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The Crystal Structure of $CsMn_4Cl_9$

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The crystal structure of $CsMn_4Cl_9$ is tetragonal with $a=11{\cdot}62$ (2) and $c=10{\cdot}28$ (2) Å. The space group is $I4_1/a$ and $Z=4$. The Cs and Cl atoms are cubic close-packed and the Mn atoms are octahedrally coordinated by Cl atoms. Each $MnCl_6$ octahedron is linked to six neighbouring octahedra by sharing five edges and one vertex.

Introduction

The authors have recently completed a study of the crystal structures of compounds in the CsCl–$MnCl_2$ system and the crystal structure of $CsMnCl_3$, which is related to that of $CsNiCl_3$, has already been described (Goodyear & Kennedy, 1973). The structures of Cs_2MnCl_4 and Cs_3MnCl_5 have been found to be similar to those of Cs_2MnBr_4 (Goodyear, Steigmann & Kennedy, 1972) and Cs_3CoCl_5 (Powell & Wells, 1935) respectively, and details of these will shortly be submitted for publication. $CsMn_4Cl_9$, however, is unique in that no other caesium complex halide of similar composition has previously been reported.

The material was prepared by heating a mixture, containing 4 molar parts of $MnCl_2$ and 1 of CsCl, in an evacuated silica tube until molten and then cooling the specimen to room temperature at the rate of about 5°/h. Red plate-like crystals were formed which were suitable for X-ray analysis. As was found with all the compounds in the series, the material was very hygroscopic and hence single crystals were examined and selected in a stream of dry nitrogen prior to mounting in sealed Lindemann-glass tubes. The density of the material was determined by weighing a sample quickly in air and in toluene.

X-ray data

The unit-cell dimensions were determined from oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation about an axis which turned out to be the a axis. The symmetry was tetragonal and the observed density could be accounted for by assigning four molecules of $CsMn_4Cl_9$ to the unit cell. The complete crystal data are shown in Table 1.

Table 1. *Crystal data*

Formula, $CsMn_4Cl_9$;	F.W. 671·78
Tetragonal;	$a=11{\cdot}62$ (2), $c=10{\cdot}28$ (2) Å
	$Z=4$, $D_o=3{\cdot}26$, $D_x=3{\cdot}22$ g cm^{-3}
Mean r (cm):	0·0096
μ (cm^{-1}):	80·3 ($\lambda=0{\cdot}7107$ Å)

Intensity data were collected from equi-inclination Weissenberg photographs taken about the a axis with Mo $K\alpha$ radiation. The intensities of 417 reflexions, on layer lines 0 to 5, were measured from multiple-film exposures using a Joyce–Loebl flying-spot microdensitometer; of these 318 were symmetrically independent. 118 reflexions were too weak to be observed.

The intensity data were corrected with the Lorentz–polarization factor and for absorption using the factors given by Bond (1959) for a cylindrical specimen. The observed reflexions satisfied the conditions $h+k+l=2n$ for hkl, $h=2n$ for $hk0$ and $l=4n$ for $00l$, which suggested $I4_1/a$ (No. 88) as the only possible space group.

Determination of the structure

The initial structure was determined from packing considerations and a knowledge of the space group.

Assuming typical values for ionic radii, the number of Cs and Cl atoms in the cell and the volume of the cell indicated that these atoms together formed a close-packed array. The relatively low Cl/Mn ratio, $\frac{9}{4}$, suggested that the structure might consist of a three-dimensional system of linked $MnCl_6$ octahedra. Following Wells (1962), it was possible to see if this ratio was consistent with the linking of topologically equivalent octahedra in the space group $I4_1/a$. In each octahedron let p_1 Cl atoms be common to one octahedron, p_2 be common to two octahedra and in general p_n be common to n octahedra, then $\sum p_n=6$ and $\sum(p_n/n)=\frac{9}{4}$. There is just one solution of these equations which is consistent with the space group. With $p_2=2$, $p_3=3$ and $p_4=1$, the numbers of p_2-type, p_3-type and p_4-type Cl atoms in the cell would be 16, 16 and 4 respectively. Thus $p_2(p_3)$-type atoms could be placed at equipoint $16(f)$ and p_4-type at $4(a)$ or $4(b)$, leaving an equipoint of rank 4 available for the location of the Cs atoms.

