

spin polaron. The binding energy and the change in the Cu–Cu separation are both quite small, since so little electronic energy (of order  $J$ ) can be gained by distorting the lattice. The distinction between spin polarons, which we believe provide the most convincing explanation of the magnetic properties, and thermal contraction then cannot be made from structural data alone. The desirability of a linear chain of copper acetate dimers with a larger value of  $J'$ , even if only by an order of magnitude, is evident both for establishing exchange striction on a structural basis and for observing triplet spin excitons in an inorganic system.

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## The Crystal Structures of $\text{Na}_6\text{MnCl}_8$ and $\text{Na}_2\text{Mn}_3\text{Cl}_8$ and Some Isostructural Compounds

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An examination of the systems  $\text{NaCl-TCl}_2$  ( $T = \text{Mg, Mn, Fe, Cd}$ ) has resulted in the discovery of compounds with the stoichiometries  $\text{NaTCl}_3$ ,  $\text{Na}_2\text{TCl}_4$ ,  $\text{Na}_6\text{TCl}_8$  and  $\text{Na}_2\text{T}_3\text{Cl}_8$ . The former three stoichiometries crystallize in structures that had been discovered before in  $\text{FeTiO}_3$  (ilmenite),  $\text{Sr}_2\text{PbO}_4$  and  $\text{Mg}_6\text{MnO}_8$  respectively.  $\text{Na}_2\text{T}_3\text{Cl}_8$  represents a new structure type and has been related to the crystal structure of  $\text{Cd}_2\text{Mn}_3\text{O}_8$ .

### Introduction

As part of a research programme on the structural relations of compounds in the system  $\text{AX-TX}_2$ , A representing Li or Na, T a first-row transition or an alkaline-earth metal and X being Cl, Br or I, we report in this paper the structures of  $\text{Na}_6\text{MnCl}_8$  and  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  and a few isostructural compounds.

Earlier we reported the crystal structure of  $\text{NaMnCl}_3$  (van Loon & Verschoor, 1973), the stoichiometry  $\text{ATX}_3$  attracting our main attention. Some isostructural compounds, together with the cell edges determined from powder diffraction data, will be given in this paper. The crystal structure of  $\text{Na}_2\text{MnCl}_4$  (Goodyear, Ali & Steigmann, 1971) was confirmed to have a  $\text{Sr}_2\text{PbO}_4$  (Trömel, 1965) structure and some other

compounds with this structure are also given here.

Our attempts to prepare  $\text{NaMn}_2\text{Cl}_5$ , mentioned in the phase-diagram of  $\text{NaCl-MnCl}_2$  (Seifert & Koknat, 1965), failed but led to the discovery of the compound  $\text{Na}_2\text{Mn}_3\text{Cl}_8$ . Searching for  $\text{Na}_4\text{MnCl}_6$  we found  $\text{Na}_6\text{MnCl}_8$  which turned out to have the cubic structure of  $\text{Mg}_6\text{MnO}_8$  (Kasper & Prener, 1954).

Experimental results and differential thermal analyses (by means of a Mettler Vacuum Thermal Analyzer TA1) revealed  $\text{NaMnCl}_3$  to be unstable below  $360^\circ\text{C}$ . Further investigations are being carried out in order to improve our knowledge of the phase system  $\text{NaCl-MnCl}_2$ .

### Experimental

$\text{NaCl}$  was dried *in vacuo* at  $200^\circ\text{C}$ .  $\text{MnCl}_2$  was obtained by dehydrating  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  in  $\text{HCl}$  atmosphere in steps up to  $350^\circ\text{C}$ , followed by melting in dry nitrogen. Molten  $\text{MgCl}_2$  was obtained by heating  $\text{Mg}$  metal at  $900^\circ\text{C}$  in a stream of dry  $\text{HCl}$  gas.  $\text{FeCl}_2$  and  $\text{CdCl}_2$  were obtained from  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and

