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*Acta Cryst.* (1973). **B29**, 1330

## The Crystal Structure of $CsMnCl_3$ and a Summary of the Structures of $RMX_3$ Compounds\*

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(Received 26 July 1972; accepted 12 February 1973)

Cesium trichloromanganate,  $CsMnCl_3$ , has been found by single-crystal X-ray diffraction studies to possess rhombohedral symmetry and to crystallize in the space group  $R\bar{3}m$ . At 23°C, the hexagonal unit-cell lattice constants are  $a = 7.290$  (5) and  $c = 27.317$  (4) Å with  $V = 1257.2$  Å<sup>3</sup>, M.W.(calc) 293.63,  $Z = 9$ ,  $D_M = 3.35$  (4),  $D_X = 3.49$  g cm<sup>-3</sup>. Full-matrix least-squares refinement of 481 observed three-dimensional diffractometer data (Mo  $K\alpha$ ) led to a final weighted residual of 0.094 on  $F$ . The compound consists of facial-bridged  $[MnCl_6]^{4-}$  octahedral trimers with each trimer linked to other trimers by sharing corners in such a way that the trimers spiral around the trigonal axis. The crystallographic site symmetries of the manganese atoms are  $D_{3d}$  for the central manganese atoms of a trimer and  $C_{3v}$  for the two terminal manganese atoms of a trimer. There are three crystallographically unique manganese-chlorine distances, 2.514 (3), 2.545 (9), and 2.557 (14) Å. The latter two facial-bridged distances compare favorably with the Mn–Cl distance 2.560 Å in  $(CH_3)_4NMnCl_3$ . The synthesis, lattice parameters, and space groups of the previously unreported compounds  $CsVI_3$ ,  $CsCrI_3$ ,  $CsNiI_3$  and  $CsMgI_3$  are described. Using the available structural data, the crystallographic properties of  $RMX_3$  (R = univalent cation, M = divalent transition metal cation, X = halogen anion) compounds can be correlated with the properties of the individual ions, R, M, and X. The relation of these properties to the structural types of  $RMX_3$  is briefly discussed.

### Introduction

Compounds with the general formula  $CsMX_3$  form a class of structurally related compounds whose crystal geometry can be described as a stacking of ordered, close-packed  $CsX_3$  layers, with the M cations filling octahedral sites between these layers. There are two possible types of stacking of  $CsX_3$  layers, cubic and hexagonal, both of which are observed (Longo & Kafales, 1969). It is also possible to have various combinations of cubic and hexagonal packing within the same crystal lattice. Complete or partial structural data published for  $CsMgCl_3$  (McPherson, Kistenmacher & Stucky, 1970),  $CsVCl_3$  (Seifert & Ehrlich, 1959),  $CsCrCl_3$  (McPherson & Stucky, 1972),  $CsFeCl_3$  (Seifert & Klatyck, 1966),  $CsCoCl_3$  (Soling, 1968),  $CsNiCl_3$  (Tishchenko, 1955), and  $CsCuCl_3$  (Schlueter, Jacobson & Rundle, 1966) show that all the complexes have the

same hexagonal close-packed structure except those of Cr(II) and Cu(II). The latter two compounds are subject to the Jahn–Teller effect and the Cu(II) complex in particular shows differences of 0.2 to 0.4 Å in metal–halogen bond distances.

In this paper, we report the results of a complete single-crystal structural investigation of  $CsMnCl_3$ . Initial preliminary results obtained from powder X-ray studies by Kestigian, Croft & Leipzig (1967) demonstrated that  $CsMnCl_3$  has hexagonal symmetry with  $a = b = 7.288$ ,  $c = 27.44$  Å, and  $Z = 9$ . This is an unusual number of molecules per unit cell for a  $CsMX_3$  system and a detailed study of the structure of this compound seemed important in order to understand the structural and magnetic properties of  $RMX_3$  complexes. It is also the purpose of this paper to show that through the correlation of the available data for known  $RMX_3$  structures, it is possible to make some generalizations concerning the factors which determine the type of structure that is obtained. Interesting magnetic and spectroscopic properties of these one-dimensional

\* This work was supported by the Advanced Research Projects Agency under Contract HC-15-67 CO221.

and highly anisotropic systems have been the subject of a number of recent studies, and it is hoped that the structural information presented here will contribute to further understanding of these data (McPherson, Kistenmacher & Stucky, 1970; Birgenau, Dingle, Hutchings, Shirane & Holt, 1970, 1971; Rinneberg & Hartman, 1970; Inoue, Kishita & Kubo, 1967).