The next step was to see if the unit-cell dimensions were simply related to those of the $MnCl_6$ octahedron. In the structure of $CsMnCl_3$ the average Cl–Cl distance in the $MnCl_6$ octahedra is 3·60 Å, so that the distance between opposite vertices is 5·09 Å. This is nearly equal to one half of the c parameter of the unit cell of $CsMn_4Cl_9$, indicating that each octahedron might be so oriented in the cell that one of the fourfold axes of the octahedron is parallel to **c**. If this is so it follows that the close-packed Cs and Cl atoms are distributed in a square array, of side 3·60 Å, in planes perpendicular to **c**, *i.e.* parallel to the XY plane. The remaining problem is to account for the a parameter in terms of the square arrangement of Cs and Cl atoms. By choosing the outline of the unit cell as shown in Fig. 1, the a parameter would be $(10\times 3{\cdot}60^2)^{1/2}=11{\cdot}38$ Å which is sufficiently close to the observed value to support the argument so far.

If Cs atoms are located at the corners of the base of the cell and the octahedrally coordinated Mn atoms are inserted at the centres of those squares which have Cl atoms at the corners, then the layer shown in Fig. 1 has the composition $CsMn_4Cl_9$ and the cell would contain 4 such layers at heights $z=0$, $z=\frac{1}{4}$, $z=\frac{1}{2}$ and $z=\frac{3}{4}$. The relative orientation of these layers which is required by the space-group symmetry is also shown in Fig. 1. This proposed structure has Cs at equipoint $4(a)$, Mn at $16(f)$, and Cl in two sets at $16(f)$ and one set at $4(b)$.

The model structure was tested by means of a two-dimensional block-diagonal least-squares refinement using $0kl$ data and assuming initial individual isotropic

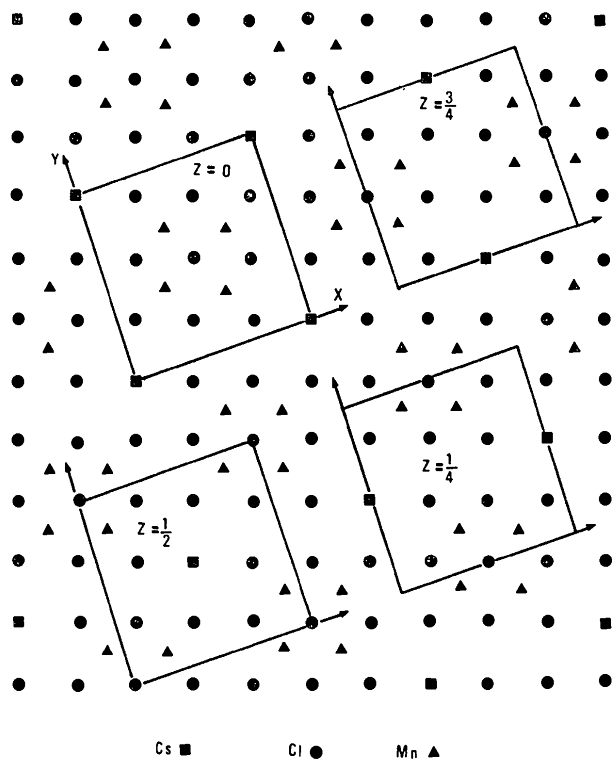

Fig. 1. Square array of Cs and Cl atoms in a plane perpendicular to the c axis. If Mn atoms are located at the centres of squares of Cl atoms, the whole layer has the composition $CsMn_4Cl_9$. The orientation of the layer at different heights in the unit cell is indicated.

