

Electronic Structure of Benzene Chromium Tricarbonyl by X-ray and Neutron Diffraction at 78°K

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The crystal structure of $C_6H_6Cr(CO)_3$ has been studied at 78°K by both X-ray and neutron diffraction. The studies indicate a lowering of the benzene-ring symmetry to C_{3v} . The C-C bonds in the ring alternate in length, the shortest bonds being *trans* to the carbonyl groups. The average difference is 0.017 (2) Å. The observed bond lengths correlate well with electron overlap populations obtained in semi-empirical molecular orbital calculations. The neutron results show the hydrogen atom to be displaced by an average of 0.03 Å from the plane of the benzene ring in a direction towards the chromium atom. X-N maps show large residual density features near the chromium nucleus, which are to be confirmed by further studies on related compounds. Other residual peaks correspond to the overlap density in the Cr-C, C-C, C-O and C-H bonds and to the lone-pair electrons on the oxygen atoms. The Cr-C(O) bond peaks are closer to the carbon atom, in agreement with theoretical predictions. This is the first combined X-ray and neutron diffraction study of a compound containing third-row atoms, and it is concluded that the bonding in transition metal complexes can now be studied by this technique. A spherical charge refinement of the X-ray data did not lead to satisfactory results. This is partly due to the lack of an appropriate X-ray form factor for chromium.

Introduction

Benzene chromium tricarbonyl (abbreviated to BCT) is one of the simplest transition metal complexes exhibiting simultaneously metal-to-carbonyl bonds and metal-to-organic ligand bonds. It has already been extensively studied, especially by infrared and Raman spectroscopy (Buttery, Keeling, Kettle, Paul & Stamper, 1969; Cataliotti, Poletti & Santucci, 1970; Brunvoll, Cyvin & Schäfer, 1972). Its crystal structure was first determined by Bailey & Dahl (1965*a*). Part of the interest in this complex arose from discussions on the symmetry of the benzene ring in chromium dibenzene. After some controversy the symmetry was determined to be D_{6h} (crystal structure at 100°K by Keulen & Jelinek, 1966; electron diffraction in gas phase by Haaland, 1965; infrared spectrum in gas phase by Ngai, Stafford & Schäfer, 1969; thermodynamic study by Andrews, Westrum & Bjerrum, 1969). The symmetry of the isolated benzene chromium tricarbonyl molecule is C_{3v} but the room-temperature study by Bailey & Dahl (1965*a*) did not show any evidence for a distortion of the benzene ring from D_{6h} symmetry.

The dual purpose of the present X-ray and neutron diffraction study is the determination of an accurate geometry, and the analysis of the difference density based on the X-ray observations and the calculated values from X-ray form factors and neutron positional and thermal parameters (X-N maps). Such difference density maps have been analyzed for a number of

molecules containing first-row atoms only (Coppens & Vos, 1971; Coppens, Sabine, Delaplane & Ibers, 1969; Hanson, Sieker & Jensen, 1973; Brill, Dietrich & Dierks, 1971 and others). It seems highly desirable to establish if similar methods can be applied to molecules containing second and third row atoms. The present work is the first part of such a study.

A preliminary report on the structure of benzene chromium tricarbonyl has been given, with emphasis on the benzene bond lengths (Rees & Coppens, 1972).

Experimental

Details of experimental procedures and data processing are given in Table 1, which also contains relevant physical and crystallographic data.

The crystals used for X-ray and neutron diffraction measurements were grown by sublimation under vacuum with a low temperature gradient, and then sealed in a Lindeman glass capillary (for X-ray diffraction), or in a small quartz tube (for neutron diffraction). The principle of the cooling device was the same in both cases: the crystal is mounted on a metallic cooling block, which is refrigerated by liquid nitrogen. Constant temperature is maintained by a heating coil, which is regulated by a temperature-sensitive resistance. The crystal and cooling block are inside an evacuated cryostat. In the X-ray case, this cryostat is made of two cylindrical beryllium cans (Cryogenics Associates). In the neutron case, there are three concentric aluminum spheres.

The X-ray diffraction measurements were performed on a PICKER four-circle diffractometer, controlled by a PDP 8 computer. The neutron diffraction data were

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collected on the four-circle diffractometer at Brookhaven National Laboratory using the computer-controlled Multi-Spectrometer Control System.

The cell dimensions were determined at 77.6°K from X-ray measurements. Since it is difficult to align the crystal in the cryostat perfectly for all diffractometer setting angles, the following procedure was used: 12 strong reflections of sufficiently high order ($2\theta > 40^\circ$, so that $\text{Mo } K\alpha_1$ and $\text{Mo } K\alpha_2$ are well separated) were selected, from different regions of reciprocal space. Each of those reflections was carefully manually centered in the counter, from both sides of the reflec-

tion plane (positive and negative 2θ), and the value considered for each setting angle was the average between the two corresponding measurements. A least-squares refinement, considering all four setting angles, was finally performed.

The difficulty in aligning a crystal in the cryostat at all possible values of the φ angle has recently been traced to a mechanical instability of the cryostat. For BCT, the effect was largely offset by recentering the crystal separately in two different regions of φ . However, it should be kept in mind that the low-temperature data used in this study are not at the limit of precision

Table 1. $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ physical and crystallographic data

