Les coordonnées atomiques ainsi que les coefficients thermiques sont reportés sur le Tableau 1.*

Discussion. La Fig. 1 donne la géométrie de la molécule. L'ensemble des atomes, excepté H(61), se trouve dans le plan miroir cristallographique $z=0,25$. Les distances interatomiques, les angles de valence sont présentés sur la Fig. 2. Les valeurs indiquent que le caractère quinonique du noyau pyridine est faible. Il n'a pas été possible de localiser le H(72) sur les cartes Fourier-différence. En fin d'affinement, sur celles-ci, les pics résiduels les plus élevés sont situés près des atomes O(72), O(71) et sur les liaisons N(1)–C(5), C(5)–C(6). Cependant, les liaisons interatomiques et les angles entre celles-ci montrent que la fonction carboxyle est intacte. Nous remarquerons la liaison intramoléculaire très courte O(1)–O(72) ($d=2{\cdot}41$ Å).

* La liste des facteurs de structure a été déposée à la British Library Lending Division (Supplementary Publication No. SUP 31230: 7 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, Angleterre.

Tableau 2. *Distances intermoléculaires inférieures à* 3,5 Å

Opérations de symétrie	(1) x, y, z (4) $\frac{1}{2}+x, \frac{1}{2}-y, -z$	
C(1)–O(1)	$\bar{1}/1,1,1$	3,314 Å
C(2)–O(72)	$\bar{4}/1,0,0$	3.275
C(4)–O(1)	$\bar{4}/\bar{1},0,0$	3,349
C(5)···O(72)	$\bar{1}/1,1,1$	3,286
C(6)–O(71)	$1/1,0,0$	3,259
C(7)–O(1)	$\bar{1}/1,1,1$	3,225
N(1)–O(72)	$\bar{1}/1,1,1$	3,209
O(1)–O(72)	$\bar{1}/1,1,1$	3,366

Les contacts intermoléculaires inférieurs à 3,5 Å sont repris dans le Tableau 2.

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Référence

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Manganese Bromide Tetrahydrate

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Abstract. $MnBr_2.4H_2O$, $P2_1/n$, $a=11{\cdot}668$ (1), $b=9{\cdot}824$ (3), $c=6{\cdot}316$ (2) Å, $\beta=99{\cdot}43°$ (4), $Z=4$. The octahedron around the Mn ion is larger and more distorted than in the isostructural $MnCl_2.4H_2O$.

Introduction. X-ray investigation of the structure of $MnBr_2.4H_2O$ was undertaken in connection with low-temperature magnetic measurements. The structure of the chloride has been determined by Zalkin, Forrester & Templeton (1964). H atoms were located by El Saffar & Brown (1970) from neutron diffraction studies. Since the bromide exhibits no magnetic spin-flop transition and its Néel temperature (2·13 K) is higher than that of the chloride (1·62 K), subtle steric differences between the two could be expected.

Crystals were prepared by evaporation of an aqueous solution. The space group was confirmed to be that reported for the chloride. A spherical single crystal of mean radius 0·23 mm was used. Lattice parameters were found from diffractometer measurements. Intensities of 605 independent reflections [in the range $0<(\sin\theta)/\lambda\leq 0{\cdot}76$] were collected with a computer-controlled four-circle diffractometer. The specimen was given a thin coating of paint to prevent it from absorbing moisture during data collection. A balanced filter (Zr and Y) ω scan technique with Mo $K\alpha$ radiation was used for the lower angle reflections for which the absorption edge of Zr fell within the scanning range for peak plus background. Zr-filtered Mo $K\alpha$ radiation and the 2θ scan method were employed for other reflections. Simultaneous diffraction effects were assessed by remeasurement of each reflection intensity after the specimen was rotated about the diffraction vector by 1°. Those intensities which, for the two settings of the crystal, differed by more than three times the standard deviation (on the basis of counting statistics) were eliminated from further consideration. Each reflection was scanned repeatedly to yield 2% statistical precision (counting statistics) in the net intensities, up to a maximum of eight times. Absorption corrections were based on the tabular data in *International Tables for X-ray Crystallography* (1959) for a spherical specimen ($\mu R=3{\cdot}2$).

