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INVESTIGATIONS ON SYSTEMS AX/MnX_2 (A = Li–Cs, Tl; X = Cl, Br, I) BY DTA AND X-RAY ANALYSIS*[1]

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ABSTRACT

A combination of differential thermal analysis and X-ray methods was used to investigate the formation of double halides from alkali halides, AX, and manganese halides, MnX_2 (X = Cl, Br, I). In complicated systems like $NaCl/MnCl_2$, $RbBr/MnBr_2$ and $CsBr/MnBr_2$, phase diagrams could only be elucidated by determining the crystal structures of the main compounds. The MnI_2 systems were investigated for the first time.

INTRODUCTION

In order to find general rules for the formation of double halides $A_nMX_{(n+2)}$ by a combination of AX (alkali chloride, bromide or iodide) and MX_2, we have elucidated several phase diagrams of such systems by DTA, and have also determined the structure of the existing compounds by X-ray methods. It was one result of our previous work that the question regarding the number of ternary compounds in a special system cannot be separated from the question regarding their structures.

X-Ray crystallography, however, can also be a very powerful investigative tool for elucidating phase diagrams, allowing, for instance, a check of the results of DTA by taking X-ray powder patterns of the solidified melts or the composition of compounds to be elucidated by structure determination. Both aspects are to be demonstrated by using some systems AX/MnX_2. Results on the systems of $MnCl_2$ and $MnBr_2$ have been published elsewhere[3] and will be covered only insofar as is required by the particular subject of this paper. Complete results on the systems of MnI_2 are presented.

INSTRUMENTATION

DTA equipment

The most important feature of the DTA cell[4] is the quartz sample holder. The sample, approximately 0.5–1 g, is homogenized after sealing the ampoules in vacuo

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by melting in a gas flame and shaking. After solidification by rapid cooling, it is sufficiently homogeneous for the determination of heating curves and for annealing experiments. (As a rule, cooling curves were determined, but in some cases undercooling was too great to get reliable results).

X-Ray equipment

Powder patterns at room temperature were taken using a goniometer equipped with a counter and a vacuum attachment (Philips, Eindhoven). High temperature patterns at varying temperatures were taken with a Simon Guinier camera, series 553 from Enraf-Nonius, Delft. Single crystal analysis was done with the 2 circle goniometer Stadi II from Stoe, Darmstadt.

SUBSTANCES

The anhydrous Mn(II) halides were prepared by dehydrating their hydrates, obtained from $MnCO_3$, in a stream of HX. $MnCO_3$ and the alkali halides were commercially available from Merck, Darmstadt.

THE SYSTEMS $ACl/MnCl_2$ AND $ABr/MnBr_2$

A reinvestigation of these systems yielded corrections in three cases.

System $CsBr/MnBr_2$

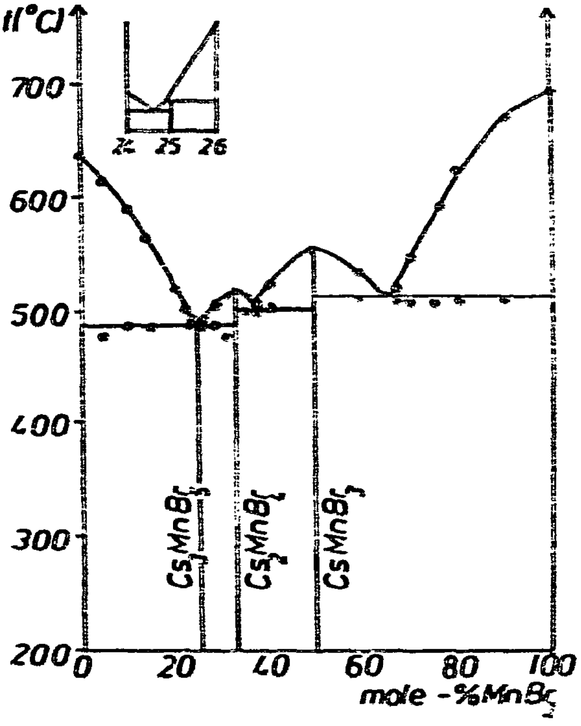
In addition to our earlier investigations[5], a compound Cs_3MnBr_5 was found. The eutectic and dystectic (or peritectic) points coincide practically. One probable form of the phase diagram is shown in the upper left part of Fig. 1. The existence of this compound could be verified only by X-ray measurements. Its structure[3] is isotypic to Cs_3CoCl_5.