### Crystal preparation

The dihydrated salt of  $\text{CsMnCl}_3$  was made by evaporating an aqueous solution containing equimolar amounts of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{CsCl}$  over a steam bath. The product was filtered and washed with cold concentrated  $\text{HCl}$ , and dried at  $120^\circ\text{C}$ . By heating it to  $600^\circ\text{C}$  in a tube furnace under a flow of dry  $\text{HCl}$ , it was completely dehydrated. It is slightly hygroscopic and red in color.

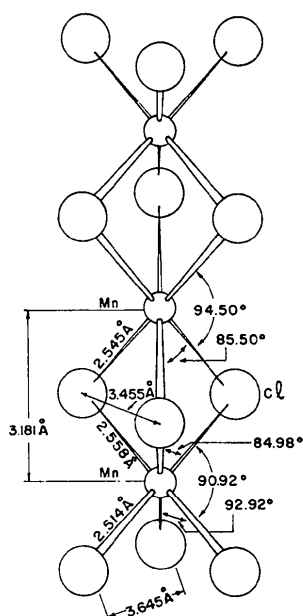


Fig. 1. A perspective view of a  $[\text{Mn}_3\text{Cl}_{12}]$  trimer unit in  $\text{CsMnCl}_3$ .

### Analysis

Calculated for  $\text{CsMnCl}_3$ : 18.67% Mn; 36.15% Cl.  
Found: 18.63% Mn; 36.41% Cl.

Crystals for the X-ray studies were grown from the melt by a vertical Bridgman method. Samples sealed in 2 mm quartz tubes were lowered through a tube furnace at an approximate rate of 9 cm/24 h.

$\text{CsMgI}_3$ ,  $\text{CsCrI}_3$  and  $\text{CsVI}_3$  were prepared by melting equimolar mixtures of cesium iodide with the transition metal diiodide in sealed and evacuated quartz tubes. The single crystals were obtained by passing the quartz tubes through a Bridgman furnace in the same manner as for  $\text{CsMnCl}_3$ .  $\text{CsNiI}_3$  was prepared by dissolving  $\text{Ni}_2\text{CO}_3$  in concentrated  $\text{HI}$  acid. A stoichiometric amount of  $\text{CsI}$  was then added and the resulting solution was slowly evaporated under a stream of nitrogen at  $80^\circ\text{C}$ . The  $\text{CsNiI}_3$  crystallized from solution as brown-black rods. All the iodides are quite hygroscopic. The crystallographic specimens were sealed in 0.3 mm glass capillary tubes. Precession photographs were taken of the zero and first levels of the  $h0l$  and  $hhl$  zones. Systematic extinctions were determined to be  $hhl$ ,  $l \neq 2n$  with Laue symmetry  $6/mmm$  symmetry. These data strongly suggest that these three complexes have the  $\text{CsNiCl}_3$  structure with the lattice parameters indicated below.

	$a$ (Å)	$c$ (Å)
$\text{CsMgI}_3$	8.20 (2)	7.01 (2)
$\text{CsCrI}_3$	8.12 (2)	6.85 (2)
$\text{CsVI}_3$	8.21 (2)	6.81 (2)
$\text{CsNiI}_3$	8.00 (2)	6.76 (2)

### Crystal data

$\text{CsMnCl}_3$ :  
Red trigonal prisms,  $a = 7.290$  (5),\*  $c = 27.317$  (4) Å  
 $t = 23$  (2)°C,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å  
 $Z = 9$

\* Numbers in parentheses here and elsewhere are estimated standard errors in the last significant figure.