	M.W. 214.14	
	Space group $P2_1/m$ ($0k0$, $k=2n$ only)	
	Cell dimensions at 77.6°K (Mo $K\alpha_1$ radiation, $\lambda=0.70926$ Å)	
	$a=6.010$ (4), $b=10.918$ (6), $c=6.504$ (4) Å	
	$\beta=100.60$ (5)°	
	Molecules per unit cell: 2	
Temperature of data collection	Neutron data 78.3 ± 0.3°K	X-ray data 77.6 ± 0.2°K
Technique of data collection		
Wavelength	1.0142 Å	0.71069 Å
Monochromator	Ge (220)	Graphite
Scan length	1.2 (1 + 8 tan θ)	2 (1.5 + 0.692 tan θ)
Scanning mode	θ - 2θ step scan (about 45 points per reflection) Monitor count: 40000	Continuous (1°/min)
Background	Determined by $\sigma(I)/I$ minimization	Measured during 10s on each side of scan
Maximum 2θ angle	86°	90°
Crystal axis near φ axis of diffractometer	c	a
Crystal shape and absorption corrections		
Crystal volume	3.64 mm ³	0.0096 mm ³
Minimum crystal thickness	1.40 mm	0.205 mm
Maximum crystal thickness	2.34 mm	0.296 mm
Number of boundary planes	13	12
Absorption coefficient	1.17 cm ⁻¹ (including incoherent scattering)	13.66 cm ⁻¹
Number of Gaussian grid-points	192	288
Range of transmission factor	0.83-0.89	0.77-0.80
Reflections and averages		
Number of reflections measured (excluding standard reflections)	1404	5066
Number of symmetry independent reflections	1112	3585
$\sum F_o^2 - \langle F_o^2 \rangle / \sum F_o^2$	0.040	0.026
Least-squares refinement		
Assumed standard deviation (σ_c from counting statistics)	$\sigma = \sigma_c(F_o^2)$	$\sigma = [\sigma_c^2 + (0.03F_o^2)^2]^{1/2}$
Rejection criteria	$F_o^2 < 3\sigma$ and $0.18 < \sin \theta / \lambda < 0.20$ $0.23 < \sin \theta / \lambda < 0.29$ $0.41 < \sin \theta / \lambda < 0.425$	$F_o^2 < 3\sigma$
Minimized quantity	$\sum \sigma^{-2}(F_o^2 - F_c ^2)^2$	$\sum \sigma^{-2}(F_o^2 - F_c ^2)^2$
Number of reflections in refinement (m)	900	2886
Number of refined parameters (n)	92	77
Agreement indices (rejection criteria as above)		
$R(F) = \sum F_o - F_c / \sum F_o$	0.053	0.035
$R(F^2) = \sum F_o^2 - F_c ^2 / \sum F_o^2$	0.050	0.052
$R_w(F^2) = [\sum \sigma^{-2}(F_o^2 - F_c ^2)^2 / \sum \sigma^{-2}F_o^2]^{1/2}$	0.049	0.078
$S = [\sum \sigma^{-2}(F_o^2 - F_c ^2)^2 / (m - n)]^{1/2}$	3.85	1.58
Isotropic extinction parameter g	0.389×10^4	0.117×10^4
F_o^2 uncorrected/ F_o^2 corrected for reflection most affected by extinction	0.69	0.88

tron case diffraction by the aluminum walls of the cryostat superimposes very broad peaks on the background. The scheme used in the background correction [$\sigma(I)/I$ minimization, Lehmann, Larsen & Hamilton, 1972] will correct for this feature in many, but not in all, cases: analysis of variance during data refinement

showed some systematic trends of the residues $|F_o^2 - |F_c|^2|/\sigma$ as a function of $\sin \theta$ when all data were included in the refinement. Three zones in $\sin \theta$, where the residues were the largest, were eventually excluded (see Table 1).

The intensities of symmetry-related reflections were

Table 4. Bond lengths (Å) and angles (°)

Corrections for thermal motion are made in the rigid-body approximation, except for the C-H bonds, for which riding motion of the hydrogen atoms was assumed.

	From neutron data		From X-ray data	
	Uncorrected	Corrected	Uncorrected	Corrected
Cr—C(1)	2.240 (3)	2.243	2.240 (2)	2.243
Cr—C(2)	2.230 (3)	2.233	2.229 (2)	2.232
Cr—C(3)	2.220 (3)	2.223	2.217 (2)	2.220
Cr—C(4)	1.842 (4)	1.845	1.842 (2)	1.845
Cr—C(5)	1.842 (3)	1.845	1.841 (1)	1.844
C(4)—O(4)	1.156 (3)	1.159	1.157 (2)	1.159
C(5)—O(5)	1.155 (2)	1.157	1.159 (2)	1.160
C(1')—C(1)	1.404 (3)	1.407	1.402 (2)	1.405
C(1)—C(2)	1.421 (2)	1.424	1.421 (2)	1.424
C(2)—C(3)	1.403 (2)	1.406	1.402 (2)	1.405
C(3)—C(3')	1.419 (3)	1.422	1.418 (2)	1.421
C(1)—H(1)	1.085 (3)	1.106	0.90 (2)	
C(2)—H(2)	1.089 (3)	1.113	0.98 (2)	
C(3)—H(3)	1.086 (3)	1.109	0.86 (2)	
Cr—C(4)—O(4)	177.95 (20)		178.18 (13)	
Cr—C(5)—O(5)	178.50 (15)		178.30 (8)	
C(4)—Cr—C(5)	89.14 (13)		89.13 (6)	
C(5)—Cr—C(5')	86.37 (14)		86.54 (8)	
C(1')—C(1)—C(2)	120.07 (7)		120.05 (6)	
C(1)—C(2)—C(3)	119.80 (11)		119.88 (10)	
C(2)—C(3)—C(3')	120.13 (7)		120.08 (6)	
C(1')—C(1)—H(1)	119.72 (15)		118.8 (10)	
C(2)—C(1)—H(1)	120.19 (18)		121.1 (10)	
C(1)—C(2)—H(2)	119.74 (17)		122.6 (10)	
C(3)—C(2)—H(2)	120.43 (17)		117.4 (10)	
C(2)—C(3)—H(3)	119.94 (18)		120.4 (11)	
C(3')—C(3)—H(3)	119.88 (16)		119.5 (11)	