System $RbBr/MnBr_2$ (Fig. 2)

Here we had found[5] the two congruently melting compounds $RbMnBr_3$ and Rb_2MnBr_4, the latter with a transition point at 230 °C. Additionally, two compounds exist which are formed by solid state reactions: Rb_4MnBr_6 is stable only below 280 °C and Rb_3MnBr_5 in the temperature range from 249 to 402 °C. The respective thermal effects could be measured only by taking heating curves of annealed samples. Again, we got the indication of the existence of these compounds by analysing powder patterns of solidified melts and, in the case of Rb_3MnBr_5, by high temperature patterns. The compositions were confirmed by determining the crystal structures[3].

System $NaCl/MnCl_2$ (Fig. 3)

The left figure shows the interpretation according to our first measurements in 1965[6]. At this time, we were not able to index any of the powder patterns. Later, van Loon and Ijdo[7] determined the structure of the two compounds Na_6MnCl_8 and $Na_2Mn_3Cl_8$. Our reinvestigation of the system with DTA[3] resulted in the correct phase diagram. The compound $NaMnCl_3$ is stable only above 360 °C but can be



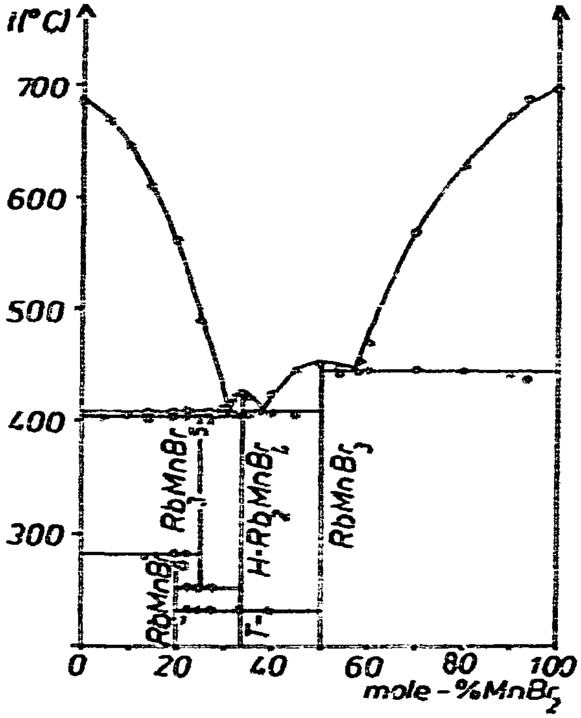


Fig. 1. System CsBr/MnBr$_2$.

Fig. 2. System RbBr/MnBr$_2$.

