

in the unit cell for the oxide prepared in the presence and absence of potassium ions and it is tentatively suggested that the ammonium ion may replace the potassium in the cryptomelane lattice.

The diffraction spots constituting the rings of Fig. 1, and similar patterns from the second preparation, show the very interesting crystal-shape effects previously described by Rees & Spink (1950) and by Burgers (1951) for the case of ZnO. From the indexed figure it is seen that in the case of planes parallel to the c axis, the diffraction spots cut the rings at right angles; with the (002) plane the spots lie along the ring and for other planes at varying angles to the c axis the diffraction spots are at oblique angles to the diffraction rings. This is explained if we assume that the minute crystals pack with the short c axis in line with the long axis of the straw-shaped aggregates as revealed in the electron micrographs. The c axis is thus parallel to the surface of the collodion film and perpendicular to the beam, and the reciprocal lattice points may be considered ap-

proximately as domains in the form of discs perpendicular to the c^* axis.

A point of further interest arising from our electron-diffraction examination of artificial manganese dioxides is that, as prepared, surface layers of MnO and Mn_3O_4 or $\gamma\text{-Mn}_2\text{O}_3$ are usually present. This may contribute significantly to the apparent oxygen deficiency as revealed by chemical analysis. A detailed paper on the work is in preparation.

References

- BURGERS, W. G. (1951). *Acta Cryst.* **4**, 502.
 DUBOIS, P. (1936). *Ann. Chim. (Phys.)* [11], **5**, 401.
 GLEMSER, O. (1939). *Ber. dtsh. chem. Ges.* **72**, 1879.
 MCMURDIE, H. F. & GOLOVATO, E. (1948). *J. Res. Nat. Bur. Stand. Wash.* **41**, 589.
 MOORE, T. E., ELLIS, M. & SELWOOD, P. W. (1950). *J. Amer. Chem. Soc.* **72**, 856.
 REES, A. L. G. & SPINK, J. A. (1950). *Acta Cryst.* **3**, 316.

Acta Cryst. (1952). **5**, 289

The crystal structure of hydrazinium bromide, N_2H_5Br . By KIICHI SAKURAI and YUJIRO TOMIIE, Faculty of Science, Osaka University, Nakanoshima, Osaka, Japan

(Received 25 January 1952)

As a part of our study on the structure of hydrazine salts ($N_2H_6SO_4$ (Nitta, Sakurai & Tomiie, 1951) and N_2H_5Cl (Sakurai & Tomiie, to appear shortly), the crystal structure of hydrazinium bromide has been determined. Crystals of hydrazinium bromide are very fine needles parallel to the monoclinic b axis, of which those about 0.08 mm. in diameter were selected for X-ray work. The procedures taken in the analysis were the same as in the case of hydrazinium chloride.

There are eight formula units in the unit cell of the dimensions

$$a = 12.85, b = 4.54, c = 11.94 \text{ \AA}, \beta = 110^\circ 16',$$

and the probable space group is C_{2h}^6-C2/c . The parameters of the atoms were determined by the Patterson maps projected on (010), electron-density projections on (010) and (001), and by the method of trial and error. They are given in Table 1.

Table 1. Atomic co-ordinates

	x	y	z
Br	0.103 ₇	0.097	0.080 ₂
N _I	0.149 ₂	0.390	0.135 ₀
N _{II}	0.141 ₀	0.620	0.216 ₅

Table 2. Interatomic distances

N _I ...N _{II}	1.45 \AA	N _I ...N _I	3.48 \AA
N _{II} H...N _I	2.93	N _{II} ...N _{II}	3.73
N _I ...Br	3.42, 3.56, 3.70	Br...Br	3.87, 4.00
N _{II} ...Br	3.29, 3.36, 3.37		

The interatomic distances are listed in Table 2. The accuracy of these values is not as high as in the chloride. Each $N_2H_5^+$ group has eight closest neighbours, six bromine and two nitrogen atoms, and their arrangement about one $N_2H_5^+$ group closely resembles that in hydrazinium chloride. The N-N distance within the $N_2H_5^+$ ion has the same value, 1.45 \AA, as found in the chloride. From a consideration of the N...Br distances, it can be concluded that N_I and N_{II} represent the $-NH_2$ group and the $-NH_3^+$ group respectively. Both N_{II}...Br and Br...Br distances are nearly equal to the corresponding values derived from the ionic radii of Br⁻ (1.95 \AA) and NH₄⁺ (1.41 \AA, corrected for coordination number four).

Cations are linked together by N⁺H...N hydrogen bonds in the same manner as in the chloride, and these hydrogen bonds form infinite spiral chains along the b axis. Owing to the presence of a centre of symmetry in this structure, however, there are two kinds of chains with opposite senses in the bromide, in contrast to the existence of one kind of chains along the polar c axis in the chloride.

We wish to thank Prof. I. Nitta for encouragement and valuable discussions. This work was supported by a grant from the Ministry of Education.

Reference

- NITTA, I., SAKURAI, K. & TOMIIE, Y. (1951). *Acta Cryst.* **4**, 289.