Table 1. Positional and temperature parameters ( $\times 10^4$ ) for  $\text{CsMnCl}_3$

Restrictions on the thermal parameters:

- (i) for Cs(1), Cs(2), Mn(1), Mn(2) and Cl(1):  $\beta_{11} = \beta_{22} = 2\beta_{12}$ ,  $\beta_{13} = \beta_{23} = 0$   
(ii) for Cl(2):  $\beta_{11} = \beta_{22} = 2\beta_{12}$ ,  $\beta_{23} = \beta_{13}$

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cs(1)	0	0	0	115 (3)	115	7 (1)	57	0	0
Cs(2)	0	0	0.2185 (1)	114 (3)	114	7 (2)	57	0	0
Mn(1)	0	0	0.5	83 (2)	83	3 (1)	41	0	0
Mn(2)	0	0	0.3836 (2)	75 (4)	75	4 (1)	37	0	0
Cl(1)	0.5	0	0	159 (4)	159	9 (2)	79	0	0
Cl(2)	0.1576 (11)	-0.1576	0.5578 (1)	102 (3)	102	5 (1)	51	2 (1)	-2
	0.150 (5)*		0.560 (5)*						

\* Parameters from Melamud, Makovsky & Shaked (1971).

$D_x = 3.49$ ,  $D_{meas} = 3.35$  (4) g cm<sup>-3</sup>  
by pycnometric technique.

Systematic absences:  $hkl$ :  $-h+k+l \neq 3n$   
Possible space groups  $R32$ ,  $R3m$ , and  $R\bar{3}m$

Probable space group  $R\bar{3}m$  because of successful refinement and intensity statistics. Linear absorption coefficient,  $\mu = 101.79$  cm<sup>-1</sup> (Mo  $K\alpha$ ).

**Intensity measurement**

A crystal approximately 0.30 mm in length and 0.20 mm in diameter was mounted on a four-circle computer-controlled diffractometer so that [0001] was offset by 1° from the  $\phi$  rotation axis. One set of intensity data was collected on a Picker-automated four-circle diffractometer, using Mo  $K\alpha$  radiation from a pyrolytic graphite monochromator (002), a scintillation counter, and a  $\theta-2\theta$  scanning technique with a scan rate of 1° (in  $2\theta$ ) per min; the background was collected for 10 sec at each end of the scanned range. A take-off angle of 1.6° was used. The total number of observations obtained was 2155. Of these, 689 reflections were found to be unique, and 481 were judged to be observed by the criteria  $I_{obsd} > 3\sigma_c$  where  $\sigma_c = [P_c + 0.25(t_c/t_b)^2 - (B_1 + B_2)]^{1/2}$ ,  $t_c$  is the total integrated counts,  $t_c/t_b$  is the ratio of the time spent counting the peak intensities to the time spent counting the background intensities, and  $B_1$  and  $B_2$  are background counts. Only these 481 reflections were used in the subsequent analysis. Two standard reflections were measured every 100 reflections in order to check the stability of the crystal. An equal and linear decrease in intensity with exposure time was observed for the standard reflections with a net decrease of 20% in intensity by the end of the data collection. We now believe that this decomposition was due to the slow hydration of the complex. The structure amplitudes were derived by application of Lorentz and polarization corrections, absorption corrections, and a linear decomposition correction.

**Solution and refinement of the structure**

All computational work was done on the Xerox Sigma V computer operated by the Materials Research Laboratory at the University of Illinois at Urbana-Champaign. The form factors for Cs<sup>+</sup>, Mn<sup>2+</sup> and Cl<sup>-</sup> were taken from the compilations of Hansen & Pohler (1966). Real and imaginary anomalous dispersion corrections for all three atoms were taken from the compilation of Cromer (1965). The function minimized in the least-squares procedure was  $\sum w(|F_o| - |F_c|)^2$  with  $w = 1/\sigma^2(F)$  and

$$\sigma(F) = \frac{1}{2F} [\sigma_c^2 + (0.05F^2)^{1/2}]$$

BaRuO<sub>3</sub> (Donohue, Katz & Ward, 1965) is reported to crystallize in the space group  $R\bar{3}m$  with a nine-layer perovskite-related structure. It seemed reasonable that CsMnCl<sub>3</sub> might be isostructural with BaRuO<sub>3</sub>, with

cesium, manganese, and chlorine atoms taking the position of barium, ruthenium and oxygen atoms respectively. The original atomic positional parameters were accordingly chosen as Cs(1) (0, 0, 0); Cs(2) (0, 0, z; z = 0.21801); Mn(1) (0, 0, 1/2); Mn(2) (0, 0, z; z = 0.558). With these six atoms, the  $R_1$  ( $R_1 = \sum ||F_o| - |F_c|| / \sum F_o$ ) value after refining the scale factor and positional pa-