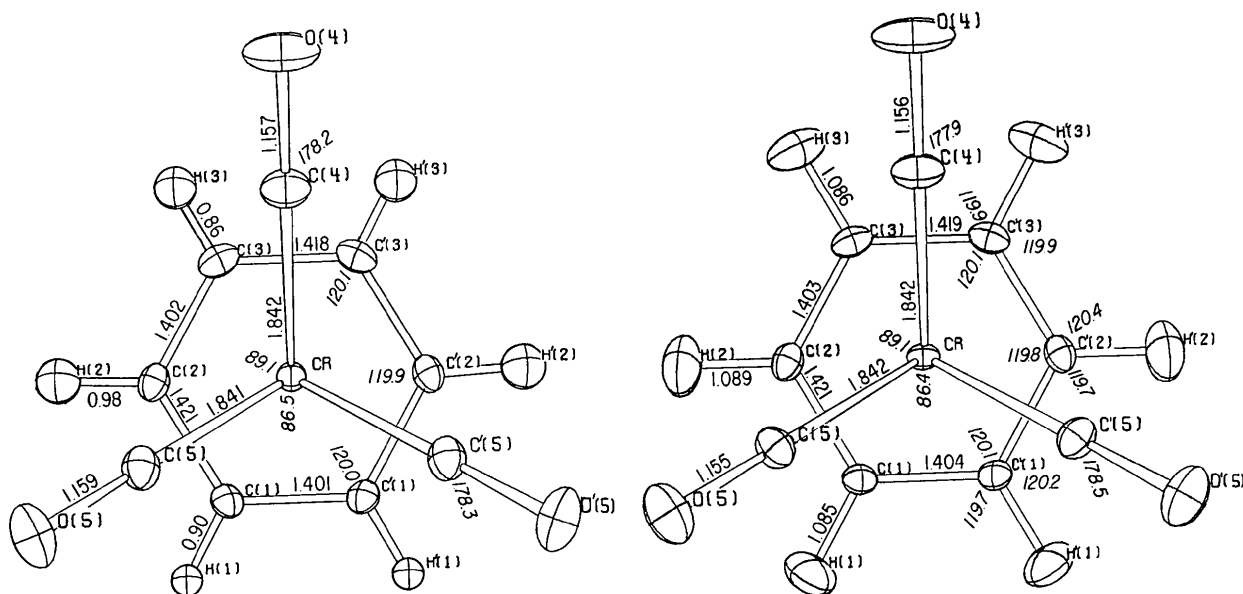


Fig. 1. Bond lengths and angles (at 78°K, uncorrected for thermal motion) in benzene chromium tricarbonyl according to the X-ray study (left) and neutron analysis (right). Ellipsoids are 50% probability surfaces.

averaged. A least-squares refinement was then performed on the positional and thermal parameters, the scale factor and the isotropic extinction coefficient. The X-ray scattering factors of Cr, O and C were taken from *International Tables for X-ray Crystallography* (1972); the values derived by Stewart, Davidson & Simpson (1965) were used for H. The anomalous scattering of Cr was taken into account (*International Tables for X-ray Crystallography*, Vol. III). The neutron coherent scattering lengths were those compiled by Shull (1972). The minimized quantity was: $\sum \sigma^{-2}(F_o^2 - |F_c|^2)^2$, with $\sigma^2 = \sigma^2(\text{counting}) + (kF_o^2)^2$, where the proportionality constant k (which is the same for all reflections in the data set) was adjusted to minimize systematic trends of $|F_o^2 - |F_c|^2|/\sigma$ as a function of $\sin \theta$ and of F_o^2 . For the neutron data this resulted in $k=0.00$, for the X-ray data in $k=0.03$.

In the neutron-data refinement, where the secondary extinction parameter was relatively large, two refinements were done on non-averaged sets of structure factors to assess the anisotropy of the extinction, for type I and type II crystals, respectively (Coppens & Hamilton, 1970). Neither of those refinements resulted in an improvement of the agreement between observed and calculated structure factors (Table 2) in comparison with the isotropic extinction model.

Results

The fractional coordinates and thermal parameters are given in Table 3. Bond lengths and bond angles are given in Table 4 and on Fig. 1. The corrections for thermal libration given in Table 4 are discussed in the next section.

The equation of the best plane through the carbon atoms of the benzene ring, as determined from the neutron diffraction data is $2.244x - 6.277z - 2.344 = 0$. The distances to this plane are given in Table 5, which contains the coordinates of the atoms in a Cartesian molecular frame.

Table 5. Cartesian coordinates of $C_6H_6Cr(CO)_3$ (\AA , from neutron diffraction results)

The origin is chosen in the best plane through the carbon atoms of the benzene ring. The z axis is perpendicular to this plane, the y axis perpendicular to the symmetry plane.

	x	y	z
Cr	0	0	1.726
C(1)	-1.242	0.702	-0.001
C(2)	-0.012	1.413	0.001
C(3)	1.201	0.709	-0.001
H(1)	-2.184	1.240	0.021
H(2)	-0.018	2.501	0.038
H(3)	2.142	1.251	0.036
C(4)	1.543	0	2.732
O(4)	2.534	0	3.328
C(5)	-0.710	1.260	2.866
O(5)	-1.150	2.032	3.604

The molecular dimensions are more precise than those determined by Bailey & Dahl (1965a) at room

temperature (the estimated standard deviations are four to five times smaller), but there are no significant differences between the two sets.

