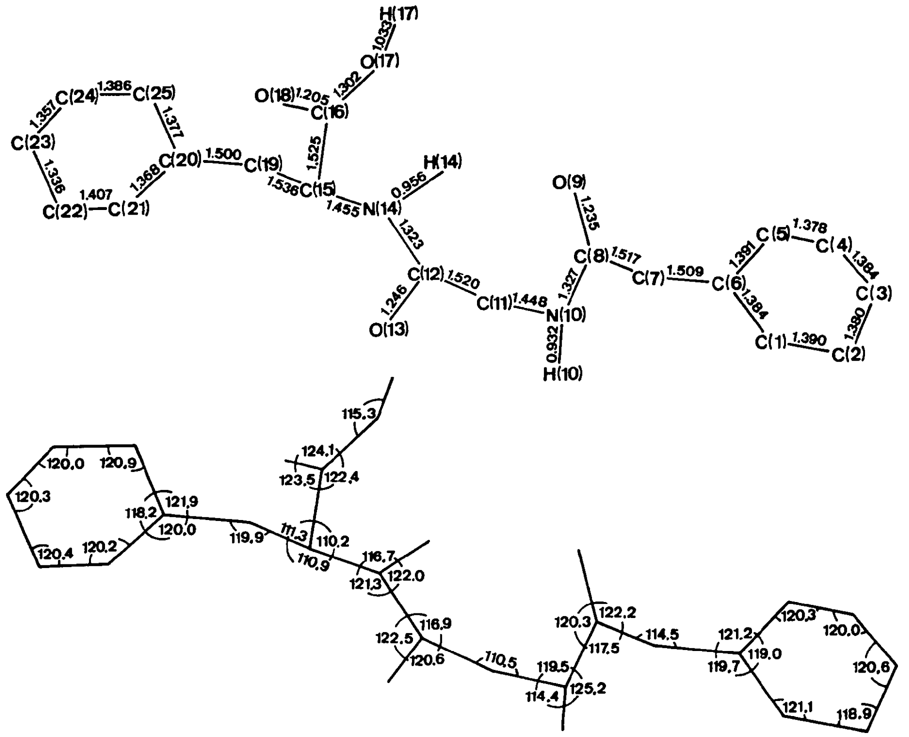

Fig. 3. Numérotation des atomes, distances intramoléculaires (Å) et angles de valence (°), σ moyens respectivement de 0,006 Å et de 0,4° pour les atomes C, N et O et de 0,04 Å et 2° pour les atomes H participant aux liaisons hydrogène.

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Crystal Structure of Cs_3MnCl_5

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Abstract. Cs_3MnCl_5: tetragonal, $I4/mcm$, $a=b=9{\cdot}21$ (2), $c=14{\cdot}97$ (5) Å, $Z=4$, $D_o=3{\cdot}35$, $D_x=3{\cdot}30$ g cm^{-3}. The structure is isomorphous with that of Cs_3CoCl_5.

Introduction. The material was prepared by heating stoichiometric amounts of CsCl and $MnCl_2$ in an evacuated sealed silica tube until molten and then cooling to room temperature at about 5°/h. Greenish-yellow crystals were formed which were of suitable size for Weissenberg photography. The crystals were very hygroscopic and had to be mounted in sealed Lindemann glass tubes for X-ray examination.

A prismatic crystal ($0{\cdot}16\times0{\cdot}14\times0{\cdot}65$ mm) was selected for intensity measurements. Data were collected from equi-inclination Weissenberg photographs taken about the elongated axis of the crystal with Mo $K\alpha$ radiation ($\mu=106{\cdot}7$ cm^{-1}). The intensities of 324 reflexions on layer lines 0–4 were measured with a

Joyce–Loebl flying-spot microdensitometer; 166 reflexions were unobserved. The data were corrected with the Lorentz–polarization factor and for absorption using the factors given by Bond (1959) for a cylindrical specimen.