Table 2. Observed and calculated structure-factor amplitudes for CsMnCl<sub>3</sub>

h	k	l	Obs	Calc	h	k	l	Obs	Calc	h	k	l	Obs	Calc	h	k	l	Obs	Calc
0	0	0	1000	1000															
0	0	1	100	100															
0	0	2	100	100															
0	0	3	100	100															
0	0	4	100	100															
0	0	5	100	100															
0	0	6	100	100															
0	0	7	100	100															
0	0	8	100	100															
0	0	9	100	100															
0	0	10	100	100															
0	0	11	100	100															
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0	0	15	100	100															
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0	0	96	100	100															
0	0	97	100	100															
0	0	98	100	100															
0	0	99	100	100															
0	0	100	100	100															

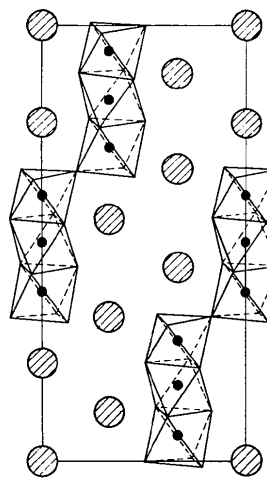


Fig. 2. A perspective view of the CsMnCl<sub>3</sub> structure in the unit cell.

rameters converged to 0.278. Refinement with isotropic temperature parameters, including the anomalous dispersion correction, gave an  $R_1$  factor of 0.195. Three more cycles of isotropic refinement gave  $R_1=0.129$ . Anisotropic thermal parameters were then included for all atoms, and four more subsequent least-squares refinements on the one scale factor, positional and thermal parameters gave as final discrepancy indices:

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.089$$

$$R_2 = \left[ \frac{\sum \omega (F_o - F_c)^2}{\sum \omega F_o^2} \right]^{1/2} = 0.094$$

$$S = \left[ \frac{\sum \omega |F_o| - |F_c|}{\sum \omega |F_o| - |F_c|} \right]^{1/2} = 2.56$$

$$N_o = 481$$

$$N_v = 18.$$

On a final difference Fourier map no peak larger than  $0.7 \text{ e } \text{Å}^{-3}$  appeared. The rather poor goodness-of-fit is attributed to systematic errors in the absorption correction and the correction for crystal decomposition.

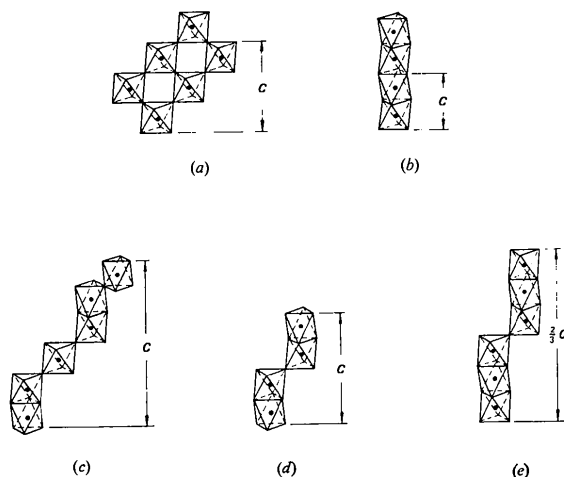


Fig. 3. Perspective projections of octahedra network in a unit cell of  $\text{RMX}_3$  complexes. (a) P. (b) 2L. (c) 6L. (d) 4L. (e) 9L.

### Results and discussion of the structure of $\text{CsMnCl}_3$

The positional and thermal parameters derived from the last cycle of least-squares refinement are presented in Table 1, along with their standard deviations. The observed and calculated structure factors for each reflection are given in Table 2. A summary of bond distances and angles and their errors appears in Table 3. Some selected non-bonded distances and angles are also given in Table 3.

