References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Moreau, S., Gaudemer, A., Lablache-Combier, A. & Biguet, J. (1976). *Tetrahedron Lett.* p. 833.

Moreau, S., Moulé, Y. & Bousquet, J. F. (1976). 3rd International IUPAC Sponsored Symposium on Mycotoxins in Foodstuffs, Sept. 16–18.

Overton, K. H. & Roberts, J. S. (1971). *Terpenoids and Steroids*, Special Periodical Reports, No. 1, p. 101. London: The Chemical Society.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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Rubidium Tetrachloromanganate

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Abstract. Rb_2MnCl_4, tetragonal, $I4/mmm$, $a = 5{\cdot}05\,(2)$, $c = 16{\cdot}14\,(5)$ Å, $D_o = 2{\cdot}96$, $D_x = 2{\cdot}97$ g cm^{-3}, $Z = 2$. Mn ions are octahedrally coordinated by Cl ions. The Cl ions at the equatorial vertices are shared with neighbouring octahedra so that each octahedron is linked to four others to form layers perpendicular to [001], the c dimension accommodating two such layers. The Cl ions at the unshared vertices are closer to the Rb ions than the others. The structure is strictly isomorphous with that of K_2NiF_4.

Introduction. On the basis of powder data, Seifert & Koknat (1965) assigned a body-centred tetragonal cell to the compound Rb_2MnCl_4. The cell parameters [$a = 5{\cdot}051\,(5)$, $c = 16{\cdot}18\,(1)$ Å] and observed density (2·96 g cm^{-3}) indicated two formula units per cell, from this evidence they concluded that the structure might be isomorphous with that found for K_2NiF_4 by Balz & Plieth (1955).

The material examined in this work was prepared by heating stoichiometric amounts of RbCl and $MnCl_2$ in an evacuated silica tube until molten and then cooling the sample at about 5°C h^{-1}. Orange crystals were formed which, although of suitable size for Weissenberg study, were quite irregular in shape. The crystal selected for X-ray examination had to be mounted in a sealed Lindemann-glass tube because of the hygroscopic nature of the material.

The dimensions of the unit cell were determined from α_1–α_2 doublet separations on a zero-layer Weissenberg photograph taken with Cu $K\alpha$ radiation ($\lambda_{\alpha_1} = 1{\cdot}54051$ Å). The unit-cell dimensions and observed density agreed, within experimental error, with the data given by Seifert & Koknat.

Intensity data were collected from equi-inclination photographs taken about the a axis with Mo $K\alpha$ radiation. The intensities of 128 reflexions were measured visually on layer lines 0–4 from accurately timed film exposures. The systematically-absent reflexions were all of the type $h + k + l = 2n + 1$, consistent with the space group ($I4/mmm$) of the K_2NiF_4 structure. These data were corrected for the Lorentz–polarization factor and an approximate correction was made for absorption by assuming the crystal to be cylindrical in shape with a μr value of 1·4.

Both the axial ratio and the number of formula units per cell suggest isomorphism between Rb_2MnCl_4 and K_2NiF_4. If this is so, the a parameter should be twice the Mn–Cl bond length in a $MnCl_6$ octahedron. Goodyear, Steigmann & Ali (1977) found the average value of the latter to be 2·51 Å in the $RbMnCl_3$ structure and this is indeed very nearly equal to $a/2$. Initially, the positional parameters of the K_2NiF_4 structure were assumed and an individual temperature factor of 2·0 Å^2 was assigned to each atom. In the first few cycles of least-squares refinement all the observed structure factors were treated as being symmetrically independent and, because of the uncertain absorption correction, the observed data were scaled to the calculated values for each layer line separately. After several cycles the residual, $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, reduced to 11·8%. The observed structure factors of symmetrically-equivalent reflexions were then averaged giving 91 independent values for the final cycles of refinement, after which R had decreased to 10·1%. At this stage the shifts in the atomic parameters were all less than 1/30 of a standard deviation. The calculated structure factors of the 42 unobserved reflexions were

