The Crystal Structure of the 1:2 Sodium Bromide–Diacetamide Complex

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The crystal structure of the complex $NaBr.2(C_4H_7NO_2)$ has been determined by three-dimensional X-ray methods. The structure is best described in terms of layers in which sodium and bromide ions are separated by diacetamide molecules chelating the sodium ions. The bromide ions are associated with sodium ions in neighbouring layers. Each sodium ion is coordinated by four oxygen atoms in the same layer at a distance of 2·3 Å, a bromide ion in the upper layer at a distance of 2·8 Å and a nitrogen atom in the lower layer at a distance of 3·86 Å. The bromide is octahedrally surrounded by one sodium ion, three nitrogen atoms and two methyl groups. No definite indication of hydrogen bonding has been found.

Introduction

Gentile & Shankoff (1965) reported the preparation of diacetamide complexes with alkali and alkaline earth metal salts of less than 64% ionic character. This contrasts strikingly with thiourea which only forms complexes with those alkali halides and related salts which have lattice energies of less than 160 kcal.mole^{-1} (Boeyens & Gafner, 1968). Whereas the thiourea complexes are stabilized by electrostatic interactions alone, additional factors seem to be of importance in the formation of the diacetamide complexes. A programme is now under way to establish the nature of the bonding in these complexes crystallographically. The results obtained for NaBr.2DA (DA = diacetamide) are reported in this paper.

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Experimental

The complex NaBr.2DA was prepared from a saturated diacetamide solution of the salt at 217°C as described by Gentile & Shankoff (1965). Single crystals were crystallized from absolute ethanol and, being very hygroscopic, hermetically sealed into Lindemann capillaries for the X-ray work.

Cell dimensions were measured from oscillation and Weissenberg photographs and intensities by visual estimation with the use of the multiple-film technique on unintegrated equi-inclination Weissenberg photographs. After a week's exposure to Cu $K\alpha$ (Ni-filter) radiation at room temperature the crystals started to disintegrate, giving diffuse spots with two or more satellites. Two different crystals were therefore used to record 809 reflexions, $hk0$ to $hk8$. No absorption corrections were applied but corrections were made for α_1–α_2 splitting, Lorentz and polarization fac-

Table 1. *Fractional coordinates and anisotropic thermal parameters*

$$T = \exp\left[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\right].$$

The standard deviations are given below each value.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0·0	0·11682	0·37359	0·01177	0·00558	0·00673	0·0	0·0	−0·00015
		0·00014	0·00015	0·00020	0·00011	0·00018			0·00008
Na	0·0	0·31946	0·37563	0·00481	0·00720	0·00659	0·0	0·0	−0·00099
		0·00050	0·00046	0·00043	0·00044	0·00055			0·00031
N(1)	0·0	0·10123	0·12883	0·00525	0·00419	0·00756	0·0	0·0	0·00023
		0·00088	0·00095	0·00110	0·00070	0·00121			0·00056
N(2)	0·0	0·36167	0·11644	0·00590	0·00518	0·00243	0·0	0·0	−0·00146
		0·00085	0·00082	0·00107	0·00071	0·00104			0·00052
O(1)	0·09902	0·12793	0·00011	0·00539	0·01014	0·00749	0·00039	0·00077	0·00079
	0·00067	0·00078	0·00096	0·00060	0·00075	0·00107	0·00054	0·00054	0·00059
O(2)	0·10020	0·35785	0·24872	0·00648	0·00956	0·00735	−0·00254	−0·00066	0·00003
	0·00069	0·00070	0·00102	0·00065	0·00070	0·00107	0·00057	0·00060	0·00062
C(1)	0·08780	0·10941	0·08332	0·00495	0·00563	0·00516	0·00106	0·00033	0·00045
	0·00092	0·00087	0·00128	0·00082	0·00067	0·00147	0·00054	0·00072	0·00056
C(2)	0·09082	0·36170	0·16290	0·00739	0·00512	0·00485	−0·00065	−0·00011	0·00016
	0·00104	0·00084	0·00131	0·00103	0·00067	0·00160	0·00062	0·00090	0·00062
Me(1)	0·17313	0·09222	0·15271	0·00643	0·00889	0·00980	0·00091	−0·00166	−0·00024
	0·00108	0·00101	0·00101	0·00107	0·00105	0·00129	0·00081	0·00074	0·00074
Me(2)	0·17193	0·37100	0·09359	0·00684	0·00976	0·00759	−0·00158	0·00236	0·00118
	0·00108	0·00111	0·00095	0·00108	0·00109	0·00122	0·00082	0·00072	0·00072

