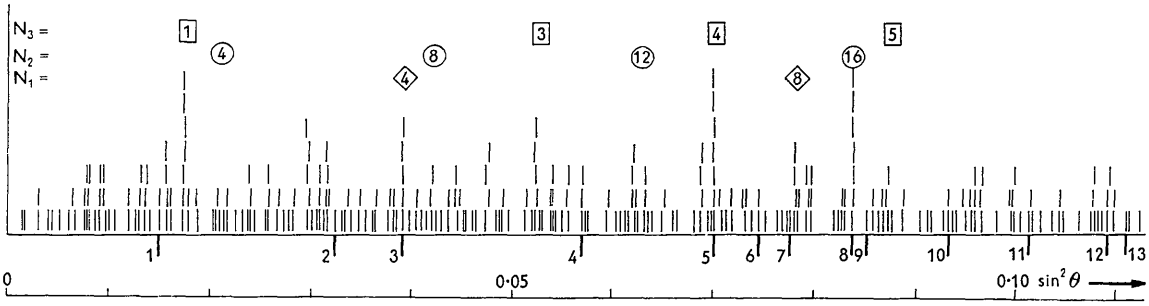

Fig. 1. The first part of the difference diagram of the powder photograph of α-$Cu(NH_3)_2Cl_2$. The unit cell is orthorhombic C centered with $a = 7{\cdot}78$, $b = 10{\cdot}65$, $c = 5{\cdot}82$ Å. Instead of Q we have used directly $\sin^2\theta$. The thick numbered lines below the horizontal axis mark the first $\sin^2\theta$ values measured, and each line above the axis represents a difference between a pair of measured $\sin^2\theta$. The whole number of the measured lines was 34.

centered cells, further values become forbidden. For example with a B centered monoclinic cell, for a given hk, l is either always even or odd. Therefore the difference of the squares is divisible by four.

For a trigonal unit cell (with hexagonal indices), the situation is more complicated. Here for a given h, k

$$l = l_0 + 3n, \quad (n = 0, \pm 1, \pm 2, \ldots) \tag{1}$$

where $l_0 = -1, 0, +1$, depending on h and k. So for example

$$\tfrac{1}{3}N_3 = \tfrac{1}{3}(l^2 - l'^2) = (n - n')[3(n + n') + 2l_0]\,. \tag{2}$$

Both factors on the right-hand side have the same parity (and are odd only when n is even and n' is odd or conversely). Using the abbreviations

$$A = n - n'; \quad B = 3(n + n') + 2l_0\,, \tag{3}$$

$$\begin{aligned}\tfrac{1}{3}N_3 &= A\,.\,B\\ &= [(A+B)/2 + (A-B)/2]\,.\,[(A+B)/2 - (A-B)/2]\,.\end{aligned} \tag{4}$$

But $A + B$ is always even, therefore $\frac{1}{2}(A \pm B)$ is integral; that is

$$\tfrac{1}{3}N_3 = (m + m')\,.\,(m - m') = m^2 - m'^2, \tag{5}$$

where m and m' are integers. It can be shown in a similar way that we can find an appropriate n and n' to each m and m'.

Now if we prepare in the usual way (see Fig. 1), the difference diagram from the data measured, we find quite a few maxima. We have to group these into two sets (tetragonal and hexagonal system) or three sets (orthorhombic system). Knowing the forbidden values mentioned above, this process is considerably facilitated. Of course there are always some accidentally appearing fortuitous maxima, and on the other hand, it can happen that no maxima belong to some permissible value.

Our experience shows, that—at least in the orthorhombic and tetragonal systems—the highest maxima belong usually to N (or N_1, N_2, N_3) = 4, 8, 16, ... and here are to be found most of the differences for the strongest lines.

The author is indebted to Prof. Dr E. Nagy for his helpful discussions.

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The crystallography of the hydrates of sodium carbonate and of sodium sulphite.

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Though the goniometric data are recorded by Groth (Vol. II, 1908), the unit-cell dimensions of common 'washing soda', $Na_2CO_3.10H_2O$, are not given in any of the standard compilations and appear not to have been measured. Whilst remedying this omission, we were led to a study of the heptahydrate, $Na_2CO_3.7H_2O$, and of the similarly hydrated sulphite, $Na_2SO_3.7H_2O$.