The  $\text{CsMnCl}_3$  structure consists of  $[\text{Mn}_3\text{Cl}_{12}]$  trimers with face-shared octahedral stacking along the trigonal axis (Fig. 1). Each trimer is linked to six other trimers by sharing a terminal chlorine atom. Within a trimer, there is a crystallographic mirror plane which passes through the center manganese atom and which is perpendicular to the axis through the three manganese atoms. The manganese–manganese distance of  $3.181 \text{ Å}$  is the longest known metal–metal distance in  $\text{CsMCl}_3$  ( $\text{M} = \text{first row transition metal}$ ) compounds, and was predicted earlier (Stucky, 1968). There are three crystallographically different manganese atom to chlorine atom distances,  $2.514$  (3),  $2.545$  (9), and  $2.557$  (14) Å as shown in Table 3 and Fig. 1. The facial-bridged chlorine manganese distances are in excellent agreement with that found for the facial-bridged  $\text{Mn–Cl}$  distance of  $2.560 \text{ Å}$  in  $(\text{CH}_3)_4\text{NMnCl}_3$  (Morosin & Graebner, 1967). The center manganese atom in a trimer has  $D_{3d}$  crystallographic symmetry, while the two terminal manganese atoms have  $C_{3v}$  symmetry. The distance between two chlorine atoms bonded to the center manganese atom is  $3.455 \text{ Å}$ , but the chlorine–chlorine distance of the terminal chlorines is a little longer,  $3.645 \text{ Å}$ .

The cesium ions are fitted into holes between the  $[\text{Mn}_3\text{Cl}_{12}]$  trimers to form a two-dimensional close-packed structure with the chlorine atoms. The distances from cesium atoms to the near neighbor atoms are given in Table 3. Fig. 2 shows a perspective view of the  $\text{CsMnCl}_3$  structure in the unit cell.

Table 3. Selected distances and angles for  $\text{CsMnCl}_3$

Bond distances (Å)		Bond angles (°)	
Mn(1)–Cl(2)	2.545 (9)	Cl(2)–Mn(1)–Cl(2')	85.50 (33)
Mn(2)–Cl(2)	2.557 (14)	Cl(2)–Mn(1)–Cl(2'')	94.50 (33)
Mn(2)–Cl(1)	2.514 (3)	Cl(2)–Mn(2)–Cl(1)	90.92 (25)
		Cl(1)–Mn(2)–Cl(1)	92.92 (5)
		Cl(2)–Mn(2)–Cl(2')	84.98 (34)
Near-neighbor distances within a trimer (Å)		Near-neighbor distances between trimers (Å)	
Mn(1)–Mn(2)	3.181 (6)	Mn(2)–Mn(2')	5.028 (5)
Cl(1)–Cl(1')	3.645 (0)		
Cl(2)–Cl(2')	3.455 (19)	Near-neighbor angle between trimers (°)	
Cl(2)–Cl(2'')	3.738 (11)	Mn(2)–Cl(1)–Mn(2')	179.88 (7)
Cl(2)–Cl(1)	3.615 (7)		
Near-neighbor distances between cesium atoms and the atoms in a trimer (Å)			
Cs(1)–Mn(2)	4.428 (2)	C(2)–Mn(2)	4.675 (3)
Cs(2)–Mn(2')	4.563 (3)	Cs(2)–Mn(2)	4.513 (7)
Cs(2)–Mn(1)	4.441 (1)	Cs(2')–Mn(1)	4.362 (1)
Cs(1)–Cl(1)	3.645 (0)	Cs(2)–Cl(1)	3.778 (3)
Cs(2)–Cl(1)	4.008 (3)		

During the final stage of our refinement, a paper was published (Melamud, Makovsky & Shaked, 1971) on the structure of CsMnCl<sub>3</sub> as obtained by neutron diffraction techniques on powder samples. Their results, based on 11 experimental lines including zero-intensity lines at room temperature, gave a final discrepancy value  $R_1=0.067$  and positional parameters essentially the same as ours (Table 1).

### Summary of structures of the type RMX<sub>3</sub>

As mentioned above, there are two types of stacking of CsX<sub>3</sub> layers in CsMX<sub>3</sub> compounds, cubic and hexagonal. If there is cubic stacking, the octahedra share corners in three dimensions to form the cubic perovskite structure. Fig. 3(a) shows a projection within a hexagonal cell. If there is hexagonal stacking, the octahedra share faces in infinite linear chains parallel to the *c* axis. The latter is referred to as the 2*L* structure (Longo & Kafales, 1969), since each unit cell contains two CsX<sub>3</sub> layers and is shown in Fig. 3(b). Although a large number of ordered structures are theoretically possible, each having a different ratio of cubic to hexagonal stackings, only three of them will be mentioned here, a two-to-one cubic-to-hexagonal stacking shown in Fig. 3(c), a one-to-one stacking shown in Fig. 3(d), and the one-to-two stacking in Fig. 3(e). From the number of layers in each model, these are designated as 6*L*, 4*L* and 9*L* stackings respectively.

