Acta Cryst. (1974). B**30**, 838

Crystal structure of bis(benzene) chromium iodide.*

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(*Received* 21 *September* 1973; *accepted* 7 *November* 1973)

The crystal structure of bis(benzene) chromium(I) iodide, $Cr(C_6H_6)_2I$, has been determined from 225 Mo $K\alpha$ intensity data. At room temperature the atoms of the benzene rings are disordered with the rotation axis of the $Cr(C_6H_6)^+$ ion along the *c* axis of the body-centered tetragonal cell ($Z=2$) of dimension $a_0=7{\cdot}031$ (3) and $c_0=11{\cdot}754$ (5) Å. Below about −95 °C, the rings evidently order, reducing the symmetry to orthorhombic, probably *Immm*.

Introduction

Very-low-temperature specific heat (Polgar & Friedberg, 1971), proton resonance (Karimov & Shchegolev, 1965), and magnetic susceptibility measurements (Smith & Friedberg, 1969) suggest that the long-range antiferromagnetic ordering near 1 °K in $Cr(C_6H_6)_2I$ may consist of spin ordering of dimensionality less than three. Preliminary room-temperature space-group determinations and unit-cell parameters (Friedberg, 1973) suggested a structure in which $Cr(C_6H_6)_2^+$ ions were oriented along the *c* axis with probably disordered benzene rings, whereas the proton resonance study was interpreted to show these ions were oriented along the *a* axis; however, no structure study had been completed to verify either arrangement. This paper reports our room-temperature structure results as well as the probable low-temperature arrangement.

Experimental details and results

Transparent orange crystals in the form of square plates, with large (001), small (110) and occasionally very small (111) faces developed, were supplied to us by Friedberg (1973). Crystals can be grown from pure methanol or other suitable solvents (methanol, ethanol, or acetone) diluted 1:1 with benzene. Crystals subjected to normal levels of room illumination will decompose; hence, unnecessary exposure to light must be avoided.

Lattice constants $a_0=7{\cdot}031$ (3) and $c_0=11{\cdot}754$ (5) Å determined on our diffractometer and possible space groups of $I\bar{4}2m$, $I\bar{4}m2$, $I422$, $I4mm$ and $I4/mmm$ based on precession photographs were in excellent agreement with previous results (Friedberg). Long-exposure Laue photographs along various directions were consistent with $4/mmm$ symmetry; however, space group $I\bar{4}m2$ was initially selected because a simple disordered model could be proposed which would, upon ordering, involve the smallest changes in order to be compatible with our low-temperature precession photographs. These low-temperature data always indicated our crystal specimens were twinned and probably belonged to space group *Immm*; cell dimensions at −100 °C were $a_0=6{\cdot}82$, $b_0=7{\cdot}04$ and $c_0=11{\cdot}64$ Å. No improvement in spot-shape, definition or sin θ dependence was observed with the low-temperature precession photographs; however, a small decrease in the diffuse pattern of Laue photographs was noted. This suggested that the small decrease in thermal motion between the room- and low-temperature structures appears to be confined to only part of the cell contents.

Room-temperature Mo $K\alpha$ intensity data were measured on a cleaved and solvent-eroded specimen ($\sim 0{\cdot}046 \times 0{\cdot}026 \times 0{\cdot}011$ cm) mounted on the long [110] direction. The θ–2θ scan technique and a scintillation detector employing pulse-height discrimination were used to measure an octant of data to 55° 2θ. Absorption corrections *A* were applied ($\mu=38{\cdot}0$ cm^{-1}) and a unique data set of 225 intensities was obtained by averaging pairs of symmetry-equivalent values whenever measured. The value of 42 intensities *I* were found to be less than 3σ, where $\sigma=A[(N_{SC}+K^2N_B)/I]n^{1/2}$ and

