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THE CRYSTAL AND MOLECULAR STRUCTURE OF TRICARBONYL(η-METHOXYTROPYLIUM)CHROMIUM TETRAFLUOROBORATE

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Summary

The structure of tricarbonyl(η-methoxytropylium)chromium tetrafluoroborate has been determined by single-crystal X-ray analysis. The salt crystallises in the triclinic space group $P\bar{1}$ with lattice constants a 740.3(2), b 956.7(3), c 1038.4(2) pm; α 89.10(2), β 73.32(2), γ 74.31(3)°; $Z = 2$. The final R index for 2914 observed reflections ($F \geq 4\sigma$) is 0.045. The cation contains an approximately planar seven-membered ring symmetrically bonded to a $Cr(CO)_3$ group. The C(1)–O(Me) distance (133.8 pm) is intermediate between usual single- and double-bond values.

Introduction

Tricarbonyl(η-tropone)chromium was first reported [1] in 1970 and its crystal structure has been determined [2]. This showed that the chromium atom is bonded to the six vinylic carbon atoms of the ligand which is folded across C(2),C(7) into an envelope conformation, the angle between the planes of C(2),C(1),C(7) and the metal-bonded carbon atoms being 28.5° with the ketonic carbon displaced away from the metal atom; i.e. the structure is better described as an (η^6-triene)chromium complex (I) rather than as an (η^7-tropylium)metal zwitterionic system (II). This complex undergoes protonation of the ketonic oxygen atom and the resulting cation is isolable in salts [1]. We recently found [3] that this cation is ca. two pK units more acidic in water than the conjugate acid (III) of tropone itself; i.e. π-complexation of tropone with a $Cr(CO)_3$ group causes a substantial enhancement of its ketonic base strength. It is known from other work [4] that the tropylium cation is strongly stabilised by π-complexation with $Cr(CO)_3$, suggesting that the protonated tropone complex may adopt an (η^7-hydroxytropylium)metal structure (IV) in preference to (η^6-triene)metal bonding (VI). In harmony with this conclusion, the spectroscopic

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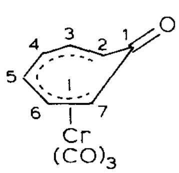
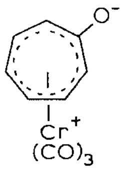
properties [3a] of this cation were found to be closer to those of the tricarbonyl(η-tropylium)chromium cation than of the tropone complex (I).



(I)



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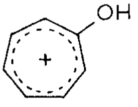

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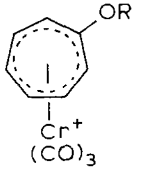
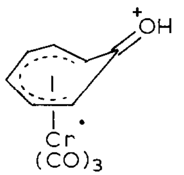
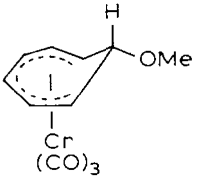


(IV, R = H
V, R = Me)



(VI)



(VII)

In order to establish the mode of metal–ligand bonding, we attempted to determine the structure of the (BF_4^-) salt of the protonated tropone complex by X-ray diffraction analysis. Unfortunately, this was unsuccessful because the crystal decomposed in the X-ray beam. However, the (BF_4^-) salt of the related cation V is more stable in this respect and we now report a determination of its crystal structure *. This salt was prepared as described earlier [1] by hydride abstraction, using (Ph_3C^+)(BF_4^-), from the (η-7-*endo*-methoxycycloheptatriene) complex VII which was synthesised by the reaction of $(MeCN)_3Cr(CO)_3$ with 7-methoxycycloheptatriene.

