

double bond character (as commonly it occurs for transition metal-chlorine or metal-bromine bonds) this amount will be reduced. The effect was demonstrated in lengthening Me-X bonds in square planar complexes of platinum and palladium, for some of which the structure is known: the anion of Zeise's salt $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ (Wunderlich & Mellor, 1954, 1955), the corresponding bromo complex $[\text{Pt}(\text{C}_2\text{H}_4)\text{Br}_3]^-$ (Bokij & Kukina, 1957), *cis*- $[\text{Pt}(\text{C}_2\text{H}_4)\text{NH}_3\text{Br}_2]$ (Kukina, Bokij & Brusentsev, 1964), the ethylene-palladium chloride complex (Dempsey & Baenziger, 1955) and the styrene-palladium chloride complex (Holden & Baenziger, 1955). This effect can probably be generalized to the present case, because Jenkins, Lupin, Shaw & Smithies (1966) have obtained infrared and nuclear magnetic resonance spectroscopic evidence for the *trans* effect in octahedral complexes of ruthenium(II). Noticing that the compound $[\text{RuBr}_2(\text{CO})_3]_2$ examined may be considered as a dimeric form of a *cis*-bromocarbonyl complex of Ru^{II} , our suggestion can be proved analysing the structure of a *trans*-bromo compound of the metal.

We are indebted to Prof. P. Pino for having supplied us with crystals of the compound, and to Prof. S. Bonatti for his encouragement and help throughout the course of the structure determination. The valuable criticism and discussion of the data by Prof. P. Corradini and Prof. O. S. Mills are gratefully acknowledged.

The three-dimensional Fourier difference synthesis was calculated with a program written by A. Domenicani and D. Giucci. All the calculations were performed on the IBM 7090 computer of the Centro Nazionale Universitario di Calcolo Elettronico (Pisa).

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The Crystal Structure of Iodine Monobromide, IBr

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The crystal structure of iodine monobromide has been determined and refined to $R=6.5\%$. The crystal is orthorhombic, $C_{2m}2_1$ (no.36), with four molecules in a unit cell of dimensions $a=4.90$, $b=6.99$, $c=8.93$ Å. All atoms lie on mirror planes and the molecules form a herringbone pattern similar to that in crystalline iodine. The intramolecular I-Br distance is 2.52 Å and the shortest intermolecular I...Br distances are 3.18 and 3.76 Å.

Introduction

The structure of iodine monobromide was studied in order to compare it with the structures of iodine and iodine monochloride. In both of the latter there are short intermolecular distances which suggest unusually strong interaction between adjacent molecules. Iodine monobromide is apparently the only iodine-bromine interhalogen compound. Its approximate structure was

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inferred (Heavens & Cheesman, 1950) on the basis of powder data from a series of solid solutions (0-38 mole % Br). No actual structure determination has been reported.

Experimental

Iodine bromide was formed by direct combination of the elements. Iodine and bromine form a nearly continuous series of solid solutions with iodine bromide.

A melt containing about 60 mole % bromine was prepared; duplicate samples were withdrawn and sealed in capillaries at intervals of several minutes as the bromine concentration decreased by evaporation. One of each pair of capillaries was broken in a bisulfite solution and analyzed for bromine and iodine by automatic potentiometric titration. If the analysis indicated an I:Br ratio of 1.00 ± 0.02 the remaining member of the pair was saved for crystallographic use. Strong evidence for formation of the compound under these conditions is the osculation of the solidus and liquidus curves on the plot of freezing point against composition (Meerum-Terwogt, 1905). Single crystals were grown within the capillaries in a miniature Bridgman (thermal gradient) furnace. After much experimentation, a single crystal formed with a useful zone axis within 5° of the capillary axis.