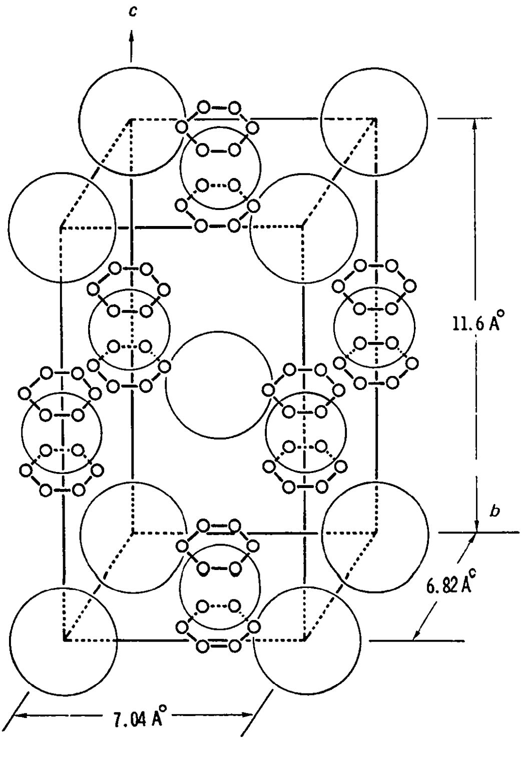

Fig. 1. Schematic representation of the proposed low-temperature structure. The benzene rings are believed to be ordered as shown in *Immm* symmetry at low temperatures, while at room temperature they are completely disordered, probably rotating, in a tetragonal structure with $a=b\simeq 7{\cdot}03$ and $c\simeq 11{\cdot}8$ Å.

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* This work was supported by the U.S. Atomic Energy Commission.

N_{SC}, N_B, K and n are the total scan count, background counts, time ratio of the scan to background and number of equivalent values, respectively; these 42 intensities were assigned a value equal to 3σ and were specially treated in subsequent calculations. (These reflections contributed to least-squares refinement and Fourier synthesis only if $F_o > F_c$; they were not included in the residual index R, where $R = \sum||F_o| - |F_c||/\sum|F_o|$.) Structure factors were calculated using scattering factors taken from Table 3·3·1A and 3·3·1B and the iodine dispersion correction from Table 3·3·2C of *International Tables for X-ray Crystallography* (1962). Since $Z=2$, the positional parameters of the chromium and iodide ions are fixed at $0,0,\frac{1}{2}$ and $0,0,0$ (plus equivalent body-centering positions), respectively; hence, the corresponding isotropic thermal parameters were refined ($R = 0{\cdot}207$). A Fourier difference synthesis based on such phases established that the benzene rings are completely disordered, probably rotating, on planes above and below the chromium ions. Attempts to fit this 'donut' of electron density using 12 carbons for each ring, with a occupation parameter $p=\frac{1}{2}$ as required by the tetragonal symmetry, were not as satisfactory as when 24 carbons were used ($p=\frac{1}{4}$). Hence, it appears that at room temperature the benzene rings are either rotating or completely disordered in the structure. No particular group or zone of intensities seem to be particularly affected by this 'two-dimensional' disorder; hence, weights for least-squares refinement were taken from counting statistics with no special emphasis to the proposed disorder. Final least-squares refinement ($R = 0{\cdot}055$) involved a 'z' parameter for the benzene ring (the C–C distance was fixed at 1·40 Å), an isotropic thermal parameter for the carbon atoms, and anisotropic thermal parameters for the chromium and iodide ions (Table 1). One notes that the thermal parameters for the chromium must be influenced by the presence of benzene rings 1·59 Å along the c axis. The relatively low value of the carbon thermal parameter appears to suggest a disordered structure rather than one involving rotating rings; the decrease in diffuse scattering appears to suggest the reverse conclusion. Very likely the actual case may be a mixture of these two models. The Cr–C separation is 2·13 (4) Å, closest I–C separation is 3·90 (4) Å, and closest intermolecular C–C separation is 3·43 (4) Å.*

Table 1. *Parameters for (bis)benzene chromium iodide*

For Cr and I, $x=y=0$, $U_{11}=U_{22}$, and $U_{12}=U_{13}U_{23}=0$ as required by symmetry.

	z	U_{11}	U_{33}
Cr	$\frac{1}{2}$	0·048 (2)	0·021 (2)
I	0	0·075 (1)	0·077 (2)
C	0·364 (4)	0·05 (1)	

Upon cooling, the benzene rings become ordered. Low-temperature data do not reveal any departures from orthorhombic symmetry; however, the chromium and iodide ions dominate the scattering and small differences may escape detection. If the assumption is made that the cell is orthorhombic at low temperature and intermolecular contact separations of the hydrogen atoms are considered, the orientation of all the benzene rings becomes fixed, as illustrated in Fig. 1. The 3% difference in the a and b axes, if maintained to temperatures below 1°K, is sufficient to explain the two proton-resonance lines observed (Karimov & Shchegolev). Because of the twinned nature of the low-temperature specimen, no further work is planned on this material.

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* A list of observed and calculated structure factors is available from the author, and has also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30279 (3 pp.). Copies may be obtained from The Executive Secretary, IUCr, 13 White Friars, Chester CH1 1NZ, England.

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