Table 4. Summary of structures of CsMX<sub>3</sub> compounds

	F (1.36)	Cl (1.81)	Br (1.95)	I (2.16)
Mg(0.65) <sup>a</sup>	—	2L <sup>b</sup>	2L <sup>c</sup>	2L <sup>d</sup>
V(0.87)	—	2L <sup>e</sup>	2L <sup>f</sup>	2L <sup>d</sup>
Cr(0.84)	—	2L <sup>g</sup>	2L <sup>h</sup>	2L <sup>d</sup>
Mn(0.80)	6L <sup>i</sup>	9L <sup>d</sup>	2L <sup>j</sup>	—
Fe(0.76)	6L <sup>k</sup>	2L <sup>l</sup>	2L <sup>j</sup>	—
Co(0.78)	9L <sup>m</sup>	2L <sup>n</sup>	—	—
Ni(0.78)	2L <sup>o</sup>	2L <sup>p</sup>	2L <sup>q</sup>	2L <sup>d</sup>
Cu(0.69)	—	2L <sup>r</sup>	4L <sup>s</sup>	—
Cd(0.97)	—	6L <sup>t</sup>	—	—

- The numbers in parentheses are the ionic radius of each atom.
- McPherson, Kistenmacher & Stucky (1970).
- McPherson & Stucky (1972).
- This work.
- Seifert & Ehrlich (1959).
- Unpublished results.
- McPherson, Kistenmacher, Folkers & Stucky (1972).
- Li & Stucky (1973b).
- Zalkin, Lee & Templeton (1962).
- Goodyear & Kennedy (1972).
- Kestigian, Leipzig, Croft & Guidoboni (1966).
- Seifert & Klatyk (1966).
- Longo & Kafales (1969).
- Seifert (1960).
- Babel (1965).
- Tischenko (1955).
- Stucky, D'Agostino & McPherson (1966).
- Hexagonal, with  $a=12.56$ ,  $c=11.56$  Å (see Babel, 1965).
- Li & Stucky (1973b).
- Siegel & Gebert (1964).

Table 5. Summaries of structures of RMCl<sub>3</sub>

	(Me) N (2.60)	Cs (1.69)	Rb (1.48)	K (1.33)
V(0.87) <sup>a</sup>	—	2L <sup>b</sup>	—	2L <sup>b</sup>
Cr(0.84)	—	2L <sup>c</sup>	—	—
Mn(0.80)	2L <sup>d</sup>	9L <sup>e</sup>	6L <sup>f</sup>	tetragonal
Fe(0.76)	—	2L <sup>g</sup>	2L <sup>g</sup>	—
Co(0.78)	—	2L <sup>h</sup>	2L <sup>i</sup>	—
Ni(0.78)	2L <sup>j</sup>	2L <sup>k</sup>	2L <sup>l</sup>	3L <sup>m</sup>
Cu(0.69)	—	2L <sup>n</sup>	—	4L <sup>o</sup>
Cd(0.97)	2L <sup>p</sup>	6L <sup>q</sup>	—	—

- The numbers in parentheses are the ionic radius of each atom or group.
- Seifert & Ehrlich (1959).
- McPherson, Kistenmacher & Stucky (1970).
- Morosin & Graebner (1967).
- This work.
- Seifert & Koknat (1965).
- Kestigian, Leipzig, Croft & Guidoboni (1966).
- Seifert (1960).
- Engberg & Soling (1967).
- Stucky (1968).
- Tishchenko (1955).
- Asmussen & Soling (1956).
- Unpublished observation.
- Schlueter, Jacobson & Rundle (1966).
- Willett, Dwiggin, Kruh & Rundle (1963).
- Morosin (1972).
- Siegel & Gebert (1964).