Systematic absences ($h+k \neq 2n$ for hkl reflections, and $l \neq 2n$ for $0kl$ reflections) are consistent with the space groups $Ccmm$ (no. 63), $Cc2m$ (no. 40) and $Ccm2_1$ (no. 36). Lattice constants were measured at 20°C by a Polaroid-precession technique described elsewhere (Swink & Carpenter, 1967) with $\text{Pb}(\text{NO}_3)_2$ ($a = 7.8566 \text{ \AA}$ at 21°C) as a standard; values in parentheses are the formal estimated standard deviations in the last place:

$$a = 4.903 (3) \text{ \AA}$$

$$b = 6.993 (6)$$

$$c = 8.931 (5)$$

$$\rho_{\text{calc}} = 4.49 \text{ g.cm}^{-3} \quad \text{for } Z = 4$$

$$\rho_{\text{obs}} = 4.41 \quad (\text{Meerum-Terwogt, 1905})$$

Intensity data were obtained at room temperature ($20\text{--}25^\circ\text{C}$) from seven layers along the $[310]$ rotation axis with use of the multiple-film equi-inclination Weissenberg technique and $\text{Mo } K\alpha$ radiation. Films were measured on a Joyce-Deeley flying-spot integrating microdensitometer. Deviations in repeated measurements of each reflection on the same film and the fit of all data to a single film factor led to the estimated weight for a single measurement of intensity:

$$w = 1/\sigma^2, \quad \text{where } \sigma(I) = 7.5 + 0.10I.$$

These weights, the single film factor, and its formal estimated standard deviation were used to compute scaled, weighted average intensities and their standard

deviations. Cylindrical absorption and Lorentz-polarization corrections were applied *via* the local intensity correction program (BXITFW).

Refinement

Packing considerations pointed to a structure with both iodine and bromine atoms in positions $4(a)$ of $Ccm2_1$. This was also the conclusion of Heavens & Cheesman. Ordered arrangements in the space groups $Cc2m$ or $Ccmm$ lead to chemically unreasonable structures.

The full-matrix least-squares program ORFLS of Busing, Martin & Levy (1962), modified for dispersion corrections (Ibers & Hamilton, 1964) was used for least-squares refinement. All refinement of the structure was based on observed reflections only. Complex scattering amplitudes were formed using HFS values (Hanson, Herman, Lea & Skillman, 1964) for f_0 , and calculated values of $\Delta f'(0)$ and $\Delta f''(0)$ (Cromer, 1965) with angular variations from values listed in *International Tables for X-ray Crystallography* (1962). The model derived from packing considerations gave a conventional $R = 0.315$ (observed reflections only). Four cycles of isotropic refinement led to a structure with $R = 0.116$, $R_w = 0.132$. Similar refinement of the enantiomorphic structure gave no significant difference in agreement. Nevertheless, the structure with slightly better agreement was picked for further refinement.

A secondary extinction correction was then applied by using the approximation:

$$|F|_{\text{corr}} \sim |F|_{\text{obs}}(1 + \beta c I_{\text{obs}})$$

(Zachariasen, 1963) with $c = 1.2 \times 10^{-4}$. Problems of radiation-independent simultaneous diffraction were fortuitously avoided by rotation about the $[310]$ axis. A further consequence of this choice of rotation axis was that the Weissenberg layers represented oblique reciprocal lattice nets, so that it was possible to refine both the seven scale factors for the individual layers and the anisotropic temperature factor parameters.

Five cycles of subsequent anisotropic refinement led to the structure described in Table 1. Final discrepancy indices for observed reflections only were $R = 0.065$, $R_w = 0.075$ and coordinate shifts on the final cycle were all less than 0.01 of the formal estimated standard deviations. Table 2 lists $|F|_{\text{obs}}$ for observed reflections, the estimated upper bound for reflections too weak to

Table 1. *Final atomic parameters*

Estimated standard deviations are in parentheses. The temperature factor has the form

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{13}hl)].$$

The z/c coordinate of the bromine atom is arbitrary.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{13}
I	0.4412 (6)	0	0.1155 (4)	0.0368 (6)	0.0138 (4)	0.0060 (3)	0.0007 (7)
Br	0.1432 (9)	0	[-0.1146]	0.0331 (20)	0.0204 (8)	0.0052 (5)	0.0009 (7)

$$\beta_{12} = \beta_{23} = 0$$

Table 1), implying that major axes of the vibration ellipsoids are approximately parallel to the crystallographic axes. Table 4 therefore presents the thermal displacements along the crystal axes, as well as the r.m.s. thermal displacements. The interatomic distances in part (b) of Table 3 are corrected for the effect of thermal motion in the manner which seems appropriate for each kind of distance; these corrected values are the ones used in figures and discussion.