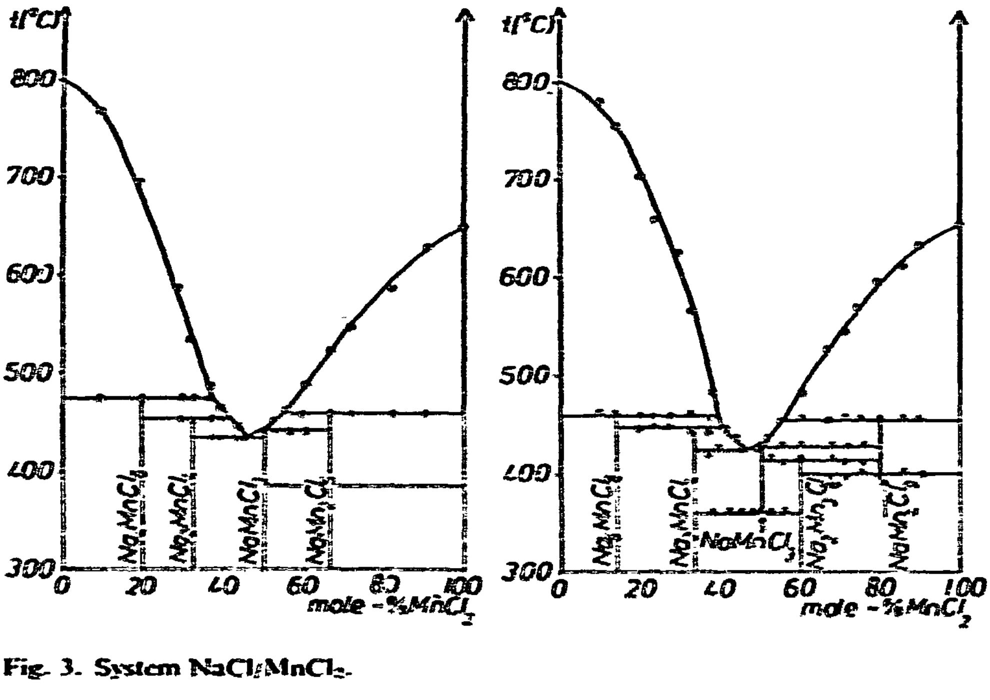
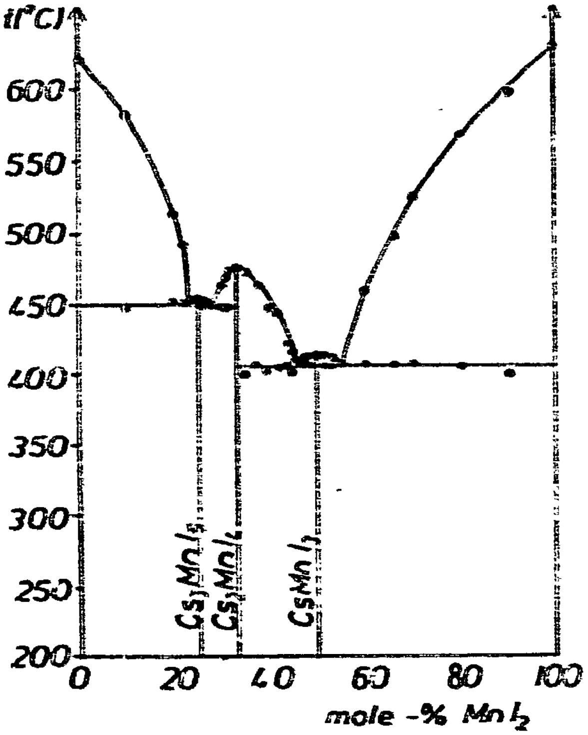


Fig. 3. System NaCl/MnCl$_2$.



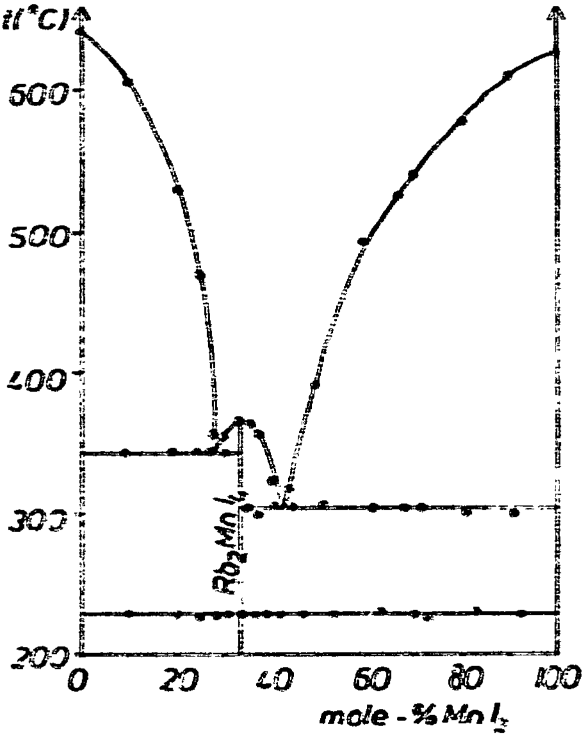


Fig. 4. System CsI/MnI$_2$.
Fig. 5. System RbI/MnI$_2$.

obtained metastably by quenching. Another high temperature compound is NaMn$_4$Cl$_9$, the crystal structure of which could not yet be determined.

