable reason for this slight deviation of the molecule from exact *m* symmetry.



Unit-cell contents projected down *c*, showing 50% thermal ellipsoids

In the organic ligand are found the usual reductions in angles from tetrahedral or trigonal values owing to ring strain; in particular, the angles C(13)–C(12)–C(8) and C(12)–C(13)–C(9) are reduced from 120 to 107 ± 1°. Although refinement of the hydrogen atoms is not highly accurate, the values for C(12)–C(13)–H(13) and C(13)–C(12)–H(12) are correspondingly large [129(6) and 134(7)°]. The olefinic C(12)–C(13) distance [1·38(1) Å] is not significantly different from that in (II) [1·36(1) Å].



(II)

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[9] G. Huttner and O. S. Mills, *J. Organometallic Chem.*, 1971, **29**, 275.

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