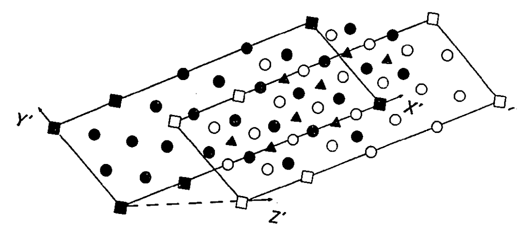

Fig. 2. The outline of a primitive unit cell whose base is parallel to the close-packed layers of Cs and Cl atoms. The Z' coordinates are indicated as follows: ● Cl, ■ $Z'=0$; ○ Cl. □ Cs $Z'=1$; ▲ Mn $Z=\frac{1}{2}$.

Table 2. *Final atomic parameters*

Origin is at $\bar{4}$. Standard deviations are given in parentheses.

	Equipoint	x/a	y/b	z/c	B(Å^2)
Cs	$4(a)$	0	0	0	2·97 (12)
Mn	$16(f)$	0·2926 (6)	0·3950 (7)	0·0073 (5)	1·60 (11)
Cl(1)	$16(f)$	0·1041 (10)	0·3021 (10)	−0·0060 (10)	1·64 (17)
Cl(2)	$16(f)$	0·2097 (9)	0·5961 (9)	−0·0057 (9)	1·35 (17)
Cl(3)	$4(b)$	$\frac{1}{2}$	$\frac{1}{2}$	0	1·71 (35)

temperature factors of 2·5 $Å^2$ for Cs and 2·0 $Å^2$ for the other atoms. After one cycle of refinement the R value, $\sum||F_o|-|F_c||/\sum|F_o|$, was 20% and this decreased to 7·3% after a further three cycles. The new atomic coordinates were then refined by the least-squares method using all the available intensity data, and after 10 cycles R was reduced to a minimum value of 9·6% and the calculated structure factor of each unobserved reflexion was less than the minimum observable value. In the final cycle of refinement, the shift in each positional parameter was less than $\frac{1}{25}$ and that in each thermal parameter less than $\frac{1}{12}$ of one standard deviation. For the structure-factor calculations the atomic scattering factors for Cs^+, Mn^{2+} and Cl^- were taken from *International Tables for X-ray Crystallography* (1962) and interlayer scaling was achieved by scaling the observed to the calculated structure factors.

The final atomic parameters are given in Table 2 and the magnitudes of the observed and calculated structure factors are compared in Table 3.

Table 3. *Magnitudes of observed and calculated structure factors on an absolute scale*

K	L	$\|F_o\|$	$\|F_c\|$
H=0			
0	8	519	472
0	12	278	252
0	16	125	117
4	0	73	73
8	0	84	90
10	0	405	414
3	1	222	223
5	1	62	66
7	1	141	150
13	1	49	58
1	3	34	29
3	3	183	171
5	3	88	90
7	3	106	112
13	3	43	51
2	4	17	18
4	4	64	59
8	4	73	76
10	4	355	363
1	5	43	41
3	5	201	180
5	5	30	25
7	5	139	137
2	6	36	30
4	6	[illegible]	34
3	7	96	90
5	7	80	80
7	7	56	52
4	8	32	33
8	8	47	43
10	8	253	254
3	9	121	111
7	9	100	95
5	11	52	53
10	12	146	146
3	13	70	60
7	13	62	56
H=1			
0	3	28	29
0	5	44	41
0	9	25	32
1	2	252	208
1	4	32	29
1	6	150	134
1	8	31	35
1	10	65	66
2	1	305	268
2	3	237	200
2	5	252	212
2	7	112	102
2	9	147	131
2	11	36	32
2	13	76	72
3	2	373	326
3	6	218	181
3	10	121	111
4	1	157	149
4	3	121	107
4	5	158	131
4	7	59	50
4	9	97	84
4	13	58	46
5	2	208	190
5	4	26	24
5	6	144	132
5	10	62	66
6	3	32	16
6	5	33	34
7	2	143	133