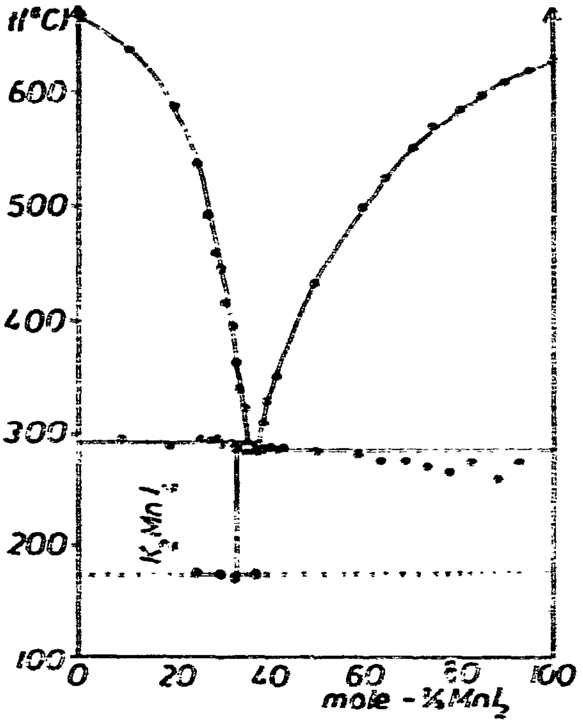
THE SYSTEMS AI/MnI$_2$

The phase diagrams are shown in Figs. 4–8; the characteristic data are compiled in Table 1.

In the systems with CsI and RbI, only congruently melting compounds exist. Rb$_2$MnI$_4$ has a transition point at 230 °C. With TlI, two compounds exist, one melting incongruently. The one K compound, K$_2$MnI$_4$, exists above 172 °C only. After annealing a sample for some days at 150 °C, a powder pattern showed the reflections of both binary iodides. When heated in the Guinier camera at ~180 °C, new reflections appeared which could be indexed in analogy to those of the low temperature Rb$_2$MnI$_4$.

The system NaI/MnI$_2$ is purely eutectic. The system LiI/MnI$_2$ is also eutectic but with an area of miscibility on the LiI-rich side which extends to ~30 mole % MnI$_2$ at 429 °C.

Table 2 gives a survey of all compounds. There is now a simple rule about a relationship between the kind of alkali or halide ions and the number of existing compounds in the single systems. The reason for that is related to the special crystal structures.



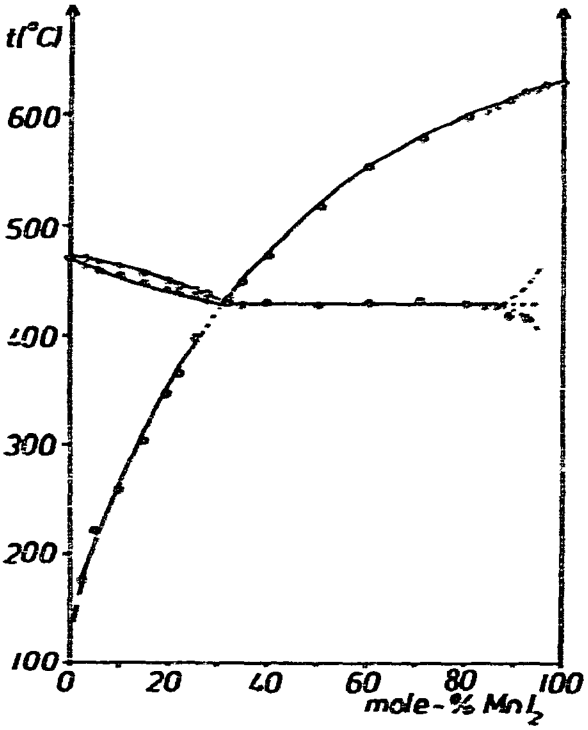


Fig. 6. System KI/MnI$_2$.

