

The shift of the Cr atoms causes a pyramidal distortion of the octahedra in the  $\text{Cr}_2\text{Cl}_9$  group, the angle  $\alpha$  being  $176^\circ$  (Fig. 3(a)); in  $\text{K}_3\text{W}_2\text{Cl}_9$  a similar distortion is found but in that case  $\alpha$  is slightly larger than  $180^\circ$ . A further distortion occurs in the group  $\text{W}_2\text{Cl}_9$  because the  $\text{Cl}_{\text{II}}$  layers are rotated about the 'axis' W-W until the upper and lower  $\text{Cl}_3$  triangles differ  $37^\circ 30'$  in azimuth (Fig. 3(b)); in the regular Cl configuration, as found in  $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ , this difference is  $60^\circ$ .

The following distances are observed in  $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ :

$\text{Cr}-\text{Cl}_I = 2.52 \text{ \AA}$	$\text{Cl}_I-\text{Cl}_I = 3.43 \text{ \AA}$	$\text{Cs}_I-\text{Cl}_I = 3.61 \text{ \AA}$
$\text{Cr}-\text{Cl}_{\text{II}} = 2.34$	$\text{Cl}_{\text{II}}-\text{Cl}_{\text{II}} = 3.40$	$\text{Cs}_I-\text{Cl}_{\text{II}} = 3.59$
$\text{Cr}-\text{Cr} = 3.12$		$\text{Cs}_{\text{II}}-\text{Cl}_I = 3.68$
		$\text{Cs}_{\text{II}}-\text{Cl}_{\text{II}} = 3.62, 3.63$

Finally, powder photographs showed that the earlier mentioned compounds  $\text{Cs}_3\text{V}_2\text{Cl}_9$  and  $\text{Cs}_3\text{Ti}_2\text{Cl}_9$  are isomorphous with the compound described above.

The dimensions of the unit cell are:

$\text{Cs}_3\text{V}_2\text{Cl}_9$ :	$a = 7.24$ ,	$c = 17.94 \text{ \AA}$ ,	$c/a = 2.48$ .
$\text{Cs}_3\text{Ti}_2\text{Cl}_9$ :	$a = 7.32$ ,	$c = 17.97 \text{ \AA}$ ,	$c/a = 2.45$ .

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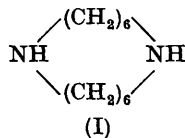
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### Elementarzelle von 1,8-Diaza-cyclo-tetradecan. Von HANS VON DIETRICH, HELMUT ZAHN und HERBERT SPOOR, *Chemisches Institut der Universität, Heidelberg, Deutschland*

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Die von Zahn & Spoor (1956) dargestellte Verbindung (I) kristallisiert in gut ausgebildeten prismatischen Nadeln, monoklin, Nadelachse [101].



Die Röntgenuntersuchung lieferte die folgenden Abmessungen der Elementarzelle:

$$c_0 = 10,20 \pm 0,03 \text{ \AA}, \quad b_0 = 15,33 \pm 0,02, \quad a_0 = 9,006 \pm 0,01, \\ \beta = 112^\circ 41' \pm 6'.$$

Bei Annahme von vier Molekülen in der Elementarzelle berechnet sich daraus die Dichte =  $1,014 \pm 0,004 \text{ g.cm.}^{-3}$ , die mit der bei  $20^\circ \text{ C.}$  gemessenen Dichte  $1,002 \text{ g.cm.}^{-3}$  hinreichend übereinstimmt.

Beim Versuch eine Kristallnadel quer zur Nadelachse durchzuschneiden, spaltet sich dieselbe sehr leicht in ein faseriges Nadelbündel, das dem Zerschneiden in der Querrichtung grossen Widerstand entgegensetzt. Diese Eigenschaft zeigt, dass die zwischenmolekularen Anziehungskräfte im Gitter in Richtung der Nadelachse offenbar wesentlich grösser sind als senkrecht dazu. Da andererseits die Methylengruppen der Moleküle im Vergleich zu den Aminogruppen nur einen kleinen Beitrag zur zwischenmolekularen Anziehung liefern dürften, kann man annehmen, dass in Richtung [101] Molekülketten im Kristallgitter vorliegen werden, deren Einzelmoleküle über N-H-N-Brücken zusammenhängen.

Eine volle Strukturbestimmung ist z. Zt. nicht beabsichtigt.

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### Polymorphism of chloroacetamide. By MIKIO KATAYAMA, *Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo, Japan*

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In the course of the analysis of the crystal structure of chloroacetamide (Katayama, 1956), the author found a new form of this compound which has strikingly almost the same cell dimensions and belongs to the same space group as the one analysed by Dejae (1955). The former was named tentatively an unstable form and the latter

the stable one. In the following, we shall call the former the  $\beta$ -form and the latter the  $\alpha$ -form.