Intermolecular distances

The distances between atoms in different molecules which are less than the sum of the van der Waals radii are shown on Fig. 2, together with the corresponding values observed at room temperature (Bailey & Dahl, 1965a). The short $O(5) \cdots H(1)$ distance (2.47 \AA) and the approximate alignment of the atoms C(5), O(5) and H(1) (the angle at O(5) is 159°) are indicative of a slightly attractive interaction. Non-bonded C-H \cdots O contacts are commonly observed, but probably should not be classified as weak hydrogen bonds (Coppens, 1964). The attractive interactions $O(5) \cdots H(1)$ and $O(5') \cdots H(1')$ and the close contacts $O(4) \cdots C(3)$ and $O(4) \cdots C(3')$ may explain the distortion of the benzene chromium tricarbonyl molecule from C_{3v} symmetry: the O(5) and O(5') atoms are further away from the benzene ring than O(4), as may be seen from Table 5. As a result the plane through the three oxygen atoms makes an angle of 4.3° with the benzene-ring plane. At room temperature, this angle is only 3.4° (Bailey & Dahl, 1965a). This may be related to the fact that, in contrast with the intramolecular bond lengths, the intermolecular distances are much shorter at 78°K than at room temperature.

Analysis of thermal motion

Rigid-body motion is described by the 12 non-vanishing elements of the T, L and S tensors (Schomaker

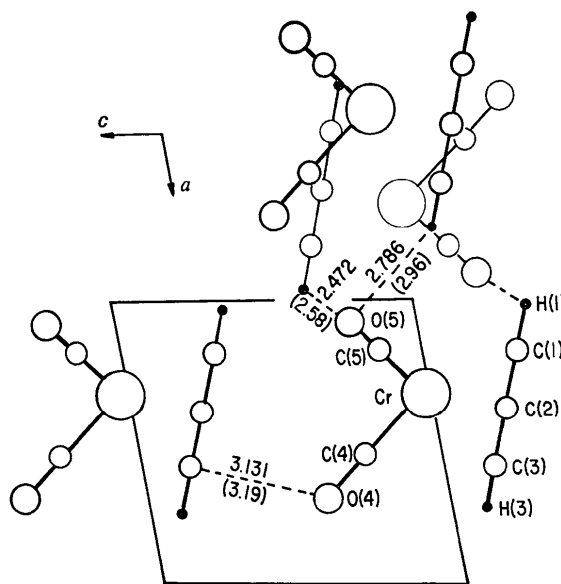


Fig. 2. Shortest intermolecular distances. Atomic positions are as determined by neutron diffraction. Values in brackets are from the room-temperature study by Bailey & Dahl (1965).

& Trueblood, 1968). Assuming a rigid-body motion of the whole BCT molecule (excepting the hydrogen atoms), and taking for the U_{obs} the mean square amplitudes determined from the neutron data, the root mean square residue $\Delta U_{\text{RMS}} = \langle (U_{\text{obs}} - U_{\text{calc}})^2 \rangle^{1/2}$ is 0.0011 \AA^2 , compared to $\sigma_{\text{RMS}}(U_{\text{obs}}) = 0.0010 \text{ \AA}^2$; and the largest individual residue is 0.0030 \AA^2 . With the thermal parameters determined from X-ray data, the magnitude of the residues is the same ($\Delta U_{\text{RMS}} = 0.0010 \text{ \AA}^2$, largest $\Delta U = 0.0026 \text{ \AA}^2$), but the standard deviations of the observed mean square amplitudes are smaller (r.m.s. value: 0.0004 \AA^2). Thus BCT behaves as a rigid body only in a first approximation. This is not surprising, since the force constants between the chromium atom and the ligands are rather small, and the relative importance of internal modes of vibration increases as the temperature is lowered. The least-squares fit is no better if one assumes a rigid-body motion of the $\text{Cr}(\text{CO})_3$ group alone, but more satisfactory results are obtained for an assumed rigid-body motion of the group CrC_6 (from neutron data: $\Delta U_{\text{RMS}} = 0.0007 \text{ \AA}^2$, largest $\Delta U = 0.0015 \text{ \AA}^2$ from X-ray data: $\Delta U_{\text{RMS}} = 0.0004 \text{ \AA}^2$, largest $\Delta U = 0.0009 \text{ \AA}^2$). All three assumptions lead to essentially the same description of rigid-body motion and the same corrections in bond lengths. The following results were obtained assuming a rigid-body motion of the whole molecule (without the hydrogen atoms).

The librational motion is strongly anisotropic. From neutron data, the r.m.s. amplitude is 3.5° around the threefold axis of the molecule, and 1.8° around the other axes. The corresponding values obtained from X-ray data are 3.4 and 1.7° . The translational motion is essentially isotropic, with an r.m.s. amplitude of 0.087 \AA ($\pm 0.013 \text{ \AA}$) from neutron data, and 0.091 \AA ($\pm 0.009 \text{ \AA}$) from X-ray data (taking the origin which symmetrizes the S matrix).

As expected the hydrogen atoms cannot be included in the rigid-body calculation from neutron data, the amplitudes of vibration due to internal modes being by no means negligible. After completion of the rigid-body analysis, the residues ΔU of the hydrogen atoms may be interpreted as the mean square amplitudes of internal motion, which should be approximately equal to the amplitudes of vibration of the CH bonds derived from infrared and Raman spectroscopic data (in this comparison, the motion of the carbon atoms may be neglected). Assuming a rigid body formed by Cr and the carbon atoms of the benzene ring, the ΔU residues lead to the following r.m.s. amplitudes for H(1), H(2) and H(3), respectively: 0.061 , 0.068 and 0.069 \AA in direction C–H; 0.094 , 0.107 and 0.083 \AA in benzene plane, perpendicular to C–H; 0.132 , 0.133 and 0.148 \AA perpendicular to benzene plane. The r.m.s. amplitudes of vibration of C–H from spectroscopic data are practically the same in benzene and in benzene chromium tricarbonyl, and almost temperature independent (Brooks, Cyvin & Kvande, 1965; Brunvoll, Cyvin & Schäfer, 1972). In benzene, at 0°K , they are: 0.077 \AA

in direction C–H, 0.118 \AA perpendicular to C–H in the plane and 0.147 \AA perpendicular to the plane. Thus, there is quite reasonable agreement between the results of the present analysis and the spectroscopic information.

