could be connected with activity of FU in some situations, for example when FU is substituted into RNA. The variety of stacking interactions observed in the FU structure demonstrates that a particular stacking geometry seems to be affected by a number of external constraints. The matter is therefore not simple, and it is difficult to generalize about the stacking geometry of FU in other environments. Interactions as strong as those observed between fluorine atoms and nitrogen atoms of adjacent pyrimidine rings have no counterpart in naturally occuring purine or pyrimidine bases. These

kinds of interaction should be investigated further, since they are liable to recur in various environments and could be connected with the mutagenic action of FU.
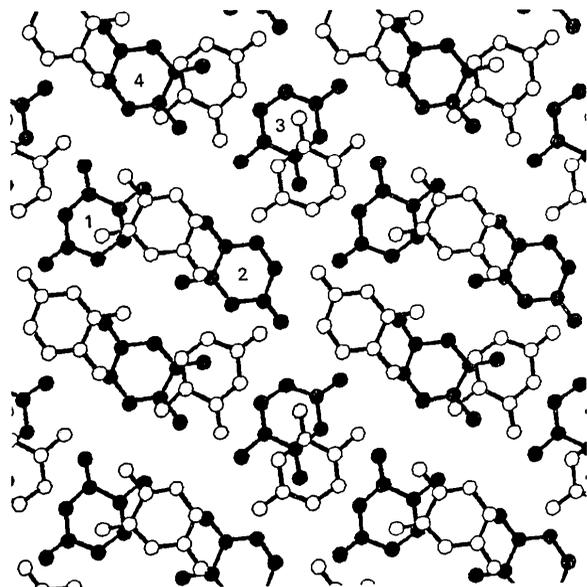
Fig. 5. Projection of molecular layer at $x \sim \frac{3}{4}$ and layer at $x \sim \frac{1}{4}$ onto (100). Black circles represent atoms in layer at $x \sim \frac{1}{4}$.

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The Crystal Structure of KIBr₂.H₂O

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Crystals of potassium dibromoiodide monohydrate, KIBr₂.H₂O, are orthorhombic, space group Pnnm, with $a = 12.183$ (5), $b = 13.046$ (5), $c = 4.390$ (3) Å, $Z = 4$. All atoms lie on mirror planes. The structure was refined from diffractometer data by least-squares methods to $R = 5.8\%$. The structure consists of nearly linear chains of halogen atoms extending infinitely along b. The two independent IBr₂⁻ anions are linear and symmetrical, both with I–Br bond lengths of 2.71 Å. The closest O···Br distance is 3.60 Å, indicative of weak hydrogen bonding.

Introduction

Wells, Wheeler & Penfield (1892) were the first to report preparing 'potassium dibromoiodide'. Later,

Cremer & Duncan (1932) proved by measurements of dissociation pressures that both hydrated and anhydrous versions of the compound exist. Although single-crystal X-ray studies of compounds containing triiodide

and dichloroiodide ions are numerous, for example, $N(C_2H_5)_4I_3$ (Migchelsen & Vos, 1967) and $N(CH_3)_4ICl_2$ (Visser & Vos, 1964), there has been only one reported investigation of the dibromoiodide ion, in $CsIBr_2$ (Davies & Nunn, 1969), where the dibromoiodide ion is unsymmetrical. In the latter study as in all the bromine- and iodine-containing trihalides (Carpenter, 1966; Tasman & Boswijk, 1955; Breneman & Willett, 1969), weak multicenter bonding between the anions is the rule. However, in $KICl_2.H_2O$ (Soled & Carpenter, 1973), there is weak hydrogen bonding between the molecules of water and the chlorine atoms, but no bonding between anions. The present study was undertaken to examine a system that might contain both weak intermolecular halogen interactions and hydrogen bonding.

Experimental

Sample preparation

Crystals of $KIBr_2.H_2O$ were obtained by slow evaporation of an aqueous solution of KNO_3, I_2 and HBr, prepared according to the procedure suggested by Wells (1901) for the preparation of $CsICl_2$. Further experimentation showed that when a twofold excess of HBr is used, anhydrous $KIBr_2$ results. Repetition of the original preparation (Wells, et al., 1892) with KBr, I_2 and Br_2 showed the product to be the hydrate.