Crystal-structure determination

Single crystals of the salt (V)(BF_4^-) were sealed under N_2 in thin-walled glass capillaries. X-ray experiments were performed using a Hilger and Watts diffractometer (temperature 20 °C; graphite-monochromated Mo-K_α radiation; $\theta/2\theta$ scan, $2\theta \leq 60°$; 2914 independent reflections with $F \geq 4\sigma$). The structure was solved by the standard heavy-atom method, and refined by full-matrix least-squares treatment. The positions of non-hydrogen atoms were refined using anisotropic temperature factors; hydrogen atoms were located with the aid of a difference Fourier map and their positions then refined isotropically. Two different orientations of the tetrahedral (BF_4^-) anion were found in the Fourier map, so two independent (BF_4) tetrahedra were refined with half weight, assuming an ideal tetrahedral geometry for every anion. The final refinement gave $R = 0.045$ (unit weights). All calculations

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* Dr. O.S. Mills (University of Manchester) has informed us that his group investigated the crystal structure of a salt of the cation V some years ago and obtained results very similar to those described herein.

TABLE 1

FRACTIONAL COORDINATES FOR $[(C_7H_6OMe)Cr(CO)_3]^+ (BF_4^-)$

Atom	x/a	y/b	z/c
Cr	0.29622(6)	0.18155(5)	0.31981(4)
C(1)	0.5591(4)	0.2530(3)	0.1795(3)
C(2)	0.3834(4)	0.3293(3)	0.1552(3)
C(3)	0.2356(5)	0.2737(4)	0.1344(3)
C(4)	0.2197(5)	0.1318(4)	0.1357(3)
C(5)	0.3478(6)	0.0075(4)	0.1635(4)
C(6)	0.5261(5)	−0.0040(4)	0.1910(3)
C(7)	0.6163(4)	0.1028(3)	0.2011(3)
O(4)	0.6828(3)	0.3217(2)	0.2032(2)
C(8)	0.6425(7)	0.4775(4)	0.1970(5)
C(9)	0.0347(4)	0.2964(4)	0.4057(3)
O(1)	−0.1206(4)	0.3646(3)	0.4572(3)
C(10)	0.2426(4)	0.0390(4)	0.4425(3)
O(2)	0.2122(4)	−0.0472(3)	0.5159(3)
C(11)	0.3727(4)	0.2684(4)	0.4516(3)
O(3)	0.4217(4)	0.3185(4)	0.5287(3)
H(1)	0.360(5)	0.418(4)	0.160(3)
H(2)	0.131(5)	0.341(4)	0.124(3)
H(3)	0.095(6)	0.124(4)	0.131(4)
H(4)	0.312(5)	−0.074(4)	0.176(3)
H(5)	0.579(5)	−0.090(4)	0.214(3)
H(6)	0.726(5)	0.074(4)	0.232(3)
H(7)	0.517(6)	0.522(4)	0.268(4)
H(8)	0.752(6)	0.505(4)	0.214(4)
H(9)	0.626(6)	0.514(4)	0.110(4)
B(1) [a]	0.0492(6)	−0.2620(4)	0.1634(4)
F(11)	0.0308(6)	−0.1431(4)	0.0907(5)
F(12)	−0.0835(11)	−0.2292(8)	0.2867(4)
F(13)	0.0171(10)	−0.3710(4)	0.0996(7)
F(14)	0.2323(8)	−0.3045(6)	0.1765(8)
B(2) [a]	0.0464(6)	−0.2826(4)	0.1869(5)
F(21)	0.2406(6)	−0.3089(6)	0.1239(6)
F(22)	−0.0211(9)	−0.1517(5)	0.2570(8)
F(23)	0.0163(8)	−0.3877(6)	0.2723(6)
F(24)	−0.0503(11)	−0.2821(10)	0.0943(7)

[a] Two disordered (BF_4) tetrahedra (weight 0.5).

were carried out with the SHELX computer programs *. Final fractional coordinates are listed in Table 1.