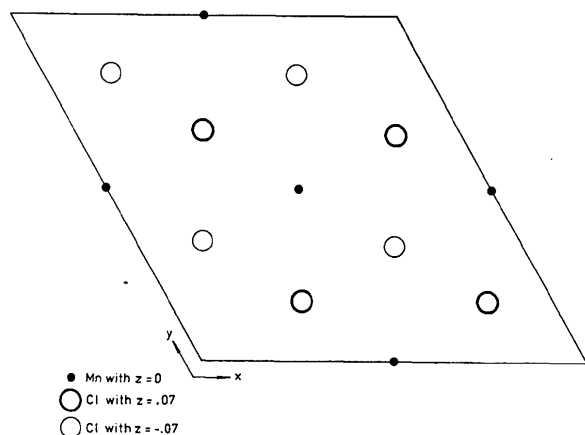


Fig. 1. Projection along the  $c$  axis of  $\text{Na}_2\text{Mn}_3\text{Cl}_8$ : a manganese layer and its nearest chlorine layers.

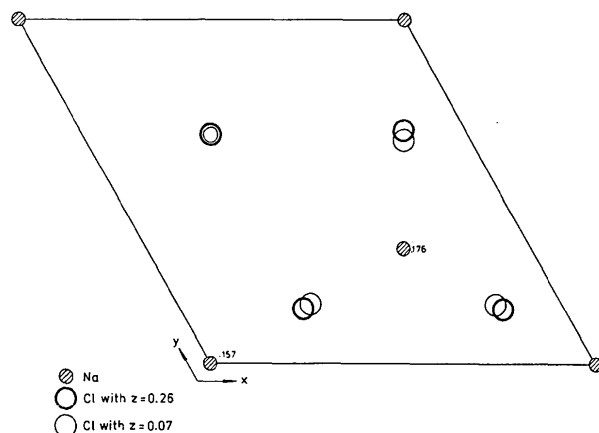


Fig. 2. Projection along the  $c$  axis of  $\text{Na}_2\text{Mn}_3\text{Cl}_8$ : a sodium layer and its nearest chlorine layers.

$\text{CdCl}_2 \cdot x\text{H}_2\text{O}$  by dehydration in a stream of dry  $\text{HCl}$  gas in steps up to  $500$  and  $350^\circ\text{C}$  respectively.

Proper amounts of the various starting materials were brought together in a glove-box filled with dry nitrogen and fused in dry nitrogen atmosphere after an evacuation up to  $10^{-5}$  torr. The samples obtained were pulverized and annealed in evacuated, sealed silica tubes for a week at temperatures between  $340$  and  $410^\circ\text{C}$ . The procedure was repeated two or three times.

The X-ray powder diffraction patterns were obtained by means of a Philips PW1050 diffractometer that was made suitable for the investigation of hygroscopic samples. The neutron diffraction diagrams were collected at  $300\text{ K}$  on the powder diffractometer at the Petten High-Flux Reactor. A wavelength of  $2.5694\text{ \AA}$  from the (111) planes of a copper monochromator was used. The complete range of data obtained ( $5.40^\circ < 2\theta < 139^\circ$ ) was used in the refinements. Absorption and extinction effects were small and no corrections were made. The samples ( $\sim 20\text{ g}$ ) were contained in a thin-walled vanadium tube. The scattering lengths ( $\times 10^{-12}$ ) were  $0.351$  for sodium,  $-0.360$  for manganese and  $0.960$  for chlorine (Neutron Diffraction Commission, 1969).

The function minimized during the full-matrix least-squares analyses of the powder diffraction profiles (Rietveld, 1967) was  $\sum w[y(\text{obs}) - 1/c y(\text{calc})]^2$ .  $y(\text{obs})$  and  $y(\text{calc})$  represent the observed and calculated intensities per measuring point in a peak,  $w$  is the statistical weight and  $c$  the scale factor.