Because of its extreme instability, the anhydrous $KIBr_2$ was not investigated further. Although $KIBr_2.H_2O$ also rapidly loses iodine and bromine on exposure to the atmosphere, it can be preserved for a few days by a coating of halocarbon grease (Kel–F).

Unit cell and space group

Crystallographic data is set out below. Unit cell and space group data were obtained from Weissenberg and precession photographs and from 14 2θ values measured with a Picker four-circle diffractometer.

System	Orthorhombic
a	12·183 (5) Å
b	13·046 (5)
c	4·390 (3)
$2c:a:b$ (X-ray)	0·7207:1:1·071
$a':b':c'$ (optical)	0·7158:1:1·1691
Absences	$0kl, k+l=2n+1$
	$h0l, h+l=2n+1$
Space group	$Pnnm$
Z	4
d_x (g cm^{-3})	3·27
μ(cm^{-1}), Mo $K\alpha$	172·2

The optical axial ratios were measured by Penfield (Wells, Wheeler & Penfield, 1892). The centrosymmetric space group $Pnnm$ was adopted during the structure determination; the subsequent refinement verifies this choice. The extreme instability of $KIBr_2.H_2O$ made a density determination impractical.

Table 1. *Final parameters and their standard deviations*

All values have been multiplied by 10^4 The temperature factor is of the form: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2hk\beta_{12})]$. $\beta_{13}=0$ and $\beta_{23}=0$ by symmetry.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}
I(1)	0·0	0·0	0·0	39 (2)	70 (3)	357 (20)	−1 (2)
I(2)	0·0	5000	0·0	78 (3)	51 (3)	375 (21)	7 (2)
Br(1)	340 (3)	2053 (3)	0·0	57 (3)	70 (3)	648 (27)	−2 (2)
Br(2)	2116 (3)	5640 (4)	0·0	71 (3)	73 (4)	771 (32)	−4 (2)
K	3238 (8)	2647 (10)	0·0	109 (8)	140 (12)	483 (59)	0 (8)
O	2192 (19)	3458 (23)	5000	61 (19)	106 (27)	856 (22)	10 (11)

Table 2. *Observed and calculated structure factors multiplied by 10*

Intensity data

Intensities were collected on a Picker automatic four-circle diffractometer with zirconium-filtered molybdenum radiation ($\lambda_\alpha = 0.7107$ Å) and θ-2θ scans. Reliable intensities were obtained for 326 independent reflections. A reflection was regarded as unobserved if its intensity was less than twice its standard deviation. During data collection, standards were monitored after every twenty five reflections. During the first two thirds of the data set (375 reflections) there was a nearly linear 19% decomposition of the crystal. For the last two hundred reflections, the rate of decomposition increased but remained approximately linear, so that when data collection was completed there had been an overall 62% decrease in the diffracting ability of the crystal. The raw intensities were corrected for the approximately segmented linear decomposition. The crystal was approximately $0.08 \times 0.10 \times 0.32$ mm and was treated as a cylinder ($\mu R = 0.82$) for an absorption correction with the local intensity correction program (*CYLLY*). The transmission coefficients ranged from 0.24 to 0.27.

Structure determination and refinement

The structure was determined by standard Patterson and Fourier methods and refined by least-squares methods with the program *BULS*, a local variation of the *ORFLS* program (Busing, Martin & Levy, 1962).