Table 4. *Thermal displacement data, with estimated standard deviations in parentheses*

(a) R.m.s. radial thermal displacements.					
I	0.322 (4) Å	Br	0.335 (5) Å		
(b) R.m.s. axial components of thermal displacement.					
I	<i>x</i>	0.212 (5) Å	Br	<i>x</i>	0.201 (6) Å
	<i>y</i>	0.185 (3)		<i>y</i>	0.225 (4)
	<i>z</i>	0.156 (4)		<i>z</i>	0.145 (7)

Fig. 2 shows that there are two pairs of iodine-bromine intermolecular distances which are considerably shorter than the sum of the negative ion radii: the distances $I \cdots Br' = I'' \cdots Br = 3.18$ Å (about 0.9 Å less than the sum of the negative ion radii) and $I \cdots Br'' = I' \cdots Br = 3.76$ Å (about 0.3 Å less than the sum of the negative ion radii). On the other hand, the distance $I-Br = 2.52$ Å is about 0.05 Å longer than the sum of the usual single bond radii. The conspicuously short $I \cdots Br'$ distances, and their symmetric equivalents, tie the I-Br molecules into planar zigzag chains running parallel to the *c* axis. This feature is similar to the chains in α - and β -iodine monochloride, but the details of the chains are different. If the slightly short $I \cdots Br''$ distances are considered, the molecules are linked into planar sheets like those in iodine.

The main features of this arrangement are consistent with a description of the bonding in terms of delocalized molecular orbitals, similar to that given for crystalline iodine (van Bolhuis *et al.*, 1967). The nearly linear set of three atoms, Br, I, and Br', can be joined by a three-center, four-electron bond composed of molecular orbitals formed from *p*-orbitals along the molecular axis. This explains the shortness of $I \cdots Br'$, the length of Br-I, and the nearly linear arrangement. On the other hand, the set of three atoms, I'', Br, I, would be expected to show much weaker bonding of this type because the lesser electronegativity of the end atoms, relative to the preceding case, raises the energy of the occupied non-bonding molecular orbital (Rundle, 1962). This is consistent with the greater deviation from linearity and the greater length of $I'' \cdots Br$ than of $I \cdots Br'$. Since $I'' \cdots Br$ is nevertheless shorter than would be expected for non-bonded atoms, a more complete description might require the use of six electrons on the four centers I'', Br, I, and Br'. The other bonds involving the same atoms are approximately perpendicular to the direction of the multicenter bonds described, as would be expected if they were formed from other *p*-orbitals on the atoms.

In iodine monobromide, every bromine atom forms a short 3.18 Å contact with an iodine atom in an adjacent molecule. In iodine monochloride, in both forms, only half of the chlorine atoms are involved in such short contacts. This seems to reflect the tighter hold which chlorine has for its unshared electron pairs, as indicated by its electronegativity slightly higher than that of bromine.

The pattern of intermolecular distances which occurs in iodine monobromide can also be explained on the basis of the expected anisotropy in polarization and repulsion forces around the atoms in the I-Br molecule. This point is to be discussed in more detail elsewhere (Swink, 1968). In any case, polarization forces undoubtedly make a significant contribution to the binding energy of the structure.

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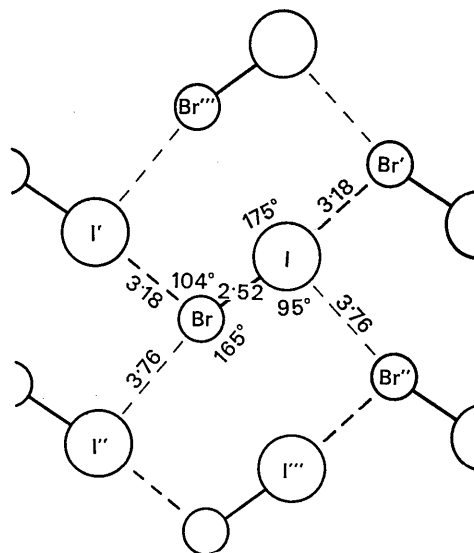


Fig. 2. One iodine monobromide molecule and its neighbors in the same mirror plane, showing important distances (Å; corrected for thermal motion) and angles.

