Low-temperature refinement of the crystal structure of α-phenazine. By F. L. Hirshfeld and

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The crystal structure of α-phenazine has recently been derived (Herbstein & Schmidt, to be published) from three-dimensional X-ray diffraction data at room temperature. The $h0l$ intensities have now been redetermined at a temperature of about 90° K. by means of several Weissenberg photographs of two different crystals cooled in a stream of boiling nitrogen. An anisotropic contraction on cooling is indicated by a change in cell dimensions from

$$a = 13\cdot21 \text{ Å}, \quad b = 5\cdot06 \text{ Å}, \quad c = 7\cdot10 \text{ Å}, \quad \beta = 109\cdot3°$$

to $a = 12\cdot97$ Å, b unmeasured, $c = 7\cdot06$ Å, $\beta = 109\cdot0°$.

Through the use of both Cu $K\alpha$ and Mo $K\alpha$ radiation, a total of 174 $h0l$ spectra have been recorded, up to a maximum value of $s = 2 \sin \theta/\lambda = 2\cdot58$ Å^{-1}, as compared with 106 spectra recorded at room temperature up to a maximum of $s = 1\cdot66$ Å^{-1}. The general increase in the intensities of the high-angle reflexions corresponds to a pronounced sharpening of the atomic electron-density maxima, permitting a more accurate determination of atomic coordinates. In the b-axis projection (Fig. 1),
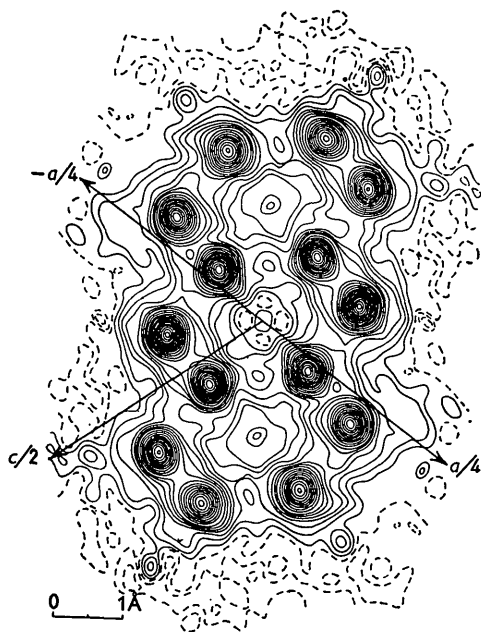

Fig. 1. Electron density projected on to (010), computed at 120ths along a and at 60ths along c. Contour intervals are 2 e.Å^{-2} above 6 e.Å^{-2}, 1 e.Å^{-2} elsewhere. Negative contours broken.

based on a Fourier summation of all observed structure factors, the average carbon peak density is 27·4 e.Å^{-2}, as compared with 8·3 e.Å^{-2} in the corresponding projection at room temperature (Herbstein & Schmidt, 1952). A slight falling off of atomic peak densities with in-

creasing distance from the molecular centre suggests an appreciable vibration of the molecule about its centre. The hydrogen atoms are readily distinguishable, with an average peak density of 2·2 e.Å^{-2}. Refinement by successive $F_o - F_c$ syntheses has led to a discrepancy factor of 0·124 for all observed spectra if the hydrogen contributions to the calculated structure factors are neglected and 0·098 if they are included.

To the observed structure factors, adjusted for the calculated contributions of the nitrogen and hydrogen atoms, has been fitted an isotropic atomic scattering-factor curve for carbon. This experimental carbon f-curve, recorded in Table 1, differs significantly both from the

Table 1. *Experimental atomic scattering factor f for carbon as a function of $s = 2 \sin \theta/\lambda$*

s (Å^{-1})	f	s (Å^{-1})	f
0	6·00	1·4	0·73
0·2	5·23	1·6	0·59
0·4	3·85	1·8	0·45
0·6	2·52	2·0	0·33
0·8	1·62	2·2	0·24
1·0	1·17	2·4	0·18
1·2	0·88	2·6	0·15

James & Brindley (1932) curve and from the McWeeny (1951) curve for valence-state carbon in a manner that cannot be accounted for by thermal vibration alone. After linear extrapolation of this curve to zero at $s = 3\cdot74$ Å^{-1}, its three-dimensional Fourier transform (Fig. 2)

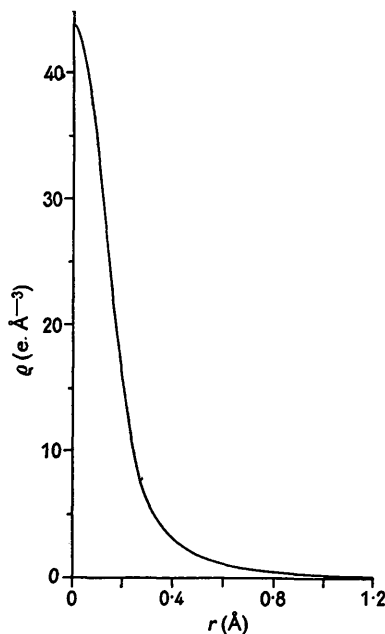Fig. 2. Three-dimensional Fourier transform of extrapolated experimental scattering-factor curve for carbon.

shows a peak electron density of 44·0 e.Å^{-3}, of which 9·6 e.Å^{-3} is due to the extrapolated portion of the f-curve, and a central curvature of 2350 e.Å^{-5}, half of which arises from the extrapolation.

