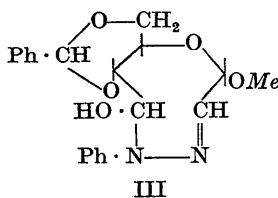


(Guthrie & Honeyman, 1959) gave yellow needle crystals from *n*-butanol.



The unit-cell dimensions were:

$$a = 16.27, b = 12.03, c = 4.95 \text{ \AA}, \gamma = 94.3^\circ;$$

the space group was  $P2_1$ . The density measured with a density-gradient column was  $1.266 \text{ g.cm.}^{-3}$ , and with  $Z=2$  the calculated molecular weight was 368.3 in agreement with 370.4 calculated for III. The correct structure of this molecule is still uncertain.

An ethanolamine derivative of compound I (Colbran, Guthrie & Parsons, 1960) was prepared but difficulty was found in elucidating its structure. X-ray work was undertaken in the hope that the determination of the molecular weight would help. Colourless needles were obtained from aqueous methanol. The unit-cell dimensions were:

$$a = 21.67, b = 16.66, c = 4.63 \text{ \AA};$$

the space group was  $P2_12_12_1$ . The density measured by flotation was  $1.302 \text{ g.cm.}^{-3}$  and assuming  $Z=4$  the calculated molecular weight was found to be 327.7. This value of the molecular weight is consistent with that derived from the elementary analysis of the compound, but despite this agreement, difficulty still exists in giving an exact formula for the compound.

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### Accuracy in structure analysis of layer silicates: Some further comments on the structure of prochlorite. By H. STEINFINK,\* *Shell Development Company, Houston, Texas, U. S. A.*

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Mathieson, Radoslovich & Walker (1959), in their criticism of the crystal structure of a monoclinic chlorite (Steinfink, 1958), assert that the data do not support the findings and that '... unwarranted structural features ...' were proposed. The contention is made that 51 positional parameters were derived from 78 reflections, although a  $R(h0l) = 0.148$  is reported in the paper and clearly indicates that additional reflections to those listed in Table 3 were used during the analysis of the structure. The primary interest in these layer silicate structures was the determination of deviations from 'ideal'  $y$  parameters. In general the  $k=3n$  reflections are relatively insensitive to these deviations, as shown below, and the 85 ( $h0l$ ) reflections in particular are not of great interest once they have been used in the refinement of the  $x$

The density-gradient columns used for the estimation of the density of compound II and III were formed from saturated aqueous solutions of inorganic salts.

	Density range
1. Water-lead nitrate	1.0-1.4 $\text{g.cm.}^{-3}$
2. Water-sodium tungstate	1.0-1.55
3. Potassium chloride-sodium iodide	1.2-1.9

Column 3 was used for compound II and columns 1 and 2 for compound III. Columns made with organic liquids were unsuitable because of the solubility of the compounds in the solvents. Details of forming and calibrating these columns are given by Linderstrøm-Lang (1937, 1938) and Preston & Nimkar (1950). The density gradient was found to be linear over small distances only, and it was therefore necessary to draw a calibration graph with values obtained with four or five reference standards placed in the region of the column where preliminary tests had shown that the crystal of unknown density would float.

The author wishes to acknowledge the helpful advice of Dr J. C. Speakman. Thanks are also due to Mr D. M. Cooke in helping to investigate the use of density-gradient columns.

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and  $z$  parameters. The 47 positional parameters (four are fixed by the space group) were therefore determined by a total of 163 reflections.

The authors also claim that the electron-density maps do not support the coordinates of Table 2. Consider the contributions to the ( $0kl$ ) structure factors from the individual atoms when they have 'ideal'  $y$  parameters. When  $k=3n$  the imaginary part of the structure factor is nearly zero, and deviations from 'ideal'  $y$  parameters will not cause large deviations from the phase angle values  $0^\circ$  or  $180^\circ$ . For the  $k \neq 3n$  reflections, the oxygens forming the base of the  $\text{SiO}_4$  tetrahedron and the silicon atom at  $y=1/6$  will cause the phase angle to assume values different from  $0^\circ$  or  $180^\circ$ , and the values of these phase angles will be sensitive to deviations from the 'ideal'  $y$  parameters of the atoms. Thus the ( $0kl$ ) projection will be heavily weighted in favor of 'ideal'  $y$  coordinates because the majority of the strong reflections are

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of the type  $k=3n$ . The most that can be obtained from this projection is an indication of the shift from the 'ideal', although it will not show the full extent.