K	L	$\|F_o\|$	$\|F_c\|$
7	6	102	94
7	8	38	38
7	10	54	49
8	1	36	43
8	3	54	61
8	7	51	56
9	2	89	91
9	6	58	62
11	2	47	46
12	1	110	124
12	3	95	105
12	5	105	112
12	7	62	66
12	9	70	81
13	2	86	90
13	6	65	74
-1	2	238	208
-1	4	27	29
-1	6	144	134
-1	8	36	35
-1	10	69	66
-2	1	76	80
-2	3	118	110
-2	5	29	28
-2	7	93	95
-2	11	54	61
-3	2	193	197
-3	6	136	133
-3	10	61	64
-4	1	32	34
-4	5	35	30
-5	2	123	136
-5	6	91	95
-5	10	40	46
-6	1	180	226
-6	3	169	183
-6	5	180	189
-6	7	102	104
-6	9	116	123
-6	11	43	42
-7	2	158	181
-7	6	132	138
-7	10	115	91
-8	1	50	63
-8	5	56	62
-8	9	44	44
-9	2	96	127
-9	6	78	90
-9	10	50	49
-11	2	51	72
-11	6	43	53
H=2			
0	2	37	15
0	4	22	18
0	6	35	30
1	3	126	110
1	5	29	28
1	7	101	95
1	11	63	61
2	4	47	43
2	6	31	32
3	1	202	187
3	3	154	134
3	5	198	162
3	7	76	63
3	9	126	104
3	13	71	59
4	4	90	81
4	8	53	47
5	1	39	34

K	L	$\|F_o\|$	$\|F_c\|$
5	5	43	34
6	4	579	555
6	8	416	361
6	12	221	202
6	16	103	95
9	1	111	124
9	3	101	105
9	5	109	105
9	7	62	63
9	9	70	70
10	4	43	32
13	1	49	53
13	5	54	56
14	4	53	51
16	4	143	147
2	0	43	52
4	0	91	101
6	0	647	671
10	0	41	39
14	0	59	58
16	0	166	164
-8	0	63	76
-10	0	34	38
-12	0	46	58
-1	3	214	200
-1	5	230	212
-1	7	109	102
-1	9	142	131
-1	13	83	72
-2	4	44	43
-2	6	31	32
-3	1	38	42
-3	5	46	42
-4	4	603	669
-4	8	430	410
-4	12	240	226
-4	16	111	105
-7	1	100	123
-7	3	85	100
-7	5	96	105
-7	7	51	53
-7	9	66	67
-8	4	54	63
-9	3	48	56
-9	7	49	50
-11	3	56	68
-11	9	64	68
-12	4	48	50
-14	4	161	204
-14	8	130	147
-16	4	54	24
H=3			
0	3	193	171
0	5	205	180
0	7	97	90
0	9	125	110
0	13	69	60
1	2	232	198
1	4	25	21
1	6	148	133
1	10	68	64
2	1	47	42
2	3	23	22
2	5	49	42
2	9	41	36
3	2	224	190
3	4	43	31
3	6	147	130
3	8	48	40
3	10	74	65

K	L	$\|F_o\|$	$\|F_c\|$
4	1	68	67
4	3	100	92
4	5	29	26
4	7	93	82
4	11	64	54
5	2	136	130
5	6	102	91
5	10	43	43
7	2	103	103
7	6	80	72
8	1	158	177
8	3	140	145
8	5	157	155
8	7	92	83
8	9	113	108
8	11	48	34
8	13	62	63
9	2	135	138
9	6	116	110
9	10	81	74
11	2	90	97
11	6	74	71
13	2	51	46
-1	2	331	326
-1	6	201	181
-1	10	130	111
-1	14	65	61
-2	1	55	187
-2	3	140	134
-2	5	182	162
-2	7	71	63
-2	9	117	104
-2	13	73	59
-3	2	[illegible]	[illegible]
-3	4	34	31
-3	6	132	130
-3	8	42	40
-3	10	71	65
-4	1	34	35
-4	5	34	33
-5	2	130	143
-5	6	102	101
-5	10	48	51
-6	1	44	47
-6	3	63	69
-6	7	61	63
-7	2	112	137
-7	6	90	94
-7	10	48	48
-9	2	60	60
-9	6	47	40
-10	1	133	149
-10	3	115	127
-10	5	119	131
-10	7	80	80
-10	9	87	92
-10	13	55	54
-11	2	106	110
-11	6	85	90
-11	10	62	60
-13	2	66	65
-13	6	48	49
H=4			
0	4	63	59
0	6	38	34
0	8	40	33
0	10	36	32
4	0	28	29
6	0	39	32
10	0	78	82