Because of the large internal thermal motion of hydrogen, the C–H bond lengths were corrected assuming a riding motion of hydrogen on the carbon atoms, whereas all other bond lengths in Table 4 are corrected in the rigid-body approximation (Johnson, 1970). The corrections of the five independent Cr–C bond lengths are essentially the same, if one assumes a riding motion of carbon on chromium instead of rigid-body motion, the differences with the rigid-body corrections being nowhere larger than 0.001 \AA . In contrast to this, the assumption of a riding motion of oxygen in the CO groups would lead to corrections as large as 0.009 and 0.014 \AA as compared to 0.002 \AA for rigid-body motion. As the earlier analysis showed that the motion can be reasonably well accounted for with a rigid-body model the latter correction is more plausible.

Geometry of the benzene ring

The symmetry of the benzene ring is C_{3v} , rather than D_{6h} as followed from the room-temperature study (Bailey & Dahl, 1965). There are clearly two types of C–C bonds of different length. Considering their position in relation to the CO groups they may be classified as *cis* and *trans* bonds (the *cis* bonds intersect the projections of the Cr–C–O bonds on the benzene plane, the *trans* bonds do not). The length of the *cis* bonds (after correction for rigid-body motion) averages 1.423 \AA , the length of the *trans* bonds, 1.406 \AA . Those values may be compared with the carbon–carbon bond length in uncomplexed benzene, and in dibenzene chromium (Table 6). The lengths of the *cis* bonds do not differ significantly from the carbon–carbon bond length observed in dibenzene chromium, but are longer by about 0.024 \AA than the bond length in uncomplexed benzene, whereas the *trans* bonds are only 0.007 \AA longer.

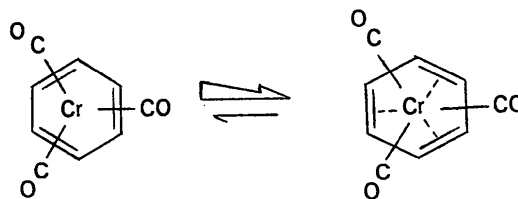
If the olefinic bond is lengthened when attached to a transition metal (Manojlovic-Muir, Muir & Ibers, 1969), it would follow that the coordination of Cr could be trigonally-prismatic rather than octahedral (Rees & Coppens, 1972). However, in all the known complexes of Cr^0 , the coordination is octahedral. Particularly interesting is the case of substituted complexes of the type $\text{R-C}_6\text{H}_5\text{Cr}(\text{CO})_3$, where R is an electron releasing radical or an electron withdrawing radical (Sim, 1967). The structure of those complexes is eclipsed and the carbon atoms which are *trans* to the CO groups are always those with the strongest negative charge induced by the substituent. As the electron withdrawing character of the $\text{Cr}(\text{CO})_3$ group is well established (see e.g. Wu, Biehl & Reeves, 1972), it seems that chromium would preferentially bind to the most negative carbon atoms of the aromatic molecule. Thus coordination in these complexes is octahedral.

An additional argument for octahedral coordination is that all the atomic orbitals of chromium used in the bonding (except the $4p$ orbitals, which probably play only a minor role), are even functions. The hybrids formed are then also approximately even, and therefore centrosymmetrical, functions.

The structure of BCT may be compared to divinylbenzene diiron hexacarbonyl and vinylnaphthalene iron tricarbonyl, where only a part of the benzene ring interacts directly with the $\text{Fe}(\text{CO})_3$ moieties (Davis & Pettit, 1970). The part which is not involved exhibits a Kekulé-type structure. This shows that the aromaticity of the benzene ring is destroyed: the π electrons are localized on double bonds in such a way that the best overlap is obtained with the iron hybrid orbitals. A similar case with a molybdenum complex was described by Cotton & La Prade (1968).

In the case of BCT, the destruction of aromaticity is only partial. In a simple valence-bond language the following interpretation may be given for the observed

bond lengths: the Kekulé form with double bonds in the *trans* position is favored for energetic reasons. This means a lengthening of the *cis* bonds and a shortening of the *trans* bonds. Upon bond formation with the chromium, the *trans* bonds are lengthened, as is the case with other olefinic bonds coordinated to metal. The resulting *trans* bond lengths are approximately equal to those in benzene, but still somewhat shorter than the *cis* bond lengths.



We performed a semi-empirical molecular orbital calculation, by the Self Consistent Charge and Configuration method (S.C.C.C.) in the way described by

Table 6. Experimental carbon-carbon bond lengths and π overlap populations, as calculated by the S.C.C.C. method

All bond lengths are corrected for thermal libration.

C-C bond	Bond length	π -population	Reference of experimental work
C_6H_6	1.398	} 0.256	Bacon, Curry & Wilson (1964)
	1.4000		Brooks, Cyvin, Kvande & Meisingseth (1963)
$\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ <i>trans</i> bond	1.406	0.235	This work
<i>cis</i> bond	1.423	0.181	
$(\text{C}_6\text{H}_6)_2\text{Cr}$	1.419, 1.420	} 0.185	Keulen & Jellinek (1966)
	1.424		Haaland (1965)

Table 7. Charge refinement

Atomic charges

Cr	1.22 (5)	$(\text{Cr}^{3+}$ core assumed)	
C(1)	-0.10 (5)	C(4)	-0.08 (8)
C(2)	-0.10 (6)	O(4)	0.04 (5)
C(3)	-0.01 (6)		
H(1)	0.02 (5)		
H(2)	0.01 (7)	C(5)	-0.33 (5)
H(3)	0.04 (5)	O(5)	-0.10 (4)

$$R(F) = 0.034$$

$$R_w(F^2) = 0.075$$

Comparison with conventional refinement

Maximum shift in atomic position (H excepted):	0.0012 Å
Maximum change in temperature parameter:	1.5%

Comparison with M.O. calculations (BCT = benzene chromium tricarbonyl)