Crystal data: $C_{11}H_9BCrF_4O_4$, M.W.: 343.99, triclinic, $P\bar{1}$, a 740.3(2), b 956.7(3), c 1038.4(2) pm; α 89.10(2), β 73.32(2), γ 74.31(3)°; V 676.7 × 10^6 pm^3, $Z = 2$; $d_{calc.}$ 1.688 g cm^{-3}; μ(Mo-K_α) 7.62 cm^{-1}; maximum crystal dimensions 0.6 × 0.2 × 0.1 mm.

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* SHELX is a system of computer programs for X-ray structure determination devised by G.M. Sheldrick, 1976.

Description of the molecular structure

The structure of the cation is shown in Fig. 1, which gives the atom-numbering system, and the bond lengths and bond angles are in Tables 2 and 3, respectively. The seven-membered ring is approximately planar, the largest deviation from the mean ring plane being that of C(1) which is displaced by ca. 3.5 pm in the direction away from the $Cr(CO)_3$ group. The ring C–C bond lengths deviate by less than 2 pm from an average value of 140 pm and the internal bond angles by less than 2.5 ° from the value (128.6 °) for a regular heptagon. As is commonly found for (η^5-cyclopentadienyl)- and (η^6-benzene)-metal complexes, the ring C–H bonds are bent by ca. 7 ° from the mean ring plane towards the metal atom. The oxygen and carbon atoms of the methoxy group lie close to the mean ring plane with displacements towards the metal-atom of 4 and 11 pm, respectively; the C(2)–C(1)–O(4)–C(8) and C(7)–C(1)–O(4)–C(8) dihedral angles are ca. 3.5 and 175 °, respectively. Whereas the O–Me bond length is normal, the C(1)–O(4) distance (133.8 pm) is intermediate between values usually associated with single and double bonds.

The $Cr(CO)_3$ group is bonded to all of the ring carbon atoms in the usual "piano-stool" geometry with a metal-ring plane separation of 157 pm, and the associated bond lengths are unexceptional. The orientations of the tetrahedral (BF_4^-) anions in the crystal lattice are disordered, as is commonly found.

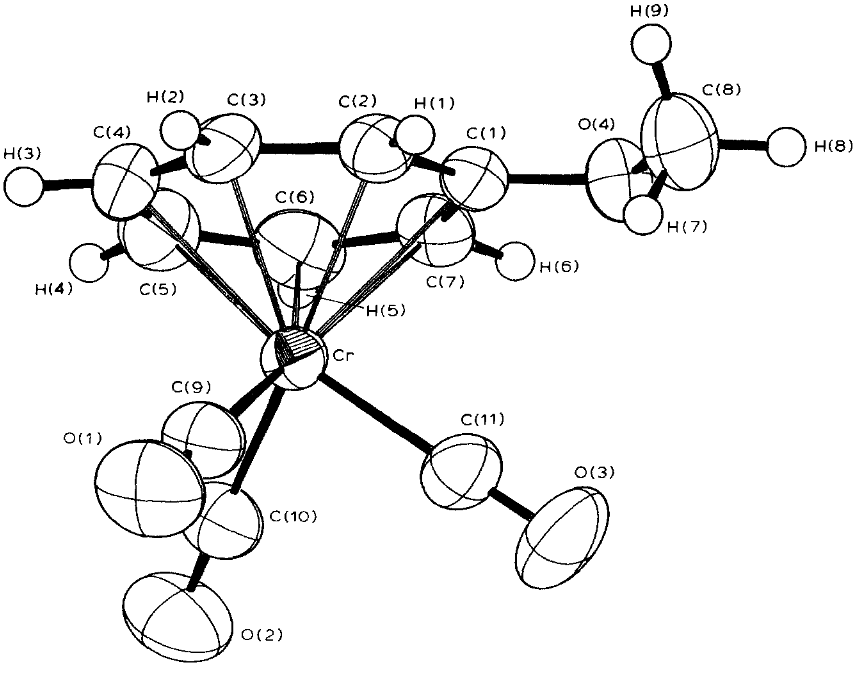

Fig. 1. ORTEP-Diagram of the molecular structure of the cation (V). The atoms are represented by their 50% probability ellipsoids for thermal motion.