Table 1. *Final atomic parameters* (*origin at centre 4/mmm*)

	Equipoint	x	y	z	B (Å^2)
Mn	2(*a*)	0	0	0	0·77 (51)
Rb	4(*e*)	0	0	0·3551 (11)	1·57 (23)
Cl(1)	4(*e*)	0	0	0·1546 (28)	2·25 (80)
Cl(2)	4(*c*)	0	$\frac{1}{2}$	0	1·55 (57)

Table 2. *Selected bond lengths* (Å)

		Multiplicity	Location of atoms			
Mn–Cl octahedron						
MnCl(1^{i})	2·50 (5)	2	Mn	0	0	0
Mn–Cl(2^{i})	2·53 (1)	4	Rb	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}-z$
Cl(1^{i})–Cl(2^{i})	3·55 (3)	8	Cl(1^{i})	0	0	z
Cl(2^{i})–Cl(2^{ii})	3·57 (1)	4	Cl(1^{ii})	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}-z$
			Cl(2^{i})	0	$\frac{1}{2}$	0
Rb–Cl distances			Cl(2^{ii})	$\frac{1}{2}$	0	0
Rb–Cl(1^{i})	3·57 (2)	4				
Rb–Cl(1^{ii})	3·24 (5)	1				
Rb–Cl(2^{i})	3·44 (2)	4				

all less than the minimum observable value. For the structure factor calculations the atomic scattering factors for Rb^+, Mn^{2+} and Cl^- were taken from *International Tables for X-ray Crystallography* (1962).*

The final atomic parameters and some selected bond lengths are listed in Tables 1 and 2 respectively.

Discussion. This work forms part of an investigation of the structures of compounds in the system $RbCl/MnCl_2$ and has shown that Rb_2MnCl_4 is strictly isomorphous with K_2NiF_4. The relation of the latter structure to that of perovskite has previously been described by Wells (1962).

In Rb_2MnCl_4, the Mn ions are surrounded octahedrally by Cl ions. Each Mn–Cl octahedron shares its four equatorial vertices [Cl(2) ions] with neighbouring octahedra to form layers of linked octahedra, of composition $MnCl_4$, perpendicular to [001]. The *c* dimension accommodates two such layers, alternate layers being displaced a distance $a/\sqrt{2}$ in the [110] direction. The Rb ions lie approximately in the same *z* planes as the unshared vertices [Cl(1) ions] of the Mn–Cl octahedra such that each Rb ion is coordinated by five Cl(1) and four Cl(2) ions.

Because of the mutual repulsion of the Mn^{2+} ions in a layer of linked octahedra, one might expect the length of the Mn–Cl(2) bond to be somewhat greater than that of the Mn–Cl(1) bond, but the observed difference is not significant when considered in relation to the estimated standard deviations. Each Cl–Mn–Cl angle is exactly 90° and the Mn–Cl octahedron is perfectly regular within the limits of the accuracy of the data. This high degree of order in the octahedral layers probably explains the relatively low temperature factors found for Mn and Cl(2).

One Rb–Cl distance (3·24 Å) is much shorter than the others because of the very unsymmetrical nature of the Cl coordination group around the Rb ion. In fact the average Rb–Cl distance (3·48 Å) is significantly shorter than the corresponding distance (3·60 Å) found in the $RbMnCl_3$ structure. On the other hand the average Mn–Cl and Cl–Cl bond lengths in the two structures agree to within 0·01 Å.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32708 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

References

BALZ, D. & PLIETH, K. (1955). *Z. Elektrochem.* **59**, 545–551.

GOODYEAR, J., STEIGMANN, G. A. & ALI, E. M. (1977). *Acta Cryst.* B**33**, 256–258.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

SEIFERT, H. J. & KOKNAT, F. W. (1965). *Z. anorg. allgem. Chem.* **341**, 269–280.

WELLS, A. F. (1962). *Structural Inorganic Chemistry*, 3rd ed. Oxford: Clarendon Press.