From a Patterson synthesis, two independent iodine atoms, both at $2/m$ positions, and the bromine atoms, also on the mirror plane, were located. The positional parameters of the bromine atoms and the isotropic temperature factor parameters of the iodine and bromine atoms were refined by four cycles of least-squares refinement to $R = 17.0\%$, $R_w = 23.6\%$. A difference map located the potassium and oxygen atoms on the mirror planes. No hydrogen atoms were located. Successive cycles of refinement, initially with isotropic and later with anisotropic temperature factors, converged to $R = 5.8\%$, $R_w = 6.8\%$. The standard deviation in F^2 was estimated from the expression

$$\sigma(F^2) = (1/\text{Lp})[C + 8.25 + (t_c/2t_b)^2(B_1 + B_2 + 16.5) + (0.07C)^2 + (0.07)^2(B_1 + B_2)^2]^{1/2}$$

where Lp is the Lorentz–polarization factor, C is the total integrated count obtained in time t_c, and B_1 and B_2 are the two background counts, each obtained in time t_b.

The final positional and thermal parameters with their e.s.d.'s are listed in Table 1 and the observed and calculated structure factors in Table 2.

Discussion

The structure is illustrated in Fig. 1 and important interatomic distances are given in Table 3. All the atoms lie on mirror planes at $z = 0$ and $z = \frac{1}{2}$, separated by 2.20 Å. There are two independent IBr₂⁻ anions, both

symmetrical and linear by virtue of lying on inversion centers and both with I–Br lengths of 2.71 Å. By contrast, the I–Br bond distances in CsIBr₂ are 2.78 Å and 2.62 Å (Davies & Nunn, 1969). The bonding in these ions is well described by three-center four-electron bonds (Rundle, 1962), symmetrical or unsymmetrical according to whether the electrostatic potential due to the surrounding ions is the same or different at the two ends of the ion (see for example, Migchelsen & Vos, 1967).

Table 3. *Interatomic distances and angles*

	x	y	z
i	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$-\frac{1}{2}-z$
ii	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
iii	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
iv	$\frac{1}{2}+x$	$\frac{3}{2}-y$	$\frac{1}{2}+z$
v	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
vi	x	y	$1+z$
vii	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$
viii	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$

I(1)———Br(1)	2.710 (6) Å	I(2)···Br(1)–I(1) 165.1 (1)°
I(2)———Br(2)	2.709 (6)	
I(2)····Br(1)	3.867 (7)	
I(1ⁱⁱ)···Br(2)	4.226 (6)	
OH····Br(2)	3.595 (24)	Br(2) ···O···Br(2ᵛⁱ) 75.2 (6)
OH····Br(2ᵛⁱ)	3.595 (24)	Br(1) ···O···Br(1ᵛⁱ) 74.1 (5)
OH····Br(1)	3.643 (22)	Br(2ᵛ)···O···Br(1ⁱⁱ) 67.2 (4)
OH····Br(1ᵛⁱ)	3.643 (22)	Br(1) ···O···Br(2) 90.8 (3)
O······Br(2ᵛ)	3.773 (30)	
O······Br(1ⁱⁱ)	3.893 (24)	
Br(1)···Kᵛⁱⁱⁱ	3.395 (9)	Br(2)···Kⁱⁱⁱ 3.444 (11) Å
Br(1)···Kᵛⁱⁱ	3.395 (9)	Br(2)···Kⁱ 3.444 (11)
Br(1)···K	3.616 (12)	

Another feature of the structure is the presence of nearly linear chains of halogen atoms along **b**. The Br(1)···I(2) distances indicated by dashed lines in Fig. 1 are 3.87 Å, about 0.2 Å less than the expected van der Waals separation, and the I(1)–Br(1)···I(2) angle is 165.1°. This suggests that the three-center bonds that
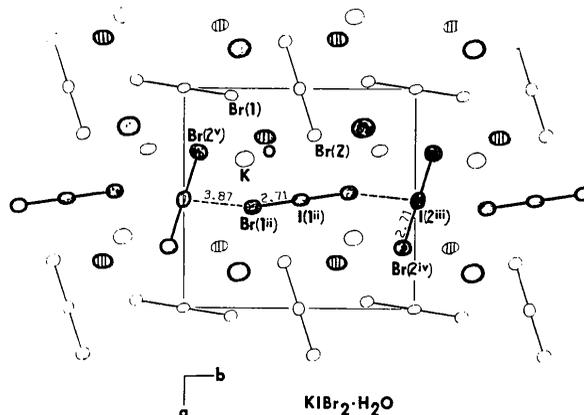
Fig. 1. The structure projected onto the *ab* plane. Shaded atoms lie on a mirror plane at $z = \frac{1}{2}$. The others are on mirror planes at $z = 0$ and $z = 1$. The oxygen atoms are striped to distinguish them from potassium atoms. Note the infinite chains formed along *b* with I(2)···Br(1) distances 3.87 Å.