	Experimental BCT (averages)	SCCC calculations			<i>ab initio</i> Calculations		
		BCT <i>a</i>	BCT <i>b</i>	BCT <i>c</i>	$\text{Cr}(\text{CO})_6$ <i>d</i>	$\text{Ni}(\text{CO})_4$ <i>d</i>	<i>e</i>
Metal	+1.22	+0.57	+0.14	+0.28	+0.70	+0.47	+0.24
Carbonyls C	-0.25	-0.02		+0.27	+0.23	+0.23	+0.29
O	-0.05	-0.30		-0.49	-0.35	-0.35	-0.35
Total	-0.30	-0.28	-0.06	-0.22	-0.12	-0.12	-0.06
Benzene C	-0.07						
H	+0.02						
Total	-0.28	+0.26	+0.04	+0.40			

- (a) Carroll & Mc Glynn (1968).
 (b) Brown & Rawlinson (1969).
 (c) Our calculation.
 (d) Hillier & Saunders (1971).
 (e) Demuyneck & Veillard (1973).

Brown & Rawlinson (1969) (the differences are that we included all ligand–ligand overlap, and that the orbitals of CO were used in the form derived by Ransil (1960), without removing the $1s$ contributions and without modifying the π orbitals). The assumed geometry of the complex was that considered by Brown & Rawlinson, with D_{6h} symmetry of benzene. This was completed by calculations on free benzene and on dibenzene chromium. The geometry of benzene was left unchanged, and in dibenzene chromium, the distance of chromium to each benzene plane was 1.609 \AA (Keulen & Jellinek, 1966). At the end of each calculation we performed a Mulliken electron population analysis in terms of the atomic orbital basis-set. Table 6 shows the results of this analysis for the carbon–carbon bonds. The correlation between overlap populations and experimental bond lengths is quite satisfactory.

Position of the hydrogen atoms

According to the neutron diffraction results, all three symmetry-independent hydrogen atoms are displaced from the plane of the benzene ring by small amounts averaging 0.03 \AA . The displacements are in the direction of the $\text{Cr}(\text{CO})_3$ group (see Table 5). The oxygen atoms of the same molecule are too far away from the hydrogen atoms to account for this deviation on the basis of an electrostatic interaction. Intermolecular interactions could perhaps account for the displacement of H(1), because of the $\text{O}(5)\cdots\text{H}(1)$ interaction, but no such explanation is available for the other hydrogen atoms. It seems more likely that the distortion indicates a slight bending of the p_π orbitals on the benzene ring carbon atoms toward the chromium atom. The trigonal hybrids which form the σ bonding orbitals lie in the nodal plane of the p_π orbital, which no longer coincides exactly with the plane of the benzene ring. This leads to a slight bending of the CC bonds and to the observed displacement of the hydrogen atoms towards the chromium. If, on the other hand, the C–Cr bond would have a certain amount of carbon s character the carbon atom would be distorted towards a tetrahedral geometry and the hydrogen atom would be displaced away from the Cr atom, in clear disagreement with the experimental results.

Hodgson & Raymond (1973) give two alternative explanations for a similar distortion observed in bis-(1,3,5,7-tetramethylcyclooctatetraenyl)uranium(IV). The first of these is substantially similar to the interpretation given above, with the distinction that a re-hybridization of the ring carbons is invoked rather than a tilt of the p_π model plane and a slight bending of the endocyclic C–C bonds.

A bending of the C–H bonds of the ligands towards the central metal atom is a commonly observed feature in the structure of ‘sandwich’ complexes like dibenzene chromium (Haaland, 1965; Keulen & Jellinek, 1966) or ferrocene (Bohn & Haaland, 1966). In those complexes, the average bending angle is about $5 \pm 2^\circ$, com-

pared with 1.7° in the present study. In bis-(1,3,5,7-tetramethylcyclooctatetraenyl)uranium(IV), Hodgson & Raymond (1973) found an inward bending of the methyl groups averaging 4.1° . One might infer that such distortions are quite general; however, it must be noted that the effect is not observed in hexamethylbenzene chromium tricarbonyl (Bailey & Dahl, 1965*b*), in which two of the six methyl group carbon atoms are displaced by 0.09 and 0.06 \AA in a direction away from the chromium. It would follow from the argument given above that the corresponding Cr–C bonds have more s character than the bonds in benzene chromium tricarbonyl. Though the deviations from the benzene ring plane in hexamethylbenzene are undoubtedly significant, it would be helpful if a more accurate analysis of this structure were available.

Charge refinement

A refinement of X-ray data was carried out, varying all structural and thermal parameters, the scale factor, isotropic secondary extinction and the valence shell occupancies of all atoms, using the extended L -shell projection method (Stewart, 1970; Coppens, Pautler & Griffin, 1971).

The core scattering factors and the L -shell scattering factors (SCF atomic orbitals) for C and O, were taken from Stewart (1970). The hydrogen scattering factor was the same as in the conventional refinement. The selection of the core and the valence shell scattering factor of Cr is more difficult. We first considered for the core the scattering factor of Cr^{2+} and for the valence shell the difference between the scattering factors of Cr and Cr^{2+} . This assumption resulted in a negative occupancy number ($-0.11e$) of the valence shell. Therefore the refinement was modified by using the scattering factor of Cr^{3+} for the ‘core’ electrons. This resulted in an occupancy number of 1.78 ($5e$) of the valence shell. As can be expected, the results depend rather strongly on the assumptions made for core and valence shell of the metal. It would be highly desirable to derive an appropriate scattering factor for a Cr atom bonded in an organometallic complex.

The results of this second refinement are given in Table 7, which also shows the results of semi-empirical calculations on benzene chromium tricarbonyl, and of *ab initio* calculations on the parent compounds $\text{Cr}(\text{CO})_6$ and $\text{Ni}(\text{CO})_4$.