K	L	$\|F_o\|$	$\|F_c\|$
12	0	271	286
3	1	39	35
5	1	189	199
7	1	37	40
9	1	76	78
1	3	24	21
5	3	178	165
7	3	57	57
9	3	53	51
6	4	37	28
10	4	70	69
12	4	247	255
1	5	39	30
3	5	39	33
5	5	193	167
9	5	88	77
5	7	111	95
7	7	58	52
2	8	473	410
10	8	46	45
12	8	181	183
1	9	33	28
5	9	125	107
9	9	68	59
5	11	51	39
2	12	269	225
12	12	105	108
5	13	72	59
2	16	123	105
-6	0	57	59
-8	0	434	476
-12	0	38	50
-14	0	38	47
-18	0	63	107
-1	3	121	107
-1	5	156	131
-1	7	60	50
-1	9	106	84
-1	13	57	46
-2	4	87	81
-2	6	38	36
-2	8	49	47
-2	10	60	35
-3	1	63	67
-3	3	92	92
-3	5	28	26
-3	7	87	81
-3	11	64	54
-5	1	171	196
-5	3	149	153
-5	5	171	172
-5	7	89	81
-5	9	121	115
-5	13	70	67
-6	4	46	50
-7	5	32	33
-8	4	379	413
-8	8	280	285
-8	12	166	163
-8	16	86	77
-11	1	35	40
-11	3	33	40
-11	5	38	43
-12	4	39	43
-15	5	41	50
-18	4	75	96
-18	8	66	71
H=5			
0	3	100	90
0	5	31	25

K	L	$\|F_o\|$	$\|F_c\|$
0	7	85	80
0	11	58	53
1	2	158	136
1	6	107	95
1	10	53	47
2	1	34	31
2	3	20	24
3	2	154	143
3	4	28	26
3	6	113	101
3	10	60	51
4	1	180	196
4	3	166	153
4	5	188	172
4	7	96	81
4	9	131	115
4	13	76	67
5	2	[illegible]	180
5	6	148	138
5	10	107	91
6	1	74	79
6	3	56	58
6	5	79	71
6	9	61	46
7	2	127	137
7	6	102	96
7	10	53	51
9	2	85	84
9	6	66	61
14	1	72	82
14	3	64	69
14	5	70	77
-1	2	201	190
-1	4	26	24
-1	6	136	132
-1	8	35	31
-1	10	71	66
-2	1	33	34
-2	3	22	20
-2	5	41	34
-3	2	[illegible]	130
-3	6	91	91
-3	10	51	43
-4	1	165	199
-4	3	151	165
-4	5	159	167
-4	7	104	95
-4	9	116	107
-4	11	47	39
-4	13	66	59
-5	2	162	130
-5	6	136	138
-5	10	99	91
-5	14	55	50
-6	1	79	87
-6	3	56	57
-6	5	88	[illegible]
-6	9	73	60
-7	2	106	122
-7	6	86	86
-7	10	53	46
-9	2	79	79
-9	6	70	58
-11	2	66	70
-11	6	41	51
-14	1	85	89
-14	3	71	77
-14	5	70	80
-14	7	50	52
-14	9	56	59
-15	2	58	59
-15	6	48	48

Description of the structure

The close packing of the Cs and Cl atoms is of the cubic variety. The indices of the close-packed planes are (132) and Fig. 2 shows a primitive cell whose base is parallel to these planes. The most interesting feature of the structure is the linking of symmetrically equivalent octahedra to form a three-dimensional complex. Cl(1), Cl(2) and Cl(3) atoms are in contact with 2 Mn, 3 Mn and 4Mn atoms respectively, so that each octahedron shares five edges and one vertex with six neighbouring octahedra. This arrangement is shown in Fig. 3.