Crystals of all three hydrates can be grown from aqueous solution. $Na_2CO_3.7H_2O$, in contact with aqueous solution, is thermodynamically stable only between 35 and 32 °C; but it was sometimes obtained at lower temperatures—presumably an example of the operation of Ostwald's law of successive reactions. Suitable fragments of $Na_2SO_3.7H_2O$ could alternatively be cut from the interior of the large crystals commercially available. All three substances effloresce rapidly when exposed to normal atmospheric conditions, and the small crystals suitable for X-ray study had immediately to be sealed into thin-walled glass tubes. Copper $K\alpha$-radiation was used. Internal calibration was procured by superposing on the same Weissenberg diagram the powder lines from a fine copper or aluminium wire, for which a at 20° was taken as 3·6149 and 4·04907 Å respectively. The new crystal data are collected in Table 1. The standard deviations shown are based, in each case, on a least-squares treatment of about 20 high-order reflexions

Table 1. *Crystal data*

(Unit-cell dimensions are expressed in Å × 10^{-3}, with their standard deviations in parentheses. Where given for angles, the standard deviations are in minutes. Z is the number of formula units per cell; D_x is the calculated density, and D_m that observed)

			D_m	Z	D_x	Space group
$Na_2CO_3.10H_2O$ (286·15)		a = 12571(10)	1·45	4	1·454	$C2/c$
		b = 9049(8)				
		c = 13469(7)				
		β = 121° 26′(3)				
$Na_2CO_3.7H_2O$ (232·10)		a = 19491(7)	1·51	8	1·559	$Pbca$
		b = 7008(3)				
		c = 14477(4)				
$Na_2SO_3.7H_2O$ (252·15)	(i)	a = 19899(9)	1·56	8	1·588	$B2_1/a$
		b = 7260(2)				
		c = 14635(9)				
		β = 94° 6′(2)				
	(ii)	a' = 12765		4	1·588	$P2_1/n$
		c' = 11922				
		β' = 107° 22′				
	(iii)	a'' = 11399		$2\frac{2}{3}$	1·588	—
		c'' = 8510				
		β'' = 93° 30′				
$Na_2SO_4.10H_2O$ (322·20)		a = 11520(3)	1·485	4	1·469	$P2_1/c$
		b = 10344(10)				
		c = 12840(3)				
		β = 107°48′(1)				

Table 2. *Axial ratios*

	Groth		X-ray
$Na_2CO_3.10H_2O$	1·4186:1:1·4828,	122°20′	1·3892:1:1·4885
$Na_2CO_3.7H_2O$	2·7747:1:2·0832 (1:0·3604:0·7508)	—	2·7813:1:2·0658
$Na_2SO_3.7H_2O$, cell (iii)	1·5728:1:1·1694,	93°36′	1·5701:1:1·1722
$Na_2SO_4.10H_2O$	1·1158:1:1·2380,	107°45′	1·1137:1:1·2413

which were compared with neighbouring lines of the standard. The density of the sulphite was determined by flotation in a chloroform–carbon tetrachloride mixture, and those cited for the other substances are taken from Groth.

Table 2 shows that the axial ratios implied by the X-ray measurements for the two carbonates agree satisfactorily with those given by Groth, after some re-allocation of axial symbols. For the sulphite the connexion was less obvious. Choice of the doubly-primitive cell (i) reveals a close relationship with the heptahydrated carbonate. This cell has equivalent positions $(0, 0, 0;\ \frac{1}{2}, 0, \frac{1}{2}) \pm (x, y, z;\ x, \frac{1}{2}-y, \frac{1}{2}+z)$, and its orientation with respect to the primitive cell (ii) is explained by Fig. 1. The intensity distribution in the $h0l$ reciprocal-net for cell (i) resembles that for $Na_2CO_3.7H_2O$, and this—together with the similar cell dimensions—suggests a structural resemblance, though the two heptahydrates belong to different crystal systems. Traube (1894) found that each will crystallize with a considerable proportion of the other in solid solution. His findings were questioned by Foerster, Brosche & Norberg-Schulz (1924), but they are in accord with the crystallographic relationship revealed by our X-ray measurements.

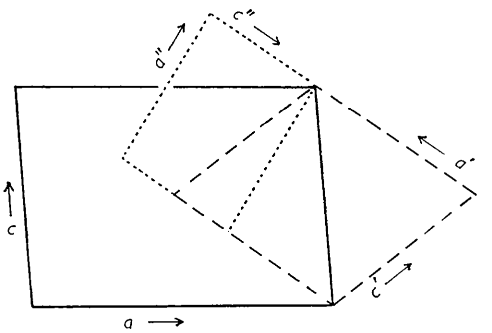

Fig. 1. Alternative unit cells for $Na_2SO_3.7H_2O$ as seen when projected along the b-axis. Cell (i) is indicated by continuous lines, cell (ii) by broken lines, and the sub-cell (iii) by dotted lines.

Neither cell (i) nor cell (ii) agrees with the goniometric ratios given by Groth. Correspondence can be achieved by relating these ratios to the sub-cell (iii) indicated by dotted lines in Fig. 1. The transformation matrix 1,0,2/0,1,0/1,0,−1 gives Miller indices for cell (i) in terms of those for (iii). Thus the most prominent forms, described by Groth as {100}, {001}, and {110}, would now be indexed as {101}, {201} and {111}.

From sodium sulphite solutions that had been exposed to the air for some time crystals were obtained having the cell dimensions given in the last row of Table 1. In fact they consist of the sulphate, $Na_2SO_4.10H_2O$, as was confirmed by comparison with the axial ratios in Table 2, and in agreement with the X-ray measurements of Ruben, Templeton, Rosenstein & Olovsson (1961).

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