The cell dimensions were determined from α_1–α_2 doublet separations on zero-layer Weissenberg photographs taken with Cu $K\alpha$ radiation [$\lambda(\alpha_1) = 1{\cdot}54051$ Å] and it was then evident that the crystal axis was along the body diagonal of a reduced orthorhombic cell whose a and b parameters were equal to within one standard deviation. The indices of the reflexions were transformed to correspond to the new cell; the systematic absences were then $h+k+l=2n+1$ for all reflexions and $l=2n+1$ for $0kl$, and for tetragonal symmetry 221 of the observed reflexions were found to be independent.

Initially the structure was assumed to be isomorphous with that of Cs_3CoCl_5, $I4/mcm$ (Powell & Wells, 1935), but a block-diagonal least-squares refinement reduced the residual, $R = \sum||F_o| - |F_c||/\sum|F_o|$, to only 33%. Attempts at refinement in other possible tetragonal space groups did not lead to any greater success. Refinement was then tried in the orthorhombic space group *Ibam* and R now reduced to 11·0%. The final parameters, however, all lay within one standard deviation of those which would correspond to the tetragonal space group $I4/mcm$. The failure to refine the structure in the tetragonal system was later found to be due to a program error. When this was corrected, refinement in the space group $I4/mcm$ was possible and several cycles led to a final reridual of 9·6% with final shifts in all the parameters of less than $\frac{1}{15}$ of a standard deviation. Atomic scattering factors for Cs^+, Mn^{2+} and Cl^- used in the structure factor calculations were taken from *International Tables for X-ray Crystallography* (1962). The final atomic parameters are given in Table 1 and selected bond lengths are listed in Table 2.*

Table 1. *Final atomic parameters* (*origin at* $4/m$)

	Equipoint	x	y	z	B(Å^2)
Cs(1)	$4a$	0	0	$\frac{1}{4}$	2·62 (27)
Cs(2)	$8h$	0·1643 (10)	0·6643 (10)	0	1·77 (14)
Mn	$4b$	0	$\frac{1}{2}$	$\frac{1}{4}$	1·54 (52)
Cl(1)	$4c$	0	0	0	1·74 (55)
Cl(2)	$16l$	0·1430 (30)	0·6430 (30)	0·6546 (27)	2·52 (55)

Table 2. *Selected bond lengths* (Å)

		Multiplicity
Mn–Cl(2) tetrahedron		
Mn–Cl(2^{i})	2·347 (40)	6
Cs(1)–Cl distances		
Cs–Cl(1)	3·742 (12)	2
Cs–Cl(2^{ii})	3·819 (30)	8
Cs(2)–Cl distances		
Cs–Cl(1)	3·442 (11)	2
Cs–Cl(2^{i})	3·661 (34)	4
Cs–Cl(2^{ii})	3·414 (41)	2

Location of atoms			
Mn	0	$\frac{1}{2}$	$\frac{1}{4}$
Cs(1)	0	0	$\frac{1}{4}$
Cs (2)	x	$\frac{1}{2}-x$	$\frac{1}{2}$
Cl(1)	0	0	$\frac{1}{2}$
Cl(2^{i})	x	$\frac{1}{2}+x$	$1-z$
Cl(2^{ii})	$\frac{1}{2}-x$	x	$1-z$

Discussion. The analysis forms part of an investigation of the crystal structures of the compounds in the system $CsCl/MnCl_2$. On the evidence of powder data, Andersen (1956) proposed a tetragonal cell for Cs_3MnCl_5 with $a=9{\cdot}21$, $c=14{\cdot}90$ Å and assumed the structure to be isomorphous with that proposed by Powell & Wells for Cs_3CoCl_5. The present work has confirmed this.

In the structure the Cl(2) ions coordinate the Mn ions to form individual $Mn–Cl_4$ tetrahedra and the structure can be considered as being composed of Cs^+, $[Mn–Cl(2)_4]^{2-}$ and $Cl(1)^-$ ions. The $Mn–Cl_4$ tetrahedron is somewhat distorted, the Cl–Mn–Cl angles ranging from 105 to 112°. The average Cs(1)–Cl distance (3·80 Å) is a little greater than and the average Cs(2)–Cl distance (3·55 Å) is a little smaller than the average length of the Cs–Cl bond (3·72 Å) found in the structure of $CsMn_4Cl_9$ (Goodyear & Kennedy, 1973).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31427 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.