Fig. 7. System LiI/MnI$_2$.

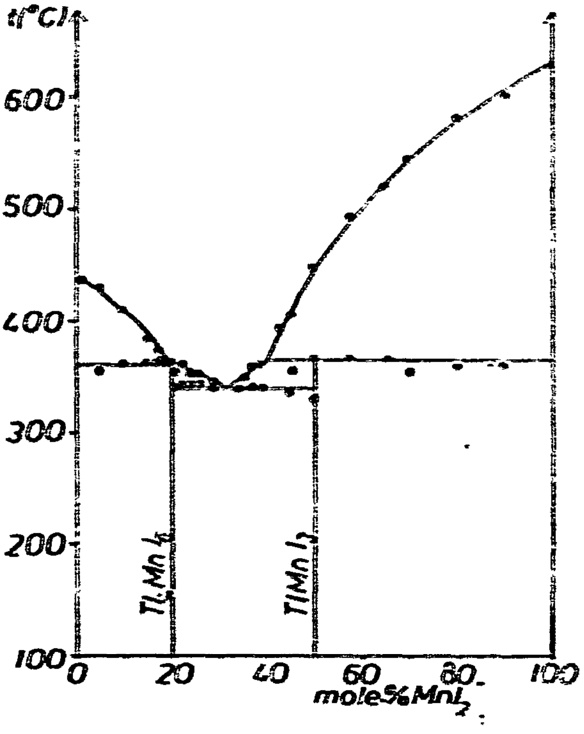


Fig. 8. System TlI/MnI$_2$.

TABLE 1

CHARACTERISTIC DATA FOR SYSTEMS AI/MnI_2

(All temperatures in °C; compositions in mole % MnI_2; m.p. = melting point; t.p. = transition point.)

System CsI/MnI_2
CsI (m.p.) = 620°
1. Eutectic point = 450°; 23.0%
Cs_3MnI_5 (m.p.) = 453°
2. Eutectic point = 445°; 28.0%
Cs_2MnI_4 (m.p.) = 472°
3. Eutectic point = 405°; 46.0%
$CsMnI_3$ (m.p.) = 413°
4. Eutectic point = 407°; 55.0%

System RbI/MnI_2
RbI (m.p.) = 642°
1. Eutectic point = 344°; 29.0%
Rb_2MnI_4 (m.p.) = 367°; t.p. = 230°
2. Eutectic point = 304°; 43.0%

System NaI/MnI_2
NaI (m.p.) = 662°
Eutectic point = 412°; 39.0%

System KI/MnI_2
KI (m.p.) = 684°
Peritect. K_2MnI_4 = 280°; 35.5%
Decomposition = 172°
Eutectic point = 270°; 38.0%

System LiI/MnI_2
LiI (m.p.) = 472°
Eutectic point = 429°; 31.0%
Miscibility gap = ~ 30%

System TlI/MnI_2
TlI (m.p.) = 442°; t.p. = 166°
1. Eutectic point = 360°; 18.5%
Tl_4MnI_6 (m.p.) = 362°
2. Eutectic point = 340°; 31.0%
Peritect $TlMnI_3$ = 365°; 38.0%

MnI_2 (m.p.) = 628°

TABLE 2

TERNARY HALIDES OF MANGANESE(II)

[( ) = incongruently melting; (d) = dimorphous; { } = exists only at high temperature.]

AX-rich	*A_2MnX_4*	*$A_3Mn_2X_7$*	*$AMnX_3$*	*MnX_2-rich*
Cs_3MnCl_5	Cs_2MnCl_4(d)		$CsMnCl_3$	($CsMn_4Cl_9$)
Cs_3MnBr_5	Cs_2MnBr_4		$CsMnBr_3$	
Cs_3MnI_5	Cs_2MnI_4		$CsMnI_3$	
	(Rb_2MnCl_4)	($Rb_3Mn_2Cl_7$)	$RbMnCl_3$	
(Rb_4MnBr_6)	Rb_2MnBr_4(d)		$RbMnBr_3$	
(Rb_3MnBr_5)	Rb_2MnI_4(d)			
(K_4MnCl_6)		($K_3Mn_2Cl_7$)	$KMnCl_3$(d)	
(K_4MnBr_6)			$KMnBr_3$	
	{(K_2MnI_4)}			
(Na_6MnCl_8)	(Na_2MnCl_4)		{($NaMnCl_3$)}	($Na_2Mn_3Cl_8$) {($NaMn_4Cl_9$)}
Tl_4MnI_6			$TlMnCl_3$	
			($TlMnBr_3$)	
			($TlMnI_3$)	