Pressure dependence studies of CsMF<sub>3</sub> (Longo & Kafales, 1969) show that this series of compounds forms a progression from 2*L* to the 9*L*, 4*L*, 6*L* and *P* structures with increasing pressure. For example, the A.P.F. (atmospheric pressure form), 2*L* CsNiF<sub>3</sub> transforms at 5 kbar to the 9*L* form, and then to the 6*L* form at 47 kbar; the A.P.F., 9*L* CsCoF<sub>3</sub> transforms to the 6*L* form at 22 kbar; the A.P.F., 6*L* CsFeF<sub>3</sub> structure transforms at about 70 kbar to the perovskite structure, while the A.P.F., 6*L* CsMnF<sub>3</sub> requires only 26 kbar for the same transformation. Longo & Kafales (1969) suggested that two dominant factors determine the phase type in this class of compounds, the electrostatic, or Madelung energies and the relative sizes of ions. The cubic form results in an increased M-M separation and reduces the electrostatic repulsion between M cations. Our studies on the structures of the CsMX<sub>3</sub> are summarized in Table 4 along with other data from the literature. Table 5 summarizes the structures of RMCl<sub>3</sub>. From Tables 4 and 5, some general trends of the properties of the RMX<sub>3</sub> compounds are implied.

1. A higher crystal field stabilization energy for M favors hexagonal stacking, e.g. CsMnF<sub>3</sub>, CsFeF<sub>3</sub>, CsCoF<sub>3</sub> and CsNiF<sub>3</sub>. We note that radius ratio effects alone cannot explain the structural data since (a) in the CsMF<sub>3</sub> series the Pauling divalent radii of the transition metals vary only slightly, with the largest variation being between Mn<sup>2+</sup> and Fe<sup>2+</sup> (0.04 Å), which have the same structure; and (b) the divalent radii of V(II), Mn(II) and Ni(II) are 0.87, 0.80 and 0.78 Å, yet CsVCl<sub>3</sub> and CsNiCl<sub>3</sub> are isostructural but different from CsMnCl<sub>3</sub>.

2. The hexagonal stacking is favored when the ionic radius of X is larger, e.g. CsMnF<sub>3</sub>, CsMnCl<sub>3</sub> and CsMnBr<sub>3</sub>.

3. The hexagonal stacking is favored when the ionic radius of R is larger, e.g. Me<sub>4</sub>NMnCl<sub>3</sub>, CsMnCl<sub>3</sub> and RbMnCl<sub>3</sub>; Me<sub>4</sub>NCdCl<sub>3</sub> and CsCdCl<sub>3</sub>.

All CsMI<sub>3</sub> compounds, CsCoBr<sub>3</sub>, and RbVCl<sub>3</sub> can be expected to have 2L structures. No obvious trends are evident for the fluorides. Possible structural forms for CsTiF<sub>3</sub>, CsVF<sub>3</sub> and CsCrF<sub>3</sub> are simple cubic perovskite (or 6L), 6L and 9L, respectively. CsMgF<sub>3</sub> is reported to be nonexistent, but the structure of Cs<sub>4</sub>Mg<sub>3</sub>F<sub>10</sub> [(CsMgF<sub>3</sub>)<sub>3</sub>·CsF<sub>n</sub>] contains perovskite layers of (CsMgF<sub>3</sub>)<sub>3</sub> groups with CsF units between the layers in agreement with (2) above. Nearly all spherical cations, such as tetramethylammonium, with an ionic radius of R larger than the cesium ion, can be expected to give structures with the 2L structure.

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*Acta Cryst.* (1973). **B29**, 1335

## Structure Cristalline de l'Hypovanadate CaV<sub>4</sub>O<sub>9</sub>

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CaV<sub>4</sub>O<sub>9</sub> is tetragonal with  $a = 8,333$  and  $c = 5,008$  Å, space group  $P4/n$ . The structure contains VO<sub>5</sub> square pyramids sharing edges and forming sheets of [V<sub>4</sub>O<sub>9</sub>]<sup>2-</sup> parallel to the  $xOy$  plane. Calcium atoms are inserted between the sheets in Archimedian square antiprisms. The reliability index is  $R = 0.038$ .

Au cours d'études cristallographiques antérieures sur les phases contenant le vanadium au seul degré d'oxydation +IV, quatre hypovanadates, appartenant au système binaire CaO-VO<sub>2</sub>, ont été synthétisés et étu-

diés sur le plan chimique et radiocristallographique: CaVO<sub>3</sub> (Chamberland & Danielson, 1971), CaV<sub>2</sub>O<sub>5</sub> (Deduit, 1961; Bouloux, 1968), CaV<sub>3</sub>O<sub>7</sub> (Deduit, 1961) et CaV<sub>4</sub>O<sub>9</sub>. La structure de CaV<sub>3</sub>O<sub>7</sub> a été précisée