The X-ray diffraction patterns of the  $\text{Na}_6\text{TCl}_8$  ( $\text{T} = \text{Mg, Mn, Fe, Cd}$ ) compounds could all be indexed in the cubic system. Systematic absences indicated a face-centred structure. The cell edges are assembled in Table 1. They appear to be twice as large as the cell edge of  $\text{NaCl}$ . Neutron diffraction experiments on  $\text{Na}_6\text{MnCl}_8$  confirmed our assumption that these compounds have the  $\text{Mg}_6\text{MnO}_8$  structure. A few cycles of full-matrix refinement of positional parameters and individual isotropic thermal parameters for all ions led to convergence at

$$R_1 = 100 \sum |I(\text{obs}) - \frac{1}{c} I(\text{calc})| / \sum I(\text{obs}) = 2.56,$$

$$R_2 = 100 \sum |y(\text{obs}) - \frac{1}{c} y(\text{calc})| / \sum y(\text{obs}) = 8.25,$$

$$R_3 = 100 \sqrt{\left\{ \sum w \left[ y(\text{obs}) - \frac{1}{c} y(\text{calc}) \right]^2 \right\} / \sum w [y(\text{obs})]^2} = 8.21.*$$

The final scale factor was  $16.9$  (1). The positional parameters and the individual isotropic thermal param-

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30744 (2pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

eters can be found in Table 1. Standard deviations given in parentheses are based on counting statistics. Interionic distances and bond angles are presented in Table 2.

Table 1. Structural data for Na<sub>6</sub>TCl<sub>8</sub> compounds

Space group: <i>Fm</i> 3 <i>m</i> , <i>Z</i> =4			
Na:	24( <i>d</i> )	0 ½ ½	Na <sub>6</sub> MgCl <sub>8</sub> : <i>a</i> =11·200 (2) Å
T:	4( <i>a</i> )	0 0 0	Na <sub>6</sub> FeCl <sub>8</sub> : <i>a</i> =11·181 (3)
Cl(1):	8( <i>c</i> )	½ ½ ½	Na <sub>6</sub> CdCl <sub>8</sub> : <i>a</i> =11·248 (3)
Cl(2):	24( <i>e</i> )	<i>x</i> 0 0	Na <sub>6</sub> MnCl <sub>8</sub> : <i>a</i> =11·2274 (4)
In Na <sub>6</sub> MnCl <sub>8</sub> :			
	<i>x</i> =0·2287 (2)		
	<i>b</i> <sub>Na</sub> =1·1 (1) Å <sup>2</sup>	<i>b</i> <sub>Cl(1)</sub> =0·8 (1) Å <sup>2</sup>	
	<i>b</i> <sub>Mn</sub> =0·6 (5)	<i>b</i> <sub>Cl(2)</sub> =0·94 (6)	

Table 2. Interionic distances (Å) and bond angles (°) in Na<sub>6</sub>MnCl<sub>8</sub>

Na—Cl(1)	2 ×	2·8069 (0)	Cl(1)—Na—Cl(1)	180·00 (0)
Na—Cl(2)	4 ×	2·8170 (2)	Cl(1)—Na—Cl(2)	90·00 (0)
Mn—Cl(2)	6 ×	2·568 (2)	Cl(2)—Na—Cl(2)	80·26 (09)
Cl(1)—Cl(2)	12 ×	3·9767 (1)	Cl(2)—Na—Cl(2)	99·74 (09)
Cl(2)—Cl(2)	4 ×	3·631 (3)	Cl(2)—Na—Cl(2)	180·00 (0)
Cl(2)—Cl(2)	4 ×	4·308 (3)	Cl(2)—Mn—Cl(2)	90·00 (0)
Na—Na	8 ×	3·9695 (0)	Cl(2)—Mn—Cl(2)	180·00 (0)
Na—Mn	2 ×	3·9695 (0)		

Table 3. Structural data for Na<sub>2</sub>T<sub>3</sub>Cl<sub>8</sub> compounds

Space group: <i>R</i> 3̄ <i>m</i> , <i>Z</i> =3			
Na:	6( <i>c</i> )	0 0 <i>z</i>	Cl(1): 6( <i>c</i> ) 0 0 <i>w</i>
T:	9( <i>e</i> )	½ 0 0	Cl(2): 18( <i>h</i> ) <i>u</i> − <i>u</i> <i>v</i>
Na <sub>2</sub> Mg <sub>3</sub> Cl <sub>8</sub>	<i>a</i> =7·355 (6) Å	<i>c</i> =19·51 (1) Å	
Na <sub>2</sub> Fe <sub>3</sub> Cl <sub>8</sub>	<i>a</i> =7·302 (2)	<i>c</i> =19·452 (5)	
Na <sub>2</sub> Cd <sub>3</sub> Cl <sub>8</sub>	<i>a</i> =7·451 (2)	<i>c</i> =19·580 (4)	
Na <sub>2</sub> Mn <sub>3</sub> Cl <sub>8</sub>	<i>a</i> =7·4563 (3)	<i>c</i> =19·591 (1)	