tors and spot shape with the computer program *COR-RECT* written by E. G. Boonstra for the IBM 360/40.

Cell data

Orthorhombic with $a = 13\cdot98 \pm 0\cdot05$, $b = 13\cdot69 \pm 0\cdot05$, $c = 13\cdot92 \pm 0\cdot05$ Å.
Measured density is $1\cdot526$ g.cm^{-3}. Calculated density for 8 molecules per unit cell is $1\cdot520$ g.cm^{-3}.
The conditions for possible reflexions are:

hkl for $h+k=2n$, $h0l$ for $l=2n$ and $hk0$ for $h=2n$, Space group: *Cmca* or *C2ca*.
The structure was solved successfully assuming *Cmca*, space group No. 64 in *International Tables for X-ray Crystallography* (1952).

Determination and refinement of the structure

The coordinates of the one Br and one Na atom in the

Table 2. *Observed and calculated structure factors on an absolute scale*

asymmetric unit were derived from a three-dimensional Patterson synthesis and all the other atomic coordinates from a three-dimensional Fourier synthesis phased on Br and Na. The Fourier syntheses were computed by means of the centrosymmetric Fourier program written by Gantzel & Hope (University of California at Los Angeles) and modified for use on the IBM 360/40 by Miss J. Hewitt.

The coordinates were refined with the full-matrix least-squares program *ORFLS* of Busing, Martin & Levy (1962) modified for use on the IBM 360/40 by H. Messerschmidt. The atomic scattering factors used were those of Hanson, Herman, Lea & Skillman (1964). The quantity minimized is $\Sigma w(F_o - kF_c)^2$. No differential weighting was applied, and $w = 1$ was used for all reflexions. The residual, defined as $R = \Sigma_{hkl}|F_o - F_c|/\Sigma F_o$, was 24% with an overall B of 3·5 Å^2 and after refining individual temperature factors isotropically it decreased to 18%.

A difference synthesis at this stage showed severe anisotropy. The anisotropic refinement gave a final R index of 11·2%. The final atomic coordinates are given in Table 1 and the observed and calculated structure factors on an absolute scale $F(000) = 1232$, in Table 2. Unobserved reflexions were given a value of $\frac{1}{3} I_{min}$ (Hamilton, 1955).

The first crystal was used to record reflexions $hk0 \rightarrow hk3$. The 104 unobserved reflexions in this region appear in Table 2 with $F_{obs} < 15$. The second crystal was used in the region $hk4–hk8$. The 165 unobserved reflexions in this region appear in Table 2 with $F_{obs} < 7$.

Description of the structure

As seen from Fig. 1 the structure, which is shown in projection along [001], consists of layers of molecules and ions. The projection along [010] of such a layer is shown in Fig. 2. Screw axes along [001] generate a similar layer at $\frac{1}{2} - y'$ (where y' is the mean y coordinate of any layer) and shifted through half a cell along [001]. The superposition of two such neighbouring layers are shown in Fig. 3. The black atoms lie in the lower, and the white atoms in the upper, layer. Screw axes along [010] generate another pair of layers at $-y'$ and $y' - \frac{1}{2}$ shifted through $c/4$ with respect to the first pair. The result is that a Na–Br pair is enclosed by ten diacetamide molecules as shown by the perspective drawing of the structure in Fig. 4. A sodium ion is seen to lie almost centrally above the plane defined by four oxygen atoms. This plane is almost parallel to the (010) plane; the equation of the normal to the plane determined by least-squares is