TABLE 2

BOND LENGTHS IN $[(C_7H_6OMe)Cr(CO)_3]^+ (BF_4^-)$

Atoms	Distance (pm)	Atoms	Distance (pm)
(a) Chromium – ring carbon distances			
Cr–C(1)	233.2(3)	Cr–C(5)	222.2(3)
Cr–C(2)	226.3(3)	Cr–C(6)	222.9(3)
Cr–C(3)	221.7(3)	Cr–C(7)	225.6(3)
Cr–C(4)	223.5(3)		
(b) Chromium – carbonyl distances			
Cr–C(9)	190.8(3)	C(9)–O(1)	113.4(3)
Cr–C(10)	189.4(3)	C(10)–O(2)	113.8(4)
Cr–C(11)	190.3(3)	C(11)–O(3)	112.9(4)
(c) Ligand distances			
C(1)–C(2)	139.8(4)	C(6)–C(7)	138.3(5)
C(2)–C(3)	140.7(4)	C(7)–C(1)	141.8(4)
C(3)–C(4)	139.4(5)	C(1)–O(4)	133.8(3)
C(4)–C(5)	138.9(5)	O(4)–C(8)	144.3(4)
C(5)–C(6)	140.4(5)		
(d) Carbon – hydrogen distances			
C(2)–H	82(4)	C(6)–H	87(4)
C(3)–H	89(4)	C(7)–H	93(4)
C(4)–H	97(4)	C(8)–H	99(4)
C(5)–H	88(4)		98(5)
			99(5)
(e) Boron – fluorine distance (average value)			
B–F	135.2(5)		

TABLE 3

SELECTED BOND ANGLES IN $[(C_7H_6OMe)Cr(CO)_3]^+ (BF_4^-)$

Atoms	Angle (degrees)	Atoms	Angle (degrees)
C(1)–C(2)–C(3)	128.3	C(2)–C(1)–O(4)	121.7
C(2)–C(3)–C(4)	130.5	C(7)–C(1)–O(4)	111.5
C(3)–C(4)–C(5)	127.7	C(1)–O(4)–C(8)	120.3
C(4)–C(5)–C(6)	127.7	Cr–C(9)–O(1)	179.7
C(5)–C(6)–C(7)	129.8	Cr–C(10)–O(2)	179.4
C(6)–C(7)–C(1)	129.5	Cr–C(11)–O(3)	178.7
C(7)–C(1)–C(2)	126.3	F–B–F	109.5 (average)

Discussion

It is clear from the crystallographic analysis that the cation in the title salt is best described as an (η^7-tropylium)chromium complex (V). The ring has a regular heptagonal geometry and the Cr–C(OMe) distance is only marginally longer than the other Cr–ring carbon distances. However, the slight shortening of the C–O(Me) bond from the usual single-bond value and the approximate coplanarity of the methoxy group and the ring plane are suggestive of $p(d)\pi$–$p\pi$ interaction between C(1) and O(4) leading to partial double-bond character; cf., the ketonic carbonyl bond lengths in tropone [5] and its $Cr(CO)_3$ complex (I) [2] are 126 and 123 pm, respectively, while normal $C(sp^2)$–O single-bond lengths are in the range 136–140 pm [6].

It is highly likely [3] that the cations IV and V have a similar metal–ligand bonding arrangement and it may be concluded that the conjugate acid of the tropone complex I has the tricarbonyl(η^7-hydroxytropylium)chromium structure. In the tropone complex I, the separation of the Cr and C(1) atoms is 264 pm [2] indicating, at best, a weak bonding interaction. Attachment of an electrophile (H^+ or, formally, $CH_3{}^+$) to the ketonic oxygen atom of this complex is accompanied by flattening of the ligand, strengthening of the Cr–C(1) bond, and removal of ring C–C bond-length alternation.

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