

M.p. 116–122°, $[\alpha]_D^{25} -11 \pm 1^\circ$ (c 0.59, ethanol). (+)-Norrangiformic acid obtained from rangiformic acid by hydrolysis had m.p. 114–122° (lit.³ m.p. 118°, $[\alpha]_D^{25} + 12.9$). The IR-spectra of the two samples were superimposable. Surprisingly, the melting point of the natural (+)-norrangiformic acid was not raised on mixing with the synthetic (–) sample (compare Ref. 2). It is possible that an increase is difficult to observe due to the unusually large melting range of the acids, which is presumably caused by anhydride formation. (Found: C 64.8; H 9.6. Calc. for $C_{20}H_{36}O_6$: C 64.5; H 9.7).

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1. Walborsky, H. M., Barash, L. and Davis, T. L. *Tetrahedron* **19** (1963) 2333.
2. Åkermark, B. *Arkiv Kemi* **27** (1967) 10.
3. Asahina, Y. and Sasaki, T. *Bull. Chem. Soc. Japan* **17** (1942) 495; Asahina, Y. and Shibata, S. *Chemistry of Lichen Compounds*, Japan Soc. for the Promotion of Science, Ueno, Tokyo 1954, p. 32.

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Thortveitite-Type Structure of $Mn_2V_2O_7$

EBBA DORM and BENGT-OLOV MARINDER

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

Several diphosphates and other $A_2B_2O_7$ compounds with thortveitite structure have been reported during recent years.¹ The main structural problem as regards the thortveitite, $Sc_2Si_2O_7$, is whether there exists a linear Si-O-Si bonding. This matter has been discussed by Cruickshank *et al.*² The thortveitite structure has now been found in dimanganesedivanadate $Mn_2V_2O_7$.

This compound was first reported by Brisi³ among other vanadates in the system Mn-V-O. The interplanar distances given by Brisi are in accordance with those found by the present authors.

The dimanganesedivanadate was synthesized by two different methods. The products gave identical powder patterns. If a sample was prepared from the oxides and vanadium in the stoichiometric composition of $MnVO_4$ — the preparation of which was the original purpose — and heated at 800°C the loss of weight corresponded exactly to one eighth of the oxygen contents. If, instead, oxides in the stoichiometric composition of $Mn_2V_2O_7$ were mixed and heated there was no loss of weight.

The cell dimensions calculated from Guinier powder photographs were refined by a least squares method program written by Werner.⁴ Strictly monochromatized $CuK\alpha_1$ radiation was used. The dimensions are

$$\begin{aligned} a &= 6.710 \pm 0.002 \text{ \AA} \\ b &= 8.726 \pm 0.002 \text{ \AA} \\ c &= 4.970 \pm 0.001 \text{ \AA} \\ \beta &= 103.57 \pm 0.01^\circ \end{aligned}$$

The unit cell contains 2 formula units (observed and calculated density values of 3.79 g/cm³ and 3.80 g/cm³, respectively). The crystals are black and inclined towards twinning.

Single crystal data were collected with a Weissenberg camera using $CuK\alpha$ radiation. The multiple film technique was applied. The intensities of the layers $hk0-hk3$ were estimated visually. The scale factors between the layers were calculated by comparing the measured intensities with those obtained from a zero layer photograph recorded around another axis. No absorption correction was made, a fact which has obviously affected the temperature factors which came out slightly negative (see Table 1).

At an early stage of the structure determination it was apparent that the structure was of the thortveitite type and thus there was a choice between the three space groups $C2/m$, $C2$, and Cm .

As an attempt to determine the space group unequivocally, refinements were carried out using the least squares method. In Table 1 the resulting distances within the V_2O_7 group and the V-O-V angle are given. The oxygen shared by the two VO_4 -tetrahedra is assigned index 11.

Table 1.

Space group	<i>C2/m</i>	<i>Cm</i>	<i>C2</i>
V ₁ -O ₁₁ ; V ₂ -O ₁₁	1.76 ± 0.006 Å	1.63 ± 0.08 Å; 1.91 ± 0.08 Å	1.76 ± 0.01 Å
V ₁ -O ₁₂ ; V ₂ -O ₂₂	1.68 ± 0.02 Å	1.60 ± 0.04 Å; 1.79 ± 0.04 Å	1.66 ± 0.05 Å
V ₁ -O ₁₃ ; V ₂ -O ₂₃	1.68 ± 0.02 Å	1.60 ± 0.04 Å; 1.79 ± 0.04 Å	1.72 ± 0.04 Å
V ₁ -O ₁₄ ; V ₂ -O ₂₄	1.71 ± 0.03 Å	1.87 ± 0.07 Å; 1.61 ± 0.07 Å	1.73 ± 0.05 Å
angle V ₁ -O ₁₁ -V ₂	180°	168 ± 6°	171 ± 4°
B(O ₁₁)	2.9 ± 1.2	1.5 ± 1.2	2.4 ± 1.2
B(Mn)	-0.3 ± 0.1		
B(V)	-0.1 ± 0.1		
B(O _{2,3})	+0.1 ± 0.3		
B(O ₄)	+0.3 ± 0.5		
R-factor	0.106	0.097	0.104

Table 2.

	<i>x</i>	<i>y</i>	<i>z</i>
Mn	0	0.3114 ± 0.0006	0.5
V	0.2354 ± 0.0009	0	0.902 ± 0.002
O ¹	0	0	0
O ²	0.232 ± 0.003	0.160 ± 0.002	0.713 ± 0.005
O ₃	0.409 ± 0.004	0	0.213 ± 0.007
Mn-O ₂₁	2 × 2.30 ± 0.02 Å		
Mn-O ₂₂	2 × 2.13 ± 0.02 Å		
Mn-O ₃	2 × 2.17 ± 0.02 Å		

Since all the refinements led to an unduly high temperature factor for the shared oxygen atom a fourth possibility was taken into account. Refinements were carried out considering a random distribution of the bridging oxygen on two positions, one on each side of the origin, *i.e.* the oxygen atom O₁₁ was allowed to split up either in the *xy* plane or along the *y* axis.

The temperature factor came out to be only slightly lower with these arrangements (1.8 ± 1.1 for both) and the resulting O₁₁ parameters are not significantly different from the position 0,0,0 in the space group *C2/m*.

As can be seen from Table 1 the refinement using space group *Cm* rendered a very unsatisfactory correspondence between the vanadium-oxygen bonding distances. The refinement applying space group *C2* gave no significant deviations from the V₂O₇-arrangement obtained with space group *C2/m*.

Considering the refinements described above there is no reason to assign to the structure a symmetry lower than *C2/m*. This should give a fairly correct picture of the atomic arrangement. Further in-

vestigations in the structural details of the compound would require experimental data of very high accuracy.

Table 2 shows the final parameters in space group *C2/m* and the resulting Mn-O distances.

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1. Lukaszewicz, K. *Roczniki Chem.* **35** (1961) 31.
Lukaszewicz, K. and Smajkiewicz, R. *Roczniki Chem.* **35** (1961) 741.
2. Cruickshank, D. W. I., Lynton, H. and Barclay, G. A. *Acta Cryst.* **15** (1962) 491.
3. Brisi, C. *Ann. Chim. (Rome)* **48** (1958) 270.
4. Werner, P.-E. *Z. Krist.* **120** (1964) 375.

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