Table 1. Refined atomic coordinates of prochlorite

Atom	X	Y	Z
A <sub>1</sub> Mg	0	0.000 <sub>6</sub>	0
A <sub>2</sub> 0.75 Mg + 0.25 Fe	0	0.333 <sub>0</sub>	0
A <sub>3</sub> 0.9 Fe	0	0.666 <sub>0</sub>	0
A <sub>4</sub> 0.75 Al + 0.25 Fe	0	0.500 <sub>4</sub>	0.5000
A <sub>5</sub> 0.75 Al + 0.25 Fe	0	0.167 <sub>3</sub>	0.5000
A <sub>6</sub> 0.75 Mg	0	0.832 <sub>3</sub>	0.5000
T <sub>1</sub> 0.30 Si + 0.70 Al	0.228 <sub>3</sub>	0.502 <sub>4</sub>	0.194 <sub>1</sub>
T <sub>2</sub> 0.80 Si + 0.20 Al	0.227 <sub>2</sub>	0.166 <sub>8</sub>	0.193 <sub>9</sub>
O <sub>1</sub>	0.186 <sub>1</sub>	0.169 <sub>3</sub>	0.075 <sub>2</sub>
O <sub>2</sub>	0.194 <sub>0</sub>	0.501 <sub>3</sub>	0.075 <sub>8</sub>
O <sub>3</sub>	0.022 <sub>3</sub>	0.074 <sub>1</sub>	0.236 <sub>2</sub>
O <sub>4</sub>	0.518 <sub>3</sub>	0.113 <sub>1</sub>	0.235 <sub>2</sub>
O <sub>5</sub>	0.194 <sub>2</sub>	0.325 <sub>7</sub>	0.235 <sub>4</sub>
OH <sub>1</sub>	0.685 <sub>2</sub>	0.313 <sub>0</sub>	0.072 <sub>6</sub>
OH <sub>2</sub>	0.125 <sub>2</sub>	0.979 <sub>4</sub>	0.433 <sub>0</sub>
OH <sub>3</sub>	0.181 <sub>3</sub>	0.327 <sub>6</sub>	0.434 <sub>1</sub>
OH <sub>4</sub>	0.132 <sub>1</sub>	0.677 <sub>0</sub>	0.431 <sub>6</sub>

The ( $hk0$ ) data, on the other hand, do not have a preponderance of reflections of the type  $k=3n$ , and the shifts are more apparent even though a large amount of overlap is present in this view of the structure. The ( $hk0$ ) electron-density map (Fig. 2, Steinfink, 1958) clearly shows that OH<sub>2</sub> is not at the 'ideal'  $y=0$  value and the deviation is not merely justified, as claimed in the criticism, on the basis of the peak asymmetry in the ( $0kl$ ) projection. Similarly the deviations of OH<sub>4</sub> and OH<sub>1</sub> are quite apparent in the original map although they are not so apparent as for OH<sub>2</sub> in the reduced reproduction. The difference electron-density maps which were used in the refinement of the structure also made it impossible to assign 'ideal' values to these atoms. When ( $0kl$ ) structure factors are computed on the basis of ideal  $y$  parameters and with weighted octahedral and tetrahedral scattering, the overall  $R=0.134$ ; the reflections  $k\neq 3n$ , however, have  $R=0.180$ . The discrepancy coefficient drops to 0.114 for  $k\neq 3n$  reflections (overall  $R(0kl)=0.087$ ) when the  $y$  coordinates of Table 2 (Steinfink, 1958) are used. Similar results were obtained for the ( $hk0$ ) reflections and were reported in the original paper. Thus the justification of the deviations from the 'ideal'  $y$  coordinates reported for seven atoms (four oxygen atoms and three hydroxyl groups) is supported by the sharp reduction in  $R$  for 38 critical ( $0kl$ ) and ( $hk0$ ) reflections for which  $k\neq 3n$ .