link the atoms into ions are further coupled, weakly, to form infinitely extended multicenter bonds. This is an extension of the four-center patterns $X–X–X\cdots X$ that occur in the isostructural cesium trihalides, CsI_3 (Tasman & Boswijk, 1955), CsI_2Br (Carpenter, 1966), $CsBr_3$ (Breneman & Willett, 1969) and $CsIBr_2$ (Davies & Nunn, 1969). Along **a** and **c** the ions are well separated. The oxygen and potassium atoms occupy holes between the dibromoiodide ions.

Each oxygen atom has six neighboring bromine atoms. There are two bromine atoms in the same plane with the oxygen atom, one 3·77 Å and one 3·89 Å away. In addition, there are two sets of two bromine atoms related by a unit-cell translation in **c**, one set 3·60 Å from the oxygen atom and one at 3·64 Å. The four shorter distances are presumably hydrogen bonds although they are 0·2–0·3 Å longer than found in such hydrogen bonded systems as $NaBr.2H_2O$ (Haaf & Carpenter, 1964) or codeine hydrobromide dihydrate (Kartha, Ahmed & Barnes, 1962). This increased length may partly be due to the reduced effective negative charge on the bromine atom compared with simple bromide ions (Elema, de Boer & Vos, 1963). Hydrogen bonding to these four bromine atoms requires a disorder of the hydrogen atoms across the mirror plane, resulting in four 'half' hydrogen bonds, each somewhat longer than a whole hydrogen bond. As in $KICl_2.H_2O$ there is no hydrogen-bonded network among the water molecules, but apparently only weak hydrogen bonding between the bromine atoms and water molecules. Unlike the chlorine atoms in $KICl_2$ and $KICl_2.H_2O$ (Soled & Carpenter, 1973), the bromine atoms in $KIBr_2.H_2O$ participate as the central atoms in a multicenter bond.

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The Crystal Structure of [Co(NH3)6]4Cu5Cl17: a Twinned Cubic Crystal

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$[Co(NH_3)_6]_4Cu_5Cl_{17}$ crystallizes in the cubic space group $Fd3$, with $a = 21·80$ Å. The structure was solved and refined by standard methods to an R of 0·148. Although the bond lengths and angles were chemically acceptable, the poor agreement suggested that the solution was only partially correct. Analysis of the intensities at this stage suggested that the crystal used was twinned and that a correction could be made for this. The structure was then refined to a final R of 0·086 with a value for the twin parameter (α) of 0·323. There was no significant change in the positional parameters after this procedure but the standard deviations decreased markedly. The method used for detecting the twinning is applicable even when systematic absences or morphology give no indication that the crystal is twinned and it differentiates between twinned and disordered crystals. The structure contains $[Co(NH_3)_6]^{3+}$ octahedra $[Co–N(av) = 1·96$ Å], isolated Cl^- ions, and $[Cu_5Cl_{16}]^{11-}$ units. The latter contain linear Cu–Cl–Cu bridges with Cu–Cl bond lengths of 2·495, 2·323 and 2·278 Å, and have 23 symmetry.

Introduction

$[Co(NH_3)_6]_4Cu_5Cl_{17}$ is of interest because of the unusual stoichiometry of the anion and also because of its very strong similarity to $[Co(NH_3)_6]CuCl_5$. The isomorphous $[Cr(NH_3)_6]CuCl_5$ has been investigated by Raymond, Meek & Ibers (1968) and shown to contain $[CuCl_5]^{3-}$ trigonal bipyramids. These two compounds