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A Case of 'Pseudo-Homometric' Structure in the Complex Nickel(II) Bis-(*N,N*-di-*n*-propyldithiocarbamate)*

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A case of 'pseudo-homometric' structure, observed in the complex nickel(II) bis-(*N,N*-di-*n*-propyldithiocarbamate), is described. The 'false' molecule ($\frac{1}{2}, \frac{1}{2}, 0$) can be roughly obtained by shifting the molecule ($\frac{1}{3}, \frac{1}{3}, \frac{2}{3}$) or by a rotation of the true molecule ($\frac{1}{2}, \frac{1}{2}, 0$).

Isovectorial structures which are different but have the same interatomic distances and, furthermore, the same structure factor values, have been defined as *homometric* (Patterson, 1944; Garrido, 1951): their solution will not be unique. Structure solutions characterized by almost identical Patterson functions have been called 'pseudo-homometric' (Luzzati, 1953; Hemily, 1957). When the chemical and geometric conditions do not allow us to discard the false solution easily, the right one may be found by using all the reflexions in a three-dimensional Patterson synthesis.

In some structures the correct solution can be obtained from the false one through crystallographic operations. In the case of *p*-nitroaniline the false structure (Abrahams & Robertson, 1948) has been corrected by shifting the origin (Donohue & Trueblood, 1956), and likewise for calcium ferrite (Decker & Kasper, 1957). The true structure of triphenylene was obtained (Pinnock, Taylor & Lipson, 1956) by simply correcting the position of the molecule which had been already correctly orientated (Klug, 1950). In other cases the true solution was reached by some rearrangement of the atoms, as in the case of DL-9,10-methyleneoctadecanoic acid (Brotherton, Craven & Jeffrey, 1958), of monoterpene isoiridomyrmecin C₁₀H₁₆O₂ (Schoenborn & McConnell, 1962), and of Na₂O·GeO₂·6H₂O (Jamieson & Glasser, 1967).

In the course of the determination of the crystal structure of nickel(II) bis-(*N,N*-di-*n*-propyldithiocarbamate), Ni[(C₃H₇)₂NCS₂]₂, rhombohedral, space group *R* $\bar{3}$, *a* = 25·20, *c* = 8·30 Å (Peyronel & Pignedoli, 1967)

we obtained a false structure by starting with a two-dimensional Patterson synthesis and by a trial-and-error method. The molecule was correctly located in the centre of symmetry. The refinement by means of three-dimensional Fourier sections gave a rather good representation of the molecule in the *XY* projection [Fig. 1(*a*)] but it was impossible to reduce *R* below 0·55. Also the interatomic distances and angles were not correct. Fig. 2 shows a combination of three-dimensional *YZ* sections in the *YZ* plane, which is arbitrarily schematic in order to avoid the atoms being superimposed as they would be in a correct projection.

From three-dimensional Patterson syntheses it was possible to obtain the correct orientation of the molecule as shown in the final composite *XY* projection of three-dimensional Fourier sections [Fig. 1(*b*)]. This structure refined satisfactorily to *R* = 0·075 (Peyronel & Pignedoli, 1967).

The false molecule appears in the *XY* projection [Fig. 1(*c*)] as having been rotated about 42–50° anticlockwise from the true position. This false orientation may also be roughly obtained by shifting the molecule (*B*) located in the ($\frac{1}{3}, \frac{1}{3}, \frac{2}{3}$) position into the ($\frac{1}{2}, \frac{1}{2}, 0$) position. This molecule has in the *XY* projection an orientation of 60° with respect to the real molecule (*A*) located in the ($\frac{1}{2}, \frac{1}{2}, 0$) position [Fig. 1(*c*)]. Therefore the false structure may be considered very roughly as 'pseudo-homometric' to the true one.

Other conditions may contribute to the rather good representation of the molecule in the false position: nickel, being in the right place, gives an important and correct contribution to the calculated structure factors of the false solution; some atomic positions in the false structure are very near to those of other atomic posi-

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