Work is proceeding on the low-temperature refinement of the other two zones in the hope of obtaining final bond lengths for comparison with those derived from the three-dimensional room-temperature analysis.

We are indebted to Messrs H. Polak and A. Rathouse of I.B.M. (Israel) Ltd, Tel Aviv, and to the computing staff of the El Al Israel Airlines, Lydda, for making available to us the I.B.M. accounting machines used in the final Fourier summations.

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A note on the crystal structure of Zeise's salt.

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Although Zeise's salt, $K(PtCl_3.C_2H_4)H_2O$, has been known for well over a century (Zeise, 1827), its constitution is still a matter of controversy. Each of the electronic structures proposed to account for the bond between Pt^{II} and ethylene implies some particular arrangement of the carbon atoms in relation to the PtCl$_3$ group (Chatt, 1949, 1951). An X-ray analysis of Zeise's salt has been undertaken in the hope of narrowing down the theories concerning its constitution.

Early morphological investigation by Jorgensen (1900) showed that the crystals belong to the monoclinic sphenoidal class.* Cell parameters, estimated from rotation and Weissenberg photographs, are

$$a = 10{\cdot}70, \ b = 8{\cdot}42, \ c = 4{\cdot}81 \ \text{Å}; \ \beta = 97° \,.$$

The density calculated for a cell containing two asymmetric units is 2·97 g.cm.$^{-3}$; the value found was slightly greater than 2·89 g.cm.$^{-3}$. Systematic absences of reflexions and a positive pyroelectric test are compatible with the space-group $P2_1$. The x, y and z co-ordinates of platinum, potassium and chlorine, determined from (010) and (001) Patterson and (010) electron-density projections are:

	x	y	z
Pt	0·106	0·000	0·771
Cl(2)	0·106	0·223	0·771
Cl(3)	0·106	0·777	0·771
Cl(1)	0·216	0·000	0·712
K	0·219	0·313	0·297

From these co-ordinates it follows that platinum and the three chlorine atoms are coplanar. While two of the Pt–Cl bond lengths are normal (2·32 Å), the third (Pt–Cl(1)) (Fig. 1), which is 'trans' to the expected posi-
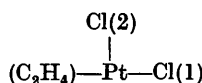
Cl(2)
|
(C$_2$H$_4$)—Pt—Cl(1)
|
Cl(3)

Fig. 1.

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* Axial ratios derived from the above cell parameters, though not identical with those determined by Jorgensen, are consistent with them.

tion of the ethylene molecule, is abnormally long (2·42 Å). Since the well known 'trans directing' influence depends on the fact that the ethylene labilizes this chlorine atom (Cl(1)), the observed increase in bond length is of considerable interest.

Owing to the small diffracting powers of carbon and oxygen, as compared with those of platinum, potassium and chlorine, the parameters of the former atoms are at present uncertain. However, it may be stated that it is highly improbable that there is any atom bound to platinum and collinear with it and Cl(1). Two of three minor peaks in the (010) projection may be interpreted as being due to carbon atoms forming a triangle with platinum which, when the PtCl$_3$ group is viewed side on, appears as shown in Fig. 2. (M represents three atoms:
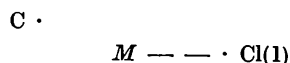
C ·

M — — · Cl(1)

C ·

Fig. 2.

Pt in the plane of the paper, Cl(2) above and Cl(3) below the plane of the paper.) The C–C axis is therefore approximately at right angles to the plane of the PtCl$_3$ group. The third peak presumably represents oxygen of the water of crystallization, an assumption which appears reasonable from atomic packing considerations.

Owing to large thermal vibrations of the atoms, the number of reflexions observed at room temperature was insufficient for satisfactory resolution of carbon and oxygen peaks. Weissenberg photographs of crystals maintained at the temperature of liquid air are being taken to obtain enough reflexions to refine the (010) projections and to investigate the (001) projection.

In summary, the results of this preliminary investigation favour a triangular arrangement of platinum and ethylene rather than the 'end on' linkage implied by Chatt's ethylidene structure (Chatt, 1951).

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