Bond lengths and angles are listed in Table 4. The average lengths of the Mn–Cl, Cl–Cl and Cs–Cl bonds are 2·54, 3·58 and 3·72 Å respectively and agree within ±0·02 Å with the corresponding distances in the $CsMnCl_3$ structure. Because of the mutual repulsions of neighbouring Mn ions, the five shared edges are all shorter (3·447–3·554 Å) than the seven unshared edges (3·611–3·673 Å) of the octahedron. The disposi-

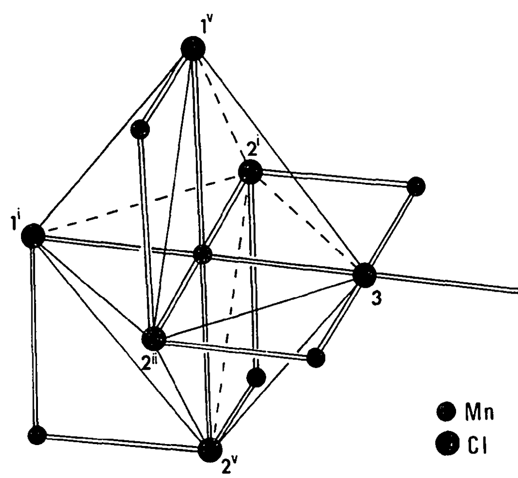

Fig. 3. The linking of the Cl atoms of one $MnCl_6$ octahedron to the Mn atoms of neighbouring octahedra. Double lines indicate Mn–Cl bonds; single lines the edges of the octahedron.

Table 4. *Bond lengths and angles*

Standard deviations, attributable to e.s.d.'s in the positional and cell parameters, are given in parentheses.

Mn–Cl octahedron			
Mn–Cl(1^i)	2·446 (14) Å	Mn–Cl(2^i)	2·532 (14)Å
Mn–Cl(1^v)	2·436 (12)	Mn–Cl(2^{ii})	2·511 (14)
Mn–Cl(3)	2·702 (9)	Mn–Cl(2^v)	2·589 (12)
Cl(1^i)–Cl(2^i)	3·630 (17)	Cl(1^i)–Mn–Cl(2^i)	93·7 (4)°
Cl(1^i)–Cl(2^{ii})	3·647 (17)	Cl(1^i)–Mn–Cl(2^{ii})	94·7 (4)
Cl(2^i)–Cl(3)	3·554 (12)	Cl(2^i)–Mn–Cl(3)	85·5 (3)
Cl(2^{ii})–Cl(3)	3·554 (12)	Cl(2^{ii})–Mn–Cl(3)	85·9 (3)
Cl(1^v)–Cl(1^i)	3·617 (12)	Cl(1^v)–Mn–Cl(1^i)	95·6 (4)
Cl(1^v)–Cl(2^i)	3·627 (16)	Cl(1^v)–Mn–Cl(2^i)	93·8 (4)
Cl(1^v)–Cl(2^{ii})	3·476 (15)	Cl(1^v)–Mn–Cl(2^{ii})	89·2 (4)
Cl(1^v)–Cl(3)	3·611 (12)	Cl(1^v)–Mn–Cl(3)	89·2 (3)
Cl(2^v)–Cl(1^i)	3·476 (15)	Cl(2^v)–Mn–Cl(1^i)	87·3 (4)
Cl(2^v)–Cl(2^i)	3·447 (20)	Cl(2^v)–Mn–Cl(2^i)	84·7 (4)
Cl(2^v)–Cl(2^{ii})	3·666 (12)	Cl(2^v)–Mn–Cl(2^{ii})	91·9 (4)
Cl(2^v)–Cl(3)	3·673 (11)	Cl(2^v)–Mn–Cl(3)	87·9 (3)