Table 1. *Comparison of unit-cell dimensions of* $MnBr_2.4H_2O$ *and* $MnCl_2.4H_2O$

Crystal	a	b	c	β
$MnBr_2.4H_2O$	11·668 (1)	9·824 (3)	6·316 (2)	99·43 (4)
$MnCl_2.4H_2O$ (Zalkin *et al.*, 1964)	11·186	9·513	6·186	99·74

Table 2. *Positional and thermal parameters*

All values are multiplied by 10^4. Standard deviations are given in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	2340 (1)	1641 (1)	9851 (2)	46 (1)	49 (1)	144 (5)	−2 (1)	22 (2)	1 (1)
Br(1)	609 (1)	3078 (1)	965 (2)	44 (1)	70 (1)	210 (5)	7 (1)	26 (2)	−14 (1)
Br(2)	3861 (1)	3635 (1)	364 (2)	47 (1)	55 (1)	188 (4)	−7 (1)	24 (2)	1 (1)
O(1)	2989 (5)	1107 (5)	3248 (10)	64 (5)	60 (6)	153 (23)	−4 (3)	20 (10)	9 (7)
O(2)	1672 (5)	2204 (6)	6520 (9)	72 (6)	84 (7)	142 (20)	−9 (4)	32 (11)	−15 (9)
O(3)	1334 (5)	9766 (6)	9625 (10)	78 (1)	75 (6)	235 (24)	−26 (4)	55 (10)	−19 (10)
O(4)	3649 (5)	315 (5)	8711 (11)	86 (6)	60 (6)	308 (26)	2 (4)	77 (12)	−19 (10)
H(11)	3889 (93)	1667 (77)	3693 (96)	59	157	236	6	5	−4
H(12)	2863 (76)	284 (82)	3526 (110)	225	80	262	−18	33	44
H(21)	806 (89)	1923 (96)	6178 (101)	54	118	234	−13	−5	4
H(22)	2094 (107)	2062 (105)	5483 (92)	85	161	176	−12	49	−22
H(31)	1008 (83)	9308 (75)	8230 (92)	100	108	329	−16	−1	−74
H(32)	1018 (75)	9408 (92)	581 (82)	169	122	525	−42	189	1
H(41)	4454 (87)	529 (101)	7967 (92)	65	149	36	−2	72	−9
H(42)	3717 (89)	9616 (78)	8797 (58)	87	83	359	106	31	−35

Full-matrix least-squares refinement of all positional and temperature parameters (except the H thermal parameters) started from the parameters of the chloride (Zalkin *et al.*, 1964). H temperature parameters were kept fixed at the values given for the chloride by El Saffar & Brown (1970). Scattering factors were from Cromer & Waber (1965) for Mn^{2+}, Cl^- and O^0. Anomalous dispersion corrections were made with values of $\Delta f'$ and $\Delta f''$ calculated by Cromer (1965). The observed structure factors were corrected for isotropic secondary exitinction. The final value of $R_1 = 2{\cdot}81$, $R_2 = 3{\cdot}69$, and $wR_2 = 4{\cdot}77\%$ where $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $R_2 = \sum(|F_o|^2 - |F_c|^2)/\sum|F_o|^2$ and $wR_2 = \{\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4\}^{1/2}$.

Table 3. *Distances and angles in the octahedron around the manganese ion**

X represents Br or Cl as appropriate.

	$MnBr_2.4H_2O$ (This work)	$MnCl_2.4H_2O$ (El Saffar & Brown, 1970)
Mn–X(1)	2·802 (2) Å	2·500 (2) Å
Mn–X(2)	2·913 (2)	2·476 (2)
Mn–O(1)	2·247 (6)	2·223 (2)
Mn–O(2)	2·221 (6)	2·218 (2)
Mn–O(3)	2·475 (6)	2·185 (6)
Mn–O(4)	2·369 (6)	2·206 (5)
X(1)–Mn–X(2)	86·8 (1)°	96·3 (1)°
X(1)–Mn–O(1)	94·0 (1)	91·5 (1)
X(1)–Mn–O(2)	84·6 (1)	86·5 (1)
X(1)–Mn–O(3)	100·9 (1)	93·4 (1)
X(1)–Mn–O(4)	174·1 (2)	173·7 (1)
X(2)–Mn–O(1)	90·6 (2)	87·5 (1)
X(2)–Mn–O(2)	88·9 (2)	94·3 (1)
X(2)–Mn–O(3)	170·7 (2)	169·0 (1)
X(2)–Mn–O(4)	98·3 (2)	89·0 (1)
O(1)–Mn–O(2)	178·6 (2)	177·4 (1)
O(1)–Mn–O(3)	83·8 (2)	86·9 (1)
O(1)–Mn–O(4)	88·6 (2)	92·0 (1)
O(2)–Mn–O(3)	96·7 (2)	91·5 (1)
O(2)–Mn–O(4)	92·7 (2)	89·7 (1)
O(3)–Mn–O(4)	74·2 (2)	81·7 (1)

Results and discussion. Table 1 compares the lattice parameters of the chloride and bromide. As expected, the bromide is isostructural with the chloride. The positional and temperature parameters are given in Table 2.*

A comparison of the interatomic distances and bond angles with those of the chloride is given in Table 3. The octahedron around Mn is slightly more distorted in the bromide and the increase in the size of the octahedron is more than can be accounted for by the larger size of the Br compared with the Cl ion. The differences in the magnetic properties can only be correlated with the larger size and the difference in the distortion of the octahedron around the Mn ion.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31237 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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