In Na<sub>2</sub>Mn<sub>3</sub>Cl<sub>8</sub>:

<i>z</i> =0·157 (1)	<i>b</i> <sub>Na</sub> =2·6 (5) Å <sup>2</sup>
<i>w</i> =0·4072 (8)	<i>b</i> <sub>Mn</sub> =−0·2 (2)
<i>u</i> =0·4987 (7)	<i>b</i> <sub>Cl(1)</sub> =1·4 (3)
<i>v</i> =0·4052 (3)	<i>b</i> <sub>Cl(2)</sub> =0·9 (1)

The X-ray diffraction patterns of the Na<sub>2</sub>T<sub>3</sub>Cl<sub>8</sub> (T = Mg, Mn, Fe, Cd) compounds were indexed with hexagonal cell parameters. The lattice parameters are given in Table 3. Systematically absent reflexions were of the type  $-h+k+l \neq 3n$ , indicating a rhombohedral symmetry. Remembering the monoclinic structure of Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> (Oswald & Wampetich, 1967) we once classified as a structure with anion layers that are alternately stacked in a close-packed way and in a simple hexagonal way, we tried to design a structure model based on such an anion distribution and having rhombohedral symmetry. Immediately a six-layer structure came out whose lattice parameters were:  $a=2a_0$  and  $c=a_0(3+\sqrt{6})$  with  $a_0$  representing the shortest anion-anion distance. Using the Ahrens (1952) radius of Cl<sup>-</sup>, 1·81 Å, the lattice parameters of the structure model become  $a=7·24$  and  $c=19·73$  Å, in agreement with the observed lattice parameters. The structure model belonged to the space group *R*3̄*m* and provided the sodium ions with a trigonal prismatic surrounding of chlorine

ions and the manganese ions with an octahedral surrounding. The chlorine ions have different coordinations: Cl(1) has a one-sided three coordination of manganese ions as is the case in MnCl<sub>2</sub>, Cl(2) has two sodium and two manganese neighbours. The space-filling polyhedron (S.F.P.) (Gorter, 1970) of the chlorine ions is used to visualize the two different anion surroundings in Fig. 4. Neutron-diffraction data were used in a refinement of the positional parameters and the individual isotropic thermal parameters. The final reliability values became  $R_1=4·99$ ,  $R_2=11·56$ ,  $R_3=11·26$  and the final scale factor was 0·196 (3). The posi-

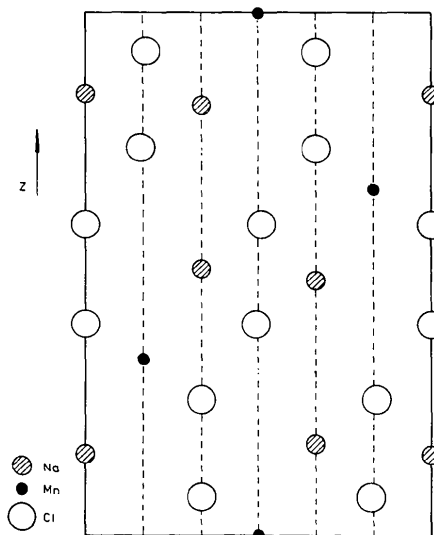


Fig. 3. (110) section in the hexagonal cell of Na<sub>2</sub>Mn<sub>3</sub>Cl<sub>8</sub>.