TABLE 3

STRUCTURE DATES FOR COMPOUNDS $A_nMnI_{(n+2)}$

[N = formula units per cell; D_x = experimental density (g cm^{-3}); D_c = calculated density; L = low temperature; H = high temperature]

Compound	*Space group*	*a* [Å]	*b* [Å]	*c* [Å]	*β* [Å]	*N*	D_x	D_c
K_2MnI_4	*P*2₁/*m*	9.719	8.229	7.922	108.3	2		3.58
L-Rb_2MnI_4	*P*2₁/*m*	10.304	8.264	7.854	109.4	2	3.85	3.86
H-Rb_2MnI_4	*Pnma*	10.540	8.502	14.725		4		3.69
Cs_3MnI_5	*I*4/*mcm*	10.215		16.623		4	4.19	4.17
Cs_2MnI_4	*Pnma*	10.859	8.433	14.737		4	4.08	4.08
$CsMnI_3$	*P*6₃/*mmc*	8.196		6.958		2	4.64	4.66
Tl_4MnI_6	*P*4/*mnc*	9.114		9.767		2	6.64	6.68
$TlMnI_3$	*Pnma*	10.116	4.317	16.258		4	6.00	5.99

THE CRYSTAL STRUCTURES

In Table 3, the lattice parameters of the iodine compounds are compiled. With one exception, $CsMnI_3$ (ref. 8), they were unknown. For $CsMnI_3$ a complete structure determination was done by single crystal methods. A small crystal was sealed into a thin-walled glass capillary under argon. De Jong-Bouman (layer 0*kl*) and precession photographs (layers *h k* 0 and *h k* 1) led to the space groups $P6_3/mmc$, $P\bar{6}2c$ or $P6_3mc$ (*hhl* only with $l = 2n$). The centrosymmetric $P6_3/mmc$ gave the best agreement with the measured intensities. They were collected with the two-circle goniometer (ω = scan, 200 steps to 0.02° in 0.5 sec; $2° \leq \theta \leq 25°$). 820 reflexes of the layers *hkl* (h = 0–5) were measured. 155 of them were symmetrically independent. After elimination of the strongest 17 reflexes, the refinement considering anisotropic temperature factors gave a *R* value of 0.074.

Results: Space group No. 194, $P6_3/mmc - D_{6h}^4$

2Cs in (d) 1/3 2/3 3/4

2Mn in (a) 0 0 0

6I in (h) x 2x 1/4 with $x = 0.1647$

Distances (Å): Mn–I 2.912

I–I 4.050 Cs–I 4.098 (in one layer ⊥ *c*)

I–I 4.191 Cs–I 4.223 (in different layers)

A survey of all crystal structures is compiled on Table 4. The compounds A_4MnX_6 contain isolated MnX_6 octahedra. The coordination number (C.N.) of the alkali ions is 6 and 8. Such compounds are not formed with the large Cs atom.

The compounds A_3MnX_5, better written $A_3[MnX_4]X$, are built up from MnX_4-tetrahedra. The same is true for many of the 2 : 1 compounds: in the K_2SO_4 type, the C.N. of the alkali ions is 9 and 10, in the Sr_2GeS_4 type (6 + 2).

