

Le rôle joué par les positions connues et inconnues devient ainsi parfaitement symétrique. La forme de (12) garantit d'ailleurs que P^+ reste toujours positif et ne peut dépasser l'unité.

Valeur probable du facteur de structure des positions inconnues

La valeur du facteur de structure des positions inconnues est $A_k - D_k$.

Sa valeur probable est:

$$\begin{aligned} \langle A_k - D_k \rangle &= P^+ (+|A_k| - D_k) + P^- (-|A_k| - D_k) \\ &= |A_k| \operatorname{th} (q_k + s_k) - D_k. \end{aligned} \quad (13)$$

Lorsque $D_k = 0$, (13) se réduit à $|A_k| \operatorname{th} s_k$ et non pas à zéro.

La meilleure série de Fourier à construire pour résoudre les positions des atomes inconnus serait dans le cas centrosymétrique

$$\sigma(\mathbf{x}) = \sum_h (|A_h| \operatorname{th} (q_h + s_h) - D_h) \cos 2\pi \mathbf{h} \cdot \mathbf{x}. \quad (14)$$

Elle complète l'expression de Woolfson (1956, cf. relation (6)) par le terme en s_h . Pour la justification de la relation (14) nous renvoyons au mémoire de Woolfson.

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The Absolute Configuration of Sodium Chlorate

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Measurements are reported of the Bijvoet inequality (difference in intensity between the reflexions hkl and $\bar{h}\bar{k}\bar{l}$) for a number of reflexions in the $[01\bar{1}]$ zone of sodium chlorate. Cu $K\alpha$ radiation was used, and the Bijvoet inequality produced by the small anomalous dispersion of chlorine atoms for this wavelength was accurately measured with a Geiger-counter spectrometer. The absolute configuration of an optically dextro-rotatory crystal was found to be described by the following parameters x, y, z with the atomic positions 12(b) of the *International Tables* for the space group No. 198 ($P2_13$) referred to a right-handed system of coordinates:

$$4 \text{ Na: } 0.064, 0.064, 0.064; \quad 4 \text{ Cl: } 0.417, 0.417, 0.417; \quad 12 \text{ O: } 0.303, 0.592, 0.500.$$

The absolute configuration determined was found to be in agreement with that deduced from the theoretical calculation of its optical activity made by Ramachandran.

1. Introduction

Sodium chlorate belongs to the cubic tetartohedral ($T-23$) class and exhibits optical activity. Its structure was worked out in complete detail by Zachariasen (1929). The space group is $P2_13$ and there are four molecules per cubic unit cell, with $a = 6.570 \text{ \AA}$. The atomic positions are:

$$\begin{aligned} x, y, z; & \quad x + \frac{1}{2}, \frac{1}{2} - y, \bar{z}; \quad \bar{x}, y + \frac{1}{2}, \frac{1}{2} - z; \quad \frac{1}{2} - x, \bar{y}, z + \frac{1}{2}; \\ & \quad y, z, x; \quad \odot; \quad \odot; \quad \odot; \\ & \quad z, x, y; \quad \odot; \quad \odot; \quad \odot. \end{aligned}$$

The values of x, y and z are

	x	y	z
4 Na	0.064	0.064	0.064
4 Cl	0.417	0.417	0.417
12 O	0.303	0.592	0.500

We shall call the structure represented by the above coordinates, referred to a right-hand system of coordinates, structure A . A unit cell of structure A is shown in Fig. 1. Since the crystal has no centre of

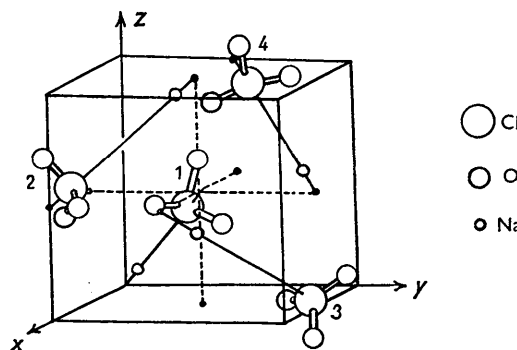


Fig. 1.

symmetry, the other enantiomorphous form could be represented by a set of coordinates related to the above by an inversion. The two structures would correspond to right- and left-rotating crystals, but it is not possible to find out from the usual X-ray methods, such as those adopted by Zachariasen, which structure corresponds to which sense of optical activity.

The structure may be considered as a slightly distorted form of the NaCl structure, with the chlorate ion replacing the chloride. However, the planes of the four O_3 groups are not parallel but have a peculiar helical configuration (Wooster, 1953), and this is what gives rise to its optical activity. The magnitude of the optical rotation has been calculated (Ramachandran, 1951b) from its structure, making use of a general theory developed for the optical activity of crystals (Ramachandran, 1951a). In this calculation, the sense of activity depends on the absolute configuration of the structure chosen. Ramachandran (1951b) made the calculations for the structure *A* and, as will be seen in a later section, it leads to dextro-rotation (clockwise for an observer looking towards the source of light).