The difference between the cell dimensions and space groups of these two forms (Table 1) is found only in the value of  $\beta$ ,  $\beta$  being  $98^\circ 49'$  in the  $\alpha$ -form and  $102.5^\circ$  in the  $\beta$ -form. Penfold & Simpson (1956) recently reported

Table 1. *The cell dimensions and the space group of chloroacetamide*

Crystal form	a (Å)	b (Å)	c (Å)	$\beta$	Space group	Author
$\alpha$	7.41	5.13	10.26	98° 49'	$P2_1/a$	Dejace (1955)
$\beta$	7.45	5.15	10.27	102.5°	$P2_1/a$	Katayama (1956)
—	7.49	5.18	10.25	102°	$P2_1/a$	Penfold & Simpson (1956)

the crystal structure of the same compound. They claim that they arrived at essentially the same structure as Dejace. However, their  $\beta$  is 102°, which may indicate they dealt with the  $\beta$ -form. Owing to the same space group and approximately the same dimensions of the unit cells, it is not easy to distinguish the two forms from the unit-cell dimensions alone. Further, inspection shows that their  $y, z$  parameter values coincide with those reported by Dejace, and their  $x, z$  parameter values coincide with those given by Katayama. The most conspicuous difference is that the strongest reflexion of the  $\alpha$ -form is (201) and of the  $\beta$ -form is (20 $\bar{2}$ ). It is confirmed that the  $\alpha$ -form is obtained from benzene solution, while the  $\beta$ -form can be obtained from aqueous solution. The difference of the two forms lies in the orientation of the molecules in the crystals: the molecules in the  $\alpha$ -form are arranged parallel to the (201) plane, while in the  $\beta$ -form they are in the (10 $\bar{1}$ ) plane.

The Debye-Scherrer patterns of these crystals were examined with a Geiger-counter spectrometer, by using Cu  $K\alpha$  radiation (Fig. 1). The patterns look almost

the same. Indeed, the strongest reflexions, (201) of the  $\alpha$ -form and (20 $\bar{2}$ ) of the  $\beta$ -form, are found at almost the same scattering angle  $2\theta = 27^\circ$ .

However, the precise measurement of these peaks reveals that the scattering angle of the (201) reflexion of the  $\alpha$ -form is slightly smaller than that of the (20 $\bar{2}$ ) reflexion of the  $\beta$ -form (Fig. 2). Hence we can easily

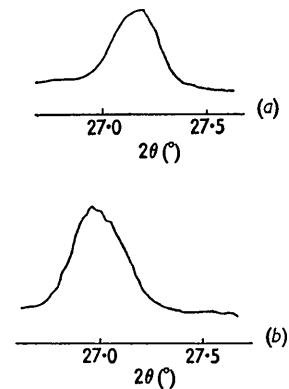


Fig. 2. Debye-Scherrer reflexions: (a) (20 $\bar{2}$ ),  $\beta$ -form; (b) (201),  $\alpha$ -form.

identify to which form the crystal belongs by observing the (201) or (20 $\bar{2}$ ) reflexion of the Debye-Scherrer pattern. Thus if a sample shows a doublet peak at this scattering angle, it indicates that the sample contains both the  $\alpha$ - and  $\beta$ -form. Fig. 1(c) shows an example which was taken with a sample crystallized from an aqueous solution.

It is found that the crystals of chloroacetamide assume either the  $\alpha$ -form or the  $\beta$ -form according to the method of crystallization. The  $\alpha$ -form is obtained from benzene or carbon tetrachloride solutions, while the crystals obtained from aqueous or ethyl alcohol solutions are mostly the  $\beta$ -form, frequently contaminated with the  $\alpha$ -form. Unfortunately, it has not been established whether both forms are crystallized simultaneously from these solutions, or whether the  $\beta$ -crystals have been deposited first and some then transform quickly into the  $\alpha$ -form.

It is also found that the crystals purified by sublimation are the  $\alpha$ -form, while those obtained by cooling the fused chloroacetamide are the  $\beta$ -form. As has been mentioned, the  $\alpha$ -form is obtained from non-polar solutions. These crystals are hard to dissolve in benzene or in carbon tetrachloride. Presumably the molecules of chloroacetamide become stable in these solutions by making dimers by hydrogen bonds, and the dimers thus formed come into the crystals having the structure shown by Dejace and confirmed by the author. The crystals are easily soluble in water or ethyl alcohol, and in these solutions the molecules are probably making hydrogen bond with the solvent molecules. This will be the reason why the crystals obtained from these solutions have a different structure.

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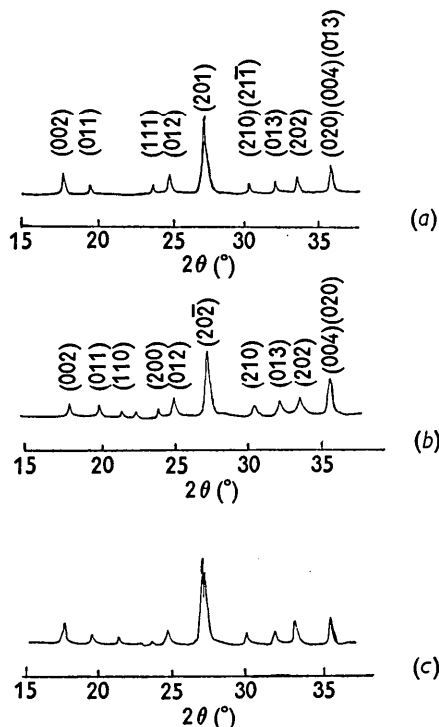


Fig. 1. Debye-Scherrer patterns of chloroacetamide: (a)  $\alpha$ -form; (b)  $\beta$ -form; (c) mixture.