In L-Cs_2MnCl_4 and in Rb_2MnCl_4, the Mn^{2+} ion is octahedrally coordinated by the chloride ions; the octahedra are connected by sharing the four coplanar

TABLE 4

CRYSTAL STRUCTURES

A_4MX_6: Tl_4MnI_6–Rb_4MnBr_6, K_4MnBr_6–K_4MnCl_6
$A_3MX_5 \equiv A_2[MX_4]X$: Cs_3MnI_5, A_3MnBr_5 (A = Cs, Rb) Cs_3MnCl_5
A_2MX_4 β-K_2SO_4 type: Cs_2MnI_4, H-Rb_2MnI_4
Cs_2MnBr_4, Rb_2MnBr_4
H-Cs_2MnCl_4
Sr_2GeS_4 type: L-Rb_2MnI_4, K_2MnI_4
K_2MgF_4 *type* $\equiv K_2MgF_{4/2}F_2$ L-Cs_2MnCl_4, Rb_2MnCl_4
Similar: $Rb_3Mn_2Cl_7$, $K_3Mn_2Cl_7$
AMX_3: NH_4CdCl_3 type: $TlMnI_3$–$TlMnBr_3$, $KMnBr_3$
$CsNiCl_3$ type: $CsMnI_3$–$CsMnBr_3$, $RbMnBr_3$
Transition types: $CsMnCl_3$, $RbMnCl_3$
Perovskites: $KMnCl_3$, $TlMnCl_3$
Similar: $CsMn_4Cl_9$
Na compounds: Na and Mn in octahedral holes

vertices forming a layer structure. In the compounds $A_3Mn_2Cl_7$, two layers are condensed. (This structural type is *not* formed if the 2 : 1-compound is built up from tetrahedra).

The 1 : 1-compounds with the more polarisable anions belong to the $CsNiCl_3$ type or, if the alkali ions are to small, to the NH_4CdCl_3 type. In the latter, double-strings of connected octahedra are held together by alkali ions, the C.N. of which is 9.

The $CsNiCl_3$ type and the structures of the trichloromanganates (Fig. 9) are perovskite variants. The A^+ and X^- form approximately close packed AX_3 layers. The Mn^{2+} ions occupy octahedral holes. In the $CsNiCl_3$ type, the $MnX_{6/2}$ octahedra share faces and built up columns which are held together by the A^+ ions. This type allows an optimal gain of polarisation energy by the asymmetrical influence of the doubly charged Mn^{2+} on the polarisable anions. In the real perovskite type, the octahedra share corners; the gain of polarisation energy is zero. The structures of $CsMnCl_3$ and $RbMnCl_3$ are links between both principles. In the sodium compound, both cations possess the C.N. 6.

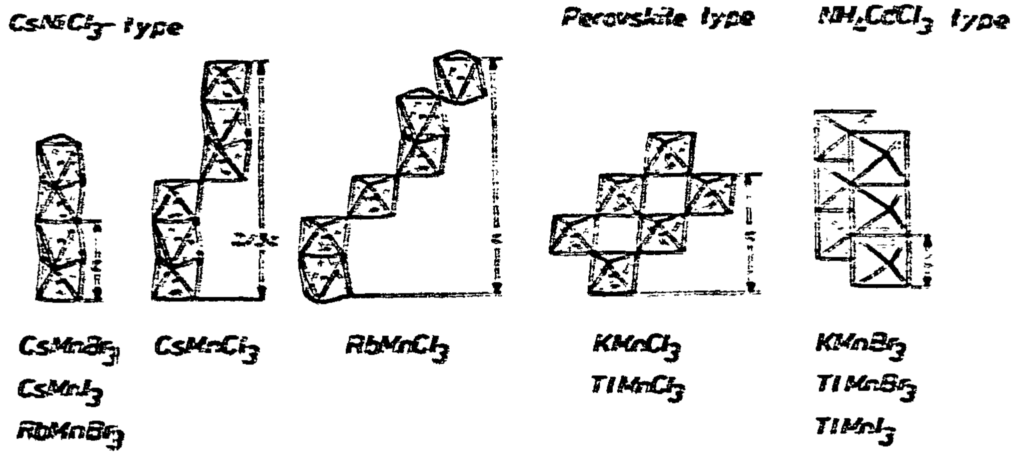


Fig. 9. Connection of octahedra in $AMnX_3$ compounds.

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