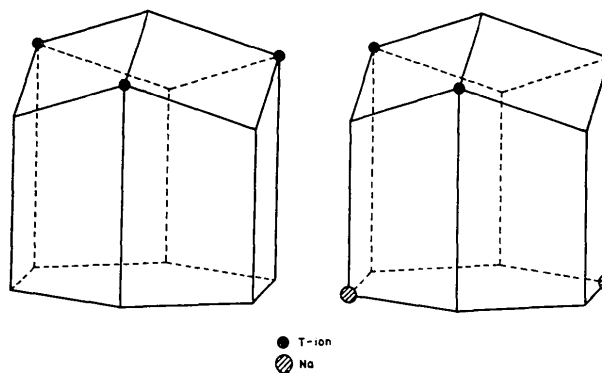


Fig. 4. Anion polyhedra in Na<sub>2</sub>T<sub>3</sub>Cl<sub>8</sub> (model).

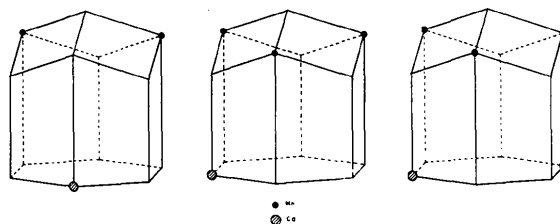


Fig. 5. Anion polyhedra in Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> (model).

tional parameters and the individual isotropic thermal parameters are given in Table 3. Interionic distances and bond angles are given in Table 4. A projection of a cation layer sandwiched between two anion layers is given for manganese and sodium in Figs. 1 and 2. Fig. 3 contains a (110) cross-section.

Table 4. *Interionic distances (Å) and bond angles (°) in Na<sub>2</sub>Mn<sub>3</sub>Cl<sub>8</sub>*

Mn—Cl(2)	4 × 2.565 (5)	Cl(2)—Na—Cl(2)	86.67 (19)
Mn—Cl(1)	2 × 2.594 (9)	Cl(2)—Na—Cl(2)	81.34 (18)
Na—Cl(2)	3 × 2.738 (6)	Cl(2)—Na—Cl(2)	135.07 (15)
Na—Cl(2)	3 × 2.957 (6)	Cl(2)—Na—Cl(2)	77.45 (19)
Cl(1)—Cl(2)	3 × 3.57 (1)	Cl(1)—Mn—Cl(1)	180.00 (0)
Cl(1)—Cl(1)	1 × 3.64 (3)	Cl(1)—Mn—Cl(2)	92.56 (23)
Cl(1)—Cl(2)	6 × 3.728 (4)	Cl(1)—Mn—Cl(2)	87.44 (23)
Cl(2)—Cl(2)	2 × 3.55 (1)	Cl(2)—Mn—Cl(2)	92.28 (28)
Cl(2)—Cl(2)	2 × 3.70 (1)	Cl(2)—Mn—Cl(2)	87.72 (28)
Cl(2)—Cl(2)	1 × 3.71 (1)	Cl(2)—Mn—Cl(2)	180.00 (0)
Cl(2)—Cl(2)	2 × 3.76 (1)	Mn—Cl(1)—Mn	91.89 (40)
Mn—Mn	4 × 3.7280 (0)	Mn—Cl(2)—Mn	93.22 (20)
Mn—Na	2 × 4.069 (2)	Na—Cl(2)—Mn	131.46 (18)
Mn—Na	4 × 4.834 (2)	Na—Cl(2)—Mn	94.66 (18)
Na—Na	3 × 4.3212 (4)	Na—Cl(2)—Na	98.66 (18)

Cell parameters together with their standard deviations of compounds with stoichiometries NaTCl<sub>3</sub> and Na<sub>2</sub>TCl<sub>4</sub>, and having the FeTiO<sub>3</sub> and the Sr<sub>2</sub>PbO<sub>4</sub> structure respectively, are given in Table 5. In this table the cell parameters of the compounds NaMnCl<sub>3</sub> and Na<sub>2</sub>MnCl<sub>4</sub> are results of single-crystal investigations by van Loon & Verschoor (1973) and Goodyear, Ali & Steigmann (1971) respectively.