Some caution is needed in the comparison of experimental and theoretical charges, not only because the molecular orbital calculations assume an isolated complex, but also because the definition of atomic charges is not the same. As an example we may consider the Cr–C(O) bonds. Theoretical calculations, as well as our experimental results (see below), show that the bonding electrons are much nearer to the carbon atom of carbonyl than to the chromium atom and our refinement will ascribe them almost completely to the carbon atom by an artificial increase of the C thermal

parameter in the direction of the bond (mean square amplitudes for C(4) and C(5) from X-ray data: 0.0099 and 0.0127 Å² respectively, compared with 0.0072 and 0.0089 Å² from neutron data). In this way also a large part of the CO bonding electrons will be assigned to carbon. On the other hand, the Mulliken population analysis divides equally the overlap population between the two atoms of the bond. Compared to a Mulliken analysis a charge refinement will thus result in more positive chromium and oxygen atoms, and a more negative carbon.

Even with this in mind, the positive charge of chromium seems to be too large. This is probably due to inadequacy of the form factors used in the charge refinement. Both the radial and the angular dependence of the form factors may be deficient. The X-N maps discussed in the next section show evidence for lack of spherical symmetry of the bonded Cr atom, large asymmetrical features being observed in its vicinity.

In a similar complex, phenol chromium tricarbonyl, Wu, Biehl & Reeves (1972) showed, by comparison of the pK_a 's of the complexed and uncomplexed phenol for a number of substituents, that a positive charge is induced on the aromatic system by the strongly electron withdrawing Cr(CO)₃ groups. This is in agreement with the semi-empirical calculations, but not with the experimental charges.

Electron density

The use of spherical isolated atom form factors introduces systematic errors in the X-ray positional and thermal parameters from the least-squares refinement, which tend to eliminate aspherical density features from the difference density maps. This result of the 'curve-fitting' procedure can be eliminated by the calculation of the X-N (X-ray-neutron) density. The X-N difference electron density is the Fourier transform of $F_o - F_c$, where F_o is the observed X-ray structure factor (with the phase of F_c and divided by a scale factor k obtained in a single cycle on k only, using the X-ray observations and neutron parameters); and F_c the calculated X-ray structure factor using the same form factors as in the conventional refinement and the positional and thermal parameters as determined by neutron diffraction. The isotropic extinction parameter was taken from the conventional X-ray refinement (a refinement on the extinction parameter, keeping the positional and thermal parameters constant at the neutron values, did not affect the density maps). Fig. 3 shows three sections of the X-N difference electron density in the benzene plane, and in two planes perpendicular to the benzene ring and passing through Cr-C(4)-O(4) and through Cr-C(5)-O(5) respectively.

The maps shown are based on the X-ray reflections with $2\theta < 55^\circ$, *i.e.* all the reflections within the copper sphere. The corresponding maps based on all reflections show the same general features, but a considerably higher level of background noise. This is attributed

to larger experimental errors in the high-order data. Modifications of the cryogenic equipment and the data collection procedure have since been made which should give increased precision in subsequent studies now underway.

As may be expected, the background noise is higher in the section containing the symmetry plane, as errors in Fourier maps accumulate in symmetry planes.

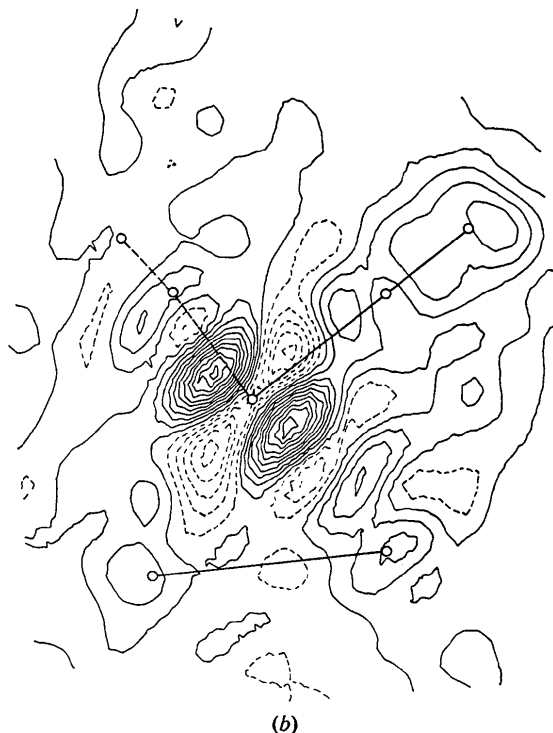
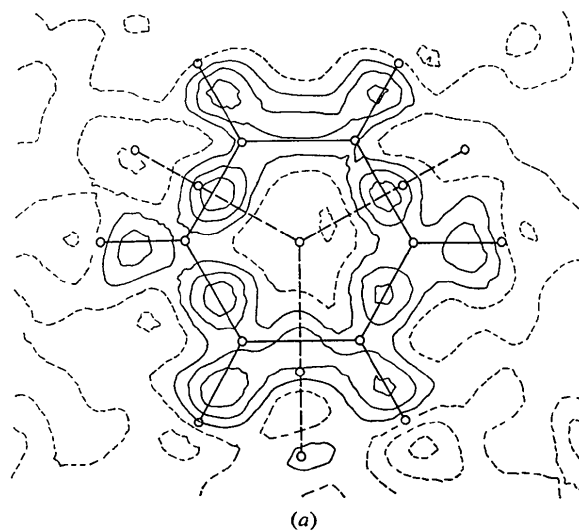


Fig. 3. Sections of the X-N difference density. Contours at 0.15 e Å⁻³. Negative contours dotted: (a) through plane of the benzene ring; (b) perpendicular to benzene ring containing Cr, C(4), O(4).