$$0.998by - 0.056cz = 4.70.$$

The Na$^+$ ion lies at a distance of 0·623 Å, in the direction of the Br$^-$, from this plane. The distance of the sodium ion from a neighbouring bromide ion is 2·775 Å and its distance from the nitrogen atom at the opposite apex of the octahedron is 3·86 Å. All other dimensions

of the coordination polyhedron are shown in Fig. 2. The important interatomic distances are given in Table 3 together with the corresponding values obtained for the NaBr.acetamide complex (Piret, Rodrique,Gobillan & van Mersche, 1966). The Na–N distance can have no chemical significance whereas the Na–Br and Na–O distances, which compare very well with the values found in the NaBr acetamide complex, are typical ion-dipole approaches. Although the sodium ion is physically surrounded by six atoms, it is chemically five-coordinated within a square pyramid of partially negatively charged atoms.
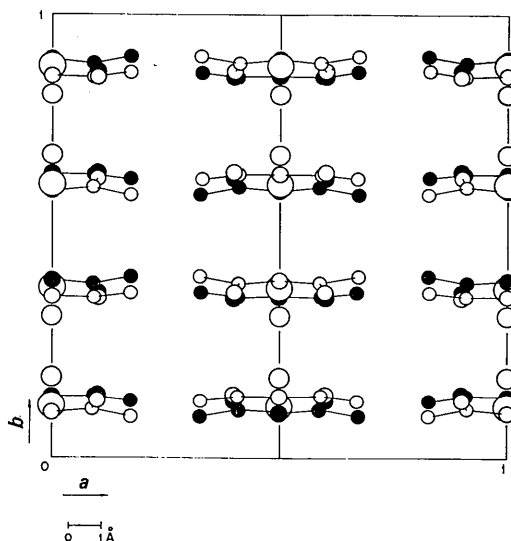

Fig. 1. Projection of the structure along [001]. All atoms are represented by circles with diameters roughly proportional to atomic numbers.
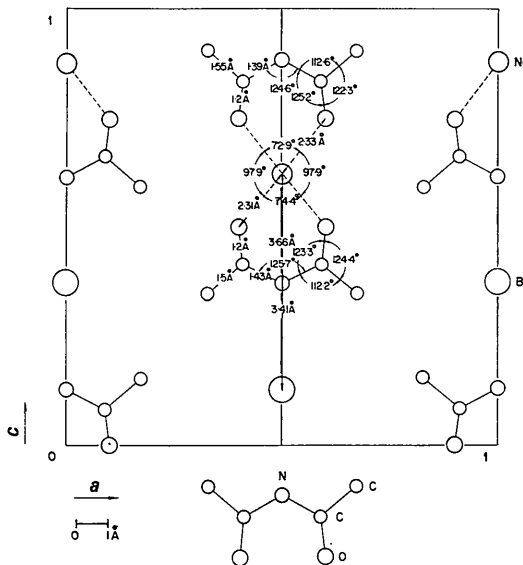

Fig. 2. One of the layers in the structure shown in projection along [010].

Table 3. *Comparison of interatomic distances with the mean values observed in the structure of* NaBr.2 *acetamide* (*Piret et al.,* 1966)

	This study	Piret *et al.* (1966)
Na——Br	2·775 ± 0·011	(2·989 ± 0·005)
N(1) –Br	3·418 ± 0·021	(3·496 ± 0·018)
N(2) –Br	3·396 ± 0·019	
N(2′)–Br	3·497 ± 0·016	
O(1) –Na	2·332 ± 0·012	(2·358 ± 0·012)
O(2) –Na	2·314 ± 0·013	
N(1) –Na	3·683 ± 0·022	
N(2) –Na	3·651 ± 0·021	
N(1′)–Na	3·859 ± 0·018	
C(1) –N(1)	1·383 ± 0·014	(1·310 ± 0·024)
C(2)—N(2)	1·423 ± 0·015	
C(1)—Me(1)	1·553 ± 0·018	(1·5 ± 0·031)
C(2):-Me(2)	1·495 ± 0·018	

Table 3 (*cont.*)

	This study	Piret *et al.* (1966)
C(2)—O(2)	1·203 ± 0·012	(1·224 ± 0·019)
C(1)—O(1)	1·196 ± 0·011	

The bromide ion is in van der Waals contact with all its neighbours except for the sodium ion. The 3·4 Å Br–N separation has, however, been interpreted as a hydrogen bond by Pimentel & McClellan (1960) and also by Piret *et al.* (1966), who claim the approach of 3·5 Å as a N–H---Br⁻ bond.

