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Preliminary communication

Benzene ring distortion in benzenechromium tricarbonyl, as determined by X-ray and neutron diffraction analyses at 78 K

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The geometry of the benzene ring in dibenzenechromium and benzenechromium tricarbonyl has been the subject of a considerable amount of study. Low-temperature crystallographic studies established the six-fold symmetry of the former compound after an earlier controversy[1]. From infrared evidence, it was concluded that the benzene ring, in benzenechromium tricarbonyl, has three-fold rather than six-fold symmetry[2], but no such distortion was found in a later crystallographic study by Bailey and Dahl[3].

We have undertaken accurate liquid-nitrogen temperature (78 K) analyses of this compound using both X-ray and neutron diffraction, as part of a program aimed at measuring electron densities by diffraction methods. Two fully three-dimensional X-ray analyses on two different crystals were undertaken, but only the results of the slightly more accurate second study are reported here, together with the neutron diffraction results. Final X-ray and neutron R factors are respectively

$$R = \frac{\Sigma \mid F_o - k \mid F_c \mid\mid}{\Sigma F_o} = 0.035 \text{ and } 0.053$$

$$R_w = \left\{ \frac{\Sigma (w \mid F_o - k \mid F_c \mid\mid)^2}{\Sigma w F_o{}^2} \right\}^{1/2} = 0.078 \text{ and } 0.049$$

The gross features of the structures agree with the earlier determination. The resulting bond lengths and angles are given in Fig. 1 and Table 1. The complex is located on a crystallographic mirror plane in the space group $P2_1/m$, so only half the molecule is determined independently.

The correction for apparent shortening due to thermal motion is small for the dimensions determined at 78 K (less than 0.003 Å for the bond lengths in the benzene ring,

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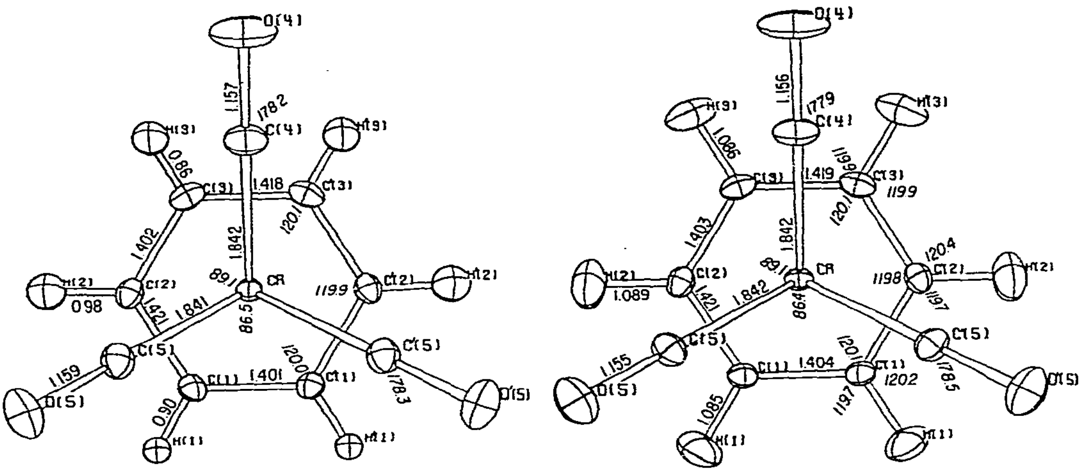

Fig. 1. Bond lengths and angles (at 78 K, uncorrected for thermal motion) in benzenechromium tricarbonyl according to X-ray study (left) and neutron analysis (right). Ellipsoids are 50% probability surfaces.

and 0.002–0.005 Å for the chromium–carbonyl and C–O bonds), and has not been applied here. There is a very close correspondence between the two sets for the dimensions not involving hydrogen atoms. When compared with the 1.398 Å C–C bond length in the benzene molecule[4], three of the bonds are lengthened by about 0.020 Å, the remaining bonds being essentially unaffected. Though the distortion is small, it is evident in both analyses (and in the earlier X-ray analysis not reported here) and clearly outside experimental errors (Table 1).

In a number of transition metal complexes of alkenes, there is a lengthening of the olefinic bond on attachment of the olefin to the metal[5], which can be rationalized by a valence-bond model involving a three-membered ring with the metal atom at an apex, or a molecular-orbital model involving antibonding orbitals[6]. It is interesting that in benzenechromium tricarbonyl the C–C bonds which in Fig. 1 project on the Cr–carbonyl bonds are lengthened. Thus, if the chromium–ring bonding is preferentially to these longer bonds, the chromium coordination would be trigonally-prismatic rather than octahedral.

A further distortion of the ring is evident from the neutron diffraction results. The three independent hydrogen atoms are displaced from the benzene ring plane by 0.021(3), 0.038(3) and 0.036(3) Å for H(1), H(2) and H(3) respectively. The displacement is towards the chromium atom, which is contrary to what would be expected from simple valence-bond considerations[7] and from comparison with other complexes, such as for example bis(t-butyl isocyanide)(tetracyanoethylene)nickel(0)[8].

Finally, we want to point out that distortions such as discussed here, will only become evident in accurate low-temperature studies. Details of the bonding in many metalloorganic complexes might be elucidated if structures analyses would be performed routinely at low temperatures.

TABLE 1. MOLECULAR DIMENSIONS

		Averaged C–C bond lengths in the benzene ring (Å)			
		X-ray data		*Neutron data*	
"Long" bond:	C(1)–C(2)	1.4208	(15)	1.4205	(18)
	C(3)–C′(3)	1.4181	(22)	1.4186	(26)
	Average	1.4194	(13)	1.4196	(16)
"Short" bond:	C(1)–C′(1)	1.4007	(19)	1.4036	(25)
	C(2)–C(3)	1.4021	(16)	1.4026	(18)
	Average	1.4014	(12)	1.4031	(15)
		$\Delta = 0.018(2)$ Å		$\Delta = 0.017(2)$ Å	

Distances from Cr to benzene ring (Å)

	X-ray data		*Neutron data*	
Cr–C(1)	2.240	(2)	2.240	(3)
Cr–C(2)	2.229	(2)	2.230	(3)
Cr–C(3)	2.217	(2)	2.220	(3)

Best plane through the carbon atoms of the benzene ring (neutron data) $2.244x - 6.377z - 2.344 = 0$

Atom	*Distance to plane (Å)*	*Atom*	*Distance to plane (Å)*
C(1)	0.001	Cr	−1.726
C(2)	−0.001	C(4)	−2.731
C(3)	0.001	O(4)	−3.327
H(1)	−0.021	C(5)	−2.865
H(2)	−0.038	O(5)	−3.603
H(3)	−0.036		

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