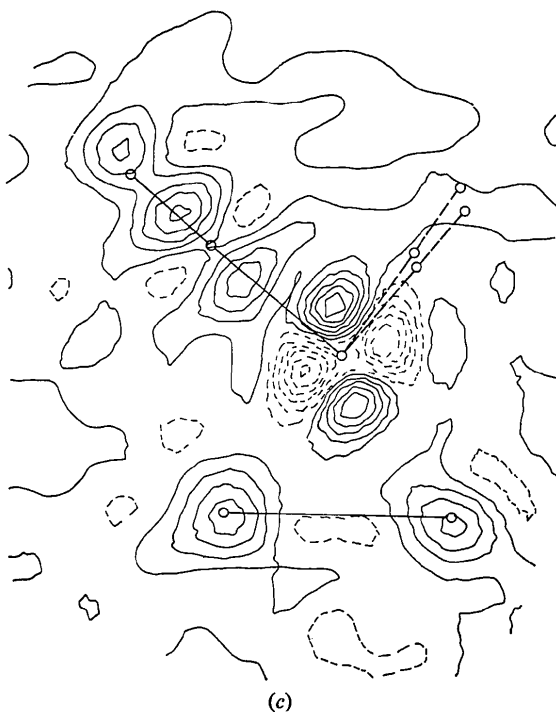


Fig. 3 (cont.) (c) Perpendicular to benzene ring containing Cr, C(5), O(5).

The bonding electrons in benzene and in the CO groups and the lone pair on the oxygen atoms are clearly apparent. So are also the bonding electrons of the Cr–C(O) bonds. The maxima of the corresponding peaks are at about 0.5 Å from C and 1.3 Å from Cr. This compares quite well with an *ab initio* calculation on Ni(CO)₄ (Demuyneck & Veillard, 1973), where it was found that the charge center of the localized orbitals representing the Ni–C bonds was at 0.46 Å from C and 1.38 Å from Ni. This is almost the same position as for the carbon lone pair in free CO for which Demuyneck & Veillard found the charge center of the localized lone pair at 0.41 Å from the carbon nucleus. In fact, the features of the X–N maps around the CO groups are quite comparable with the theoretical difference electron density computed by Hazelrigg & Politzer (1969) for carbon monoxide. The differences between this theoretical map and our X–N section through C(5)–O(5) are chiefly that the experimental residual peaks are lower by about 30% than the theoretical ones and are elongated in a direction perpendicular to the bond, features which may both be ascribed to thermal motion.

The main feature in the difference maps that is not readily explainable is the large density maximum ($> 1e \text{ \AA}^{-3}$) in the vicinity of the chromium atom. Comparable residual features are observed in X-ray difference density maps on Co(NH₃)₆Co(CN)₆ (Iwata & Saito, 1972). It seems probable that the map contains information on the nature of the transition-metal lig-

and bonding, but we feel that a confirmation by low-temperature studies of better accuracy is required before conclusions are drawn. This conviction is based in part on a comparison of the U_{ii} values from the X-ray and neutron experiments. Since the U_{ii} 's from X-ray data include bonding effects, they are generally found to be larger than the corresponding neutron values. This is so in the present study for most U_{11} and U_{33} values, but not for U_{22} : the neutron U_{22} values are always higher than the corresponding X-ray parameters, indicating the presence of systematic errors. To analyze the effect on the difference density, the X–N maps were recalculated with neutron U_{ii} values re-scaled: the neutron U_{ii} parameters were multiplied by a constant k_i ($i=1,2,3$) such that $\sum k_i U_{ii}$ (neutron) = $\sum U_{ii}$ (X-ray), where the sums are over all non-hydrogen atoms. In these maps the density in the benzene ring C–C bonds conforms better to sixfold symmetry, but the agreement between the C–H bonds is somewhat poorer. The features around the chromium atom are largely preserved, and are therefore not an artifact of the difference in the U_{22} values. Chromium hexacarbonyl is presently under study, and we hope better insight will be gained when this work is completed.

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The Crystal Structure of Wittichenite, $\text{Cu}_3\text{BiS}_3^*$

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Wittichenite, Cu_3BiS_3 , from the type locality in Wittichen, West Germany is orthorhombic, $a = 7.723$ (10), $b = 10.395$ (10), $c = 6.716$ (5) Å; $D_{\text{meas}} = 6.01$, $D_{\text{calc}} = 6.11$ g cm $^{-3}$; $Z = 4$; space group $P2_12_12_1$. The structure was solved by the heavy-atom method from 695 observed symmetry-independent reflexions $F_0^2 \geq 2\sigma F_0^2$ collected on a Picker four-circle FACS-1 diffractometer using Zr-filtered Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation. Spherical absorption corrections were applied to the data ($\mu R = 10.5$) and the structure was refined by full-matrix least-squares using anisotropic temperature factors to an R value of 4.9% ($R_w = 6.7\%$). The structure consists of infinite BiCu_3S_3 chains parallel to [001] which are linked by Cu–S bonds to form continuous sheets normal to [010]. Adjacent sheets are related by the 2_1 axes parallel to [100] and are linked by Cu–S and Bi–S bonds. Cu is in nearly trigonal planar coordination with S (Cu–S distances 2.255 to 2.348 Å; S–Cu–S angles 110.8 to 131.8°). The packing of CuS_3 polyhedra in the structure yields short Cu–Cu contacts ranging from 2.61 to 2.94 Å. Bi is trigonally coordinated by S (Bi–S distances 2.569 to 2.608 Å; S–Bi–S angles 94.2 to 98.7°). S is tetrahedrally coordinated by three copper atoms and one bismuth atom.

Introduction

Wittichenite is a bismuth sulphosalt of copper, apparently first described in 1805 by Selb (Hintze, 1904)

from Wittichen in Baden, Germany, under the name Kupferwismuthertz. The original chemical analysis, which established the composition as Cu_3BiS_3 , was performed by Klaproth in about 1807. Later the mineral was renamed wittichit and finally wittichenit (wittichenite) in 1853.

The early mineralogists recognized a second copper bismuth sulphosalt in the ores from Wittichen, namely

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