Table 5. *NaTCl<sub>3</sub> and Na<sub>2</sub>TCl<sub>4</sub> compounds*

NaMnCl <sub>3</sub> *	<i>a</i> = 6.591 (3) Å	<i>c</i> = 18.627 (9) Å	
NaMgCl <sub>3</sub>	<i>a</i> = 6.506 (3)	<i>c</i> = 18.586 (7)	
NaCdCl <sub>3</sub>	<i>a</i> = 6.759 (2)	<i>c</i> = 18.666 (5)	
Na <sub>2</sub> MnCl <sub>4</sub> *	<i>a</i> = 6.93 (1)	<i>b</i> = 11.86 (2)	<i>c</i> = 3.86 (2) Å
Na <sub>2</sub> MgCl <sub>4</sub>	<i>a</i> = 6.904 (3)	<i>b</i> = 11.899 (5)	<i>c</i> = 3.816 (2)
Na <sub>2</sub> FeCl <sub>4</sub>	<i>a</i> = 6.901 (3)	<i>b</i> = 11.732 (4)	<i>c</i> = 3.830 (2)
Na <sub>2</sub> CdCl <sub>4</sub>	<i>a</i> = 7.020 (2)	<i>b</i> = 11.970 (3)	<i>c</i> = 3.9360 (8)

\* Single-crystal data from literature.

### Discussion

The crystal structure of the Na<sub>6</sub>TCl<sub>8</sub> compounds can be classified among the structures with anions in a cubic close-packed lattice and with cations that occupy octahedral sites in an ordered way. Pauling's (1929) second and fifth rules are obeyed if six chlorine ions have a five-coordination, consisting of four sodium and one divalent ion, and the two other chlorine ions have six sodium neighbours as in NaCl. In the five-coordinated polyhedron the divalent ion and the vacancy are on opposite corners of an octahedron.

The chlorine lattice in Na<sub>2</sub>T<sub>3</sub>Cl<sub>8</sub> can be regarded as a mixed lattice, composed of an equal contribution of close-packed stacking and simple hexagonal stacking. The anion-layer sequence is ...CCA(ABBCCA)ABB.... Between identical layers the sodium ions occupy sites that have a trigonal prismatic surrounding. The di-

valent T ions occupy three-quarters of the octahedral sites between different anion layers. The ordering pattern of one vacancy and three T ions in the octahedral layer corresponds to the triangular (T) type of order, introduced earlier (Schippers, Brandwijk & Gorter, 1973). In the structure of Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> the octahedral layers adopt the rectangular type of order (R), thereby destroying the trigonal symmetry.

The polyhedra of the anions in the model of Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> are given in Fig. 5 in order to show the differences from the anion polyhedra in Na<sub>2</sub>T<sub>3</sub>Cl<sub>8</sub>. In the latter the second and fifth rules of Pauling are obeyed, whereas in Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> the one-sided three-coordination has been avoided in favour of less asymmetric environments. The polarizability of Cl<sup>-</sup> being larger than that of O<sup>2-</sup>, one expects the polarization energy to be of greater importance in Na<sub>2</sub>T<sub>3</sub>Cl<sub>8</sub> than in Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>. The anion surroundings in both structures agree with this expectation. The question why the anions adopt the lattice described above instead of a close-packed lattice with both cations octahedrally coordinated may possibly be answered by means of a structure derivation for A<sub>2</sub>T<sub>3</sub>X<sub>8</sub> compounds as has been done before for <sup>xii</sup>ABX<sub>3</sub> and <sup>xii</sup>A<sub>2</sub>BX<sub>6</sub> compounds (Schippers, Brandwijk & Gorter, 1973) and for <sup>vi</sup>A<sup>vi</sup>BX<sub>3</sub> compounds (van Loon, 1974).

The computations were carried out partly at the computing division of the Reactor Centre in Petten, partly at the computing institute of Leiden University. The authors are indebted to Mr J. de Jong and Mr D. W. Zandbergen for the neutron diffraction experiments and the calculations, performed at the Reactor Centre, and to Dr E. C. Kruissink for the d.t.a. measurements. The investigations were supported in part by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

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