During the investigation of the prochlorite structure additional reflections consisting of  $h1l$ ,  $h2l$ ,  $h3l$ , and  $1kl$  had been recorded but were not used in the refinement of the structure. Because the results have been questioned by Mathieson *et al.* it was decided to use these reflections together with the  $hk0$ ,  $h0l$  and  $0kl$  reflections in a refinement of the positional parameters of the structure which had been reported (Steinfink, 1958). The 336 independent reflections which were available constitute approximately 40% of the reflections which are within the Cu sphere. Through the courtesy of Prof. G. A. Jeffrey & Dr R.

Shiono (1959) computer programs were obtained which refine atomic coordinates by differential synthesis. Four cycles of differential synthesis refinements were carried out starting with the published coordinates. The refined atomic parameters are listed in Table 1, and a comparison with Table 2 (Steinfink, 1958) shows that appreciable changes occurred only in the  $x$  parameters of the hydroxyl groups.

The standard deviations of the atomic parameters were computed using the formulae by Cruickshank (1949, 1950) and the average values for each atom type are shown in Table 2.

Table 2. Standard deviations of atomic parameters

	$\sigma(X)$	$\sigma(Y)$	$\sigma(Z)$
O, OH	0.020 Å	0.022 Å	0.015 Å
T	0.008	0.010	0.007
A	0.006	0.008	0.005

The revised bond lengths together with their standard deviations are shown in Table 3.

Table 3. Interatomic distances

$\sigma = 0.024$					
	T <sub>1</sub> -O <sub>5</sub>	1.76	T <sub>2</sub> -O <sub>5</sub>	1.61	
	T <sub>1</sub> -O <sub>4</sub>	1.71	T <sub>2</sub> -O <sub>4</sub>	1.67	
	T <sub>1</sub> -O <sub>3</sub>	1.76	T <sub>2</sub> -O <sub>3</sub>	1.57	
Average	T <sub>1</sub> -O	1.74	Average	T <sub>2</sub> -O	1.62
	T <sub>1</sub> -O <sub>2</sub>	1.68		T <sub>2</sub> -O <sub>1</sub>	1.68
$\sigma = 0.023$ Å					
A <sub>1</sub> -O <sub>1</sub>	2.09	A <sub>3</sub> -O <sub>1</sub>	2.10	A <sub>5</sub> -OH <sub>2</sub>	2.14
A <sub>1</sub> -O <sub>2</sub>	2.06	A <sub>3</sub> -O <sub>2</sub>	2.09	A <sub>5</sub> -OH <sub>3</sub>	2.06
A <sub>1</sub> -OH <sub>1</sub>	2.21	A <sub>3</sub> -OH <sub>1</sub>	1.93	A <sub>5</sub> -OH <sub>4</sub>	2.11
A <sub>2</sub> -O <sub>1</sub>	2.06	A <sub>4</sub> -OH <sub>2</sub>	2.14	A <sub>6</sub> -OH <sub>2</sub>	1.84
A <sub>2</sub> -O <sub>2</sub>	2.11	A <sub>4</sub> -OH <sub>3</sub>	2.15	A <sub>6</sub> -OH <sub>3</sub>	1.86
A <sub>2</sub> -OH <sub>1</sub>	2.08	A <sub>4</sub> -OH <sub>4</sub>	2.07	A <sub>6</sub> -OH <sub>4</sub>	1.92

The discrepancy coefficient for the 336 reflections used in the refinement was 0.131 with  $B=1.6$  Å<sup>2</sup>.

None of the conclusions which were based on the previously published data and which were questioned by Mathieson *et al.* need to be changed because of revisions in coordinates or bond lengths. The application of the significance criterion of  $2.3\sigma$  confirms that the differences in bond lengths within the tetrahedral layer are significant and are due to the preferential concentration of aluminum in site T<sub>1</sub>. Similarly the shortening of the bonds about A<sub>6</sub> is confirmed. The implications from the structure analysis presented in the previously published discussion remain valid.

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