Cs–Cl distances

Cs–Cl($1^{i,ii,iii,iv}$)	3·713 (13) Å
Cs–Cl($1^{vi,vii,viii,ix}$)	3·698 (12)
Cs–Cl($2^{iii,iv,vi,vii}$)	3·755 (11)

Table 4 (*cont.*)

Idealized positions of atoms

Cs at (0,0,0)			Mn at (0·3,0·4,0)					
Cl at $z=0$			$z=\frac{1}{4}$			$z=-\frac{1}{4}$		
	x	y		x	y		x	y
(1^{i})	0·1	0·3	(1^{v})	0·3	0·4	(1^{viii})	0·2	0·1
(1^{ii})	−0·3	0·1	(1^{vi})	−0·1	0·2	(1^{ix})	−0·2	−0·1
(1^{iii})	−0·1	−0·3	(1^{vii})	0·1	−0·2	(2^{v})	0·3	0·4
(1^{iv})	0·3	−0·1	(2^{iii})	0·2	0·1	(2^{vi})	−0·1	0·2
(2^{i})	0·2	0·6	(2^{iv})	−0·2	−0·1	(2^{vii})	0·1	−0·2
(2^{ii})	0·4	0·2						
(3)	0·5	0·5						

Table 5. *Distortion of the* Cl–Mn–Cl *angle*

Column (*a*): due to the contraction (or extension) of the Cl–Cl bond
Column (*b*): due to the displacement of the Mn ion

Angle subtended by	(*a*)	(*b*)		(*a*)	(*b*)		(*a*)	(*b*)
(1^{i})–(2^{i})	+1·6°	+2·0°	(1^{v})–(1^{i})	+1·0°	+4·4°	(2^{v})–(1^{i})	−3·5°	+0·7°
(1^{i})–(2^{ii})	+2·1	+2·5	(1^{v})–(2^{i})	+1·3	+2·3	(2^{v})–(2^{i})	−4·4	−1·2
(2^{i})–(3)	−1·0	−3·7	(1^{v})–(2^{ii})	−3·5	+2·8	(2^{v})–(2^{ii})	+2·6	−0·8
(2^{ii})–(3)	−1·0	−3·3	(1^{v})–(3)	+0·8	−1·8	(2^{v})–(3)	+2·8	−4·8

tion of the neighbouring Mn ions (see Fig. 3) suggests that in an octahedron the Mn ion would be repelled in a direction predominantly away from Cl(3) and somewhat towards the Cl(1^{i})–Cl(1^{v}) edge. This explains the very long Mn–Cl(3) and the relatively long Mn–Cl(2^{v}) bonds, and to some extent the wide variation in the shared Cl–Cl distances.

The magnitudes of the Cl–Mn–Cl angles of the octahedron can best be accounted for by considering separately departures from the ideal value of 90° due to (*a*) the contraction (or extension) of the Cl–Cl edge and (*b*) the displacement of the Mn ion from the centre of the octahedron. These distortions, which are listed in Table 5, were calculated by assuming a constant Mn–Cl distance of 2·536 Å in case (*a*) and a constant Cl–Cl distance of 3·582 Å in case (*b*).

Finally all attempts at preparing the compound $CsMn_4Br_9$ failed. Although trigonally distorted $MnBr_6$ octahedra are found in the structure of $CsMnBr_3$ (Goodyear & Kennedy, 1972), it appears that the Mn^{2+} ion is not large enough to be in contact with six Br^- ions at the vertices of an octahedron which is distorted similarly to the $MnCl_6$ octahedron found in the $CsMn_4Cl_9$ structure.

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