The diacetamide molecule

Molecular parameters for two independent diacetamide molecules have been obtained and are summarized in Fig.2. Except for the methyl groups the molecules are almost flat; the deviations from the best plane being: O= −0·003, C=0·009, N= −0·011, C(methyl)=0·042 and O= −0·003, C=0·010, N= −0·012, C(methyl)=0·105 Å.

Discussion

In simple ion-dipole complexes such as the ionic thiourea complexes (Boeyens & Herbstein, 1967) the cations and anions are segregated and bridged by the oriented dipoles. In the present structure, however, NaBr units are enclosed in a diacetamide matrix with bidentation of the Na⁺ ion by pairs of oxygen atoms. This structure is determined not only by ion-dipole interactions, but also by chemical interaction within the NaBr unit. This interaction must be related to the observation that only those salts of less than 64% ionic character form complexes with diacetamide (Gentile & Shankoff, 1965). The structure can formally be described as a chemically interacting ion pair clathrated as a unit within a matrix of oriented dipoles. The nearest neighbours of a Na⁺ ion are four oxygen atoms at a separation of 2·3 Å, one bromide ion at a distance of 2·8 Å and a nitrogen atom at 3·86 Å.
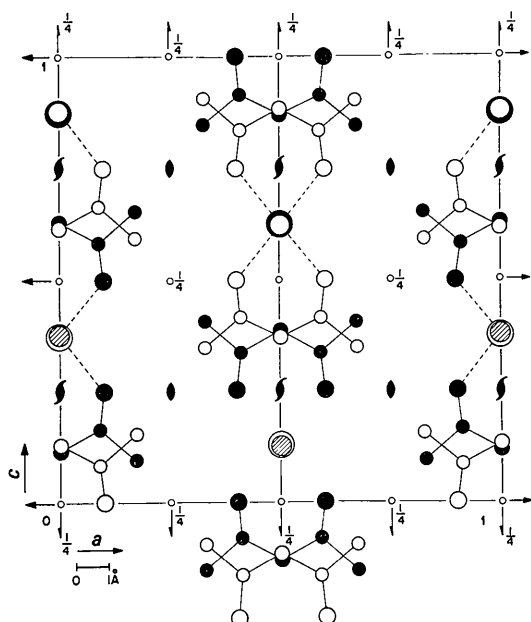

Fig. 3. The superposition of two neighbouring layers related by a screw axis parallel to [001], shown in projection along [010].
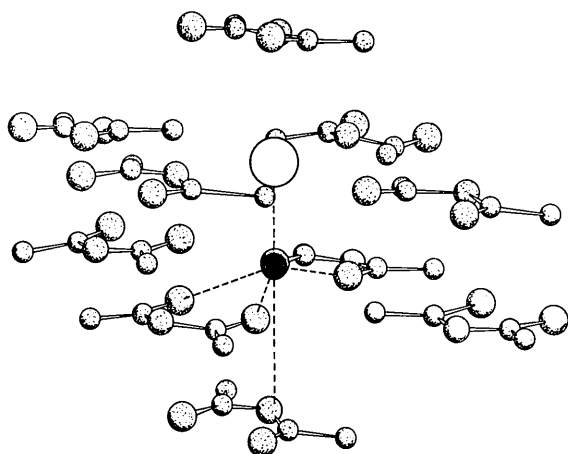

Fig. 4. Perspective drawing of a Na–Br unit clathrated by ten diacetamide molecules.

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