The object of the present work was to check the result in a direct manner, using the anomalous dispersion of X-rays. Bijvoet and his collaborators (Peerdeman, Bommel & Bijvoet, 1951) were the first to use the anomalous dispersion technique for determining the absolute configuration of crystal structures. In their study of sodium rubidium tartarate, use was made of the large magnitude of the imaginary component of the scattering factor of Rb owing to the closeness of the exciting radiation Zr $K\alpha$ ($\lambda=0.786 \text{ \AA}$) to the *K* absorption edge of the anomalous scatterer (Rb $\lambda_R = 0.816 \text{ \AA}$). Large differences were observed in the intensities of reflexions hkl and $\bar{h}\bar{k}\bar{l}$, since Friedel's law fails under such conditions*. This technique has also been utilized by others (Trommel & Bijvoet, 1954; Saito, Nakatsu, Shiro & Kuroya, 1955) for the determination of absolute configuration.

Recently Peterson (1955) pointed out that appreciable Bijvoet inequalities are found for some reflexions in tyrosine hydrochloride and hydrobromide, even when the wavelength of exciting radiation was not so close to the absorption edge. This technique has been adopted here for the study of sodium chlorate. Unambiguous evidence for the absolute configuration could be obtained with Cu $K\alpha$ radiation (1.54 \AA) although the *K* edge of the anomalous scatterer (λ_R for chlorine is 4.40 \AA) is relatively far away. The absolute configuration thus determined was found to be in agreement with that deduced from the theory of optical activity.

The authors have also applied the method to D(+) glucosamine hydrochloride with a view to checking

the configuration assigned to this molecule by the chemists, and have found that the latter was correct. The details will be reported separately.

2. Specification of coordinate axes

In a well developed crystal, the two enantiomorphous forms may be distinguished by the distribution of the $\{210\}$ faces (Groth, 1908), but in the crystals grown for these studies only the $\{100\}$ faces were developed. The optical activity of the crystal was therefore used to determine its 'hand', and an X-ray method was used to define the coordinate axes.

Although the *x, y, z* axes are equivalent for the point group $T-23$, only a cyclic permutation between them is allowed by symmetry and not an interchange of a pair of them. Thus, if *OX* is chosen arbitrarily, *OY* and *OZ* are automatically fixed. The principle of fixing the directions of the axes has been explained by Ramachandran & Chandrasekharan (1951) in their work on the photoelastic constants of the crystal. A Laue picture is obtained with X-rays travelling along a cubic direction, arbitrarily called *OX*. Then from the picture, *OY* and *OZ* directions are fixed, making use of the following inequalities of intensities (Zachariasen, 1929):

$$I_{150} > I_{105}; \quad I_{140} > I_{104}; \quad I_{270} < I_{207}.$$

(These inequalities arise from the symmetry of the crystal and have nothing to do with the Bijvoet inequality.)

Having thus obtained the directions of the axes, it is further necessary to specify the sense, in order to describe the absolute configuration. For a right-handed system, the positive directions of the axes are so chosen that, looking from any point in the positive octant towards the origin, the sequence *OX, OY, OZ* is anticlockwise. This is in accordance with the convention adopted in the *International Tables* (1952). Four choices* are possible for orthogonal coordinate systems (orthorhombic, tetragonal and cubic symmetry), but the four are equivalent, being related by the elements of symmetry of the point group 222 , and so any one of them may be adopted.

The above method of defining the coordinate axes was used for both dextro- and laevo-rotatory crystals, and a right-handed system was used in both cases. The fact that, once the axis *OX* is fixed, then *OY* and *OZ* cannot be interchanged and that their directions are specified in the same way for both enantiomers, is confirmed also by the photoelastic properties of the crystal (Ramachandran & Chandrasekharan, 1951). It is found that $q_{12} \neq q_{13}$ and $(q_{11}-q_{12}) > (q_{11}-q_{13})$ for both enantiomers, when the axes are defined as above.

* In this paper the reflexions hkl and $\bar{h}\bar{k}\bar{l}$ will be referred to as 'inverse reflexions' and the inequality in their intensities owing to anomalous dispersion as the 'Bijvoet inequality'.

* It can be readily verified that the number of such equivalent choices of right-handed system is only two for monoclinic and hexagonal systems and only one for rhombohedral and triclinic systems.

3. Choice of reflexions for study

Since the cubic axes are twofold axes of symmetry, any reflexion hkl , with any one of the indices zero, will not exhibit any Bijvoet inequality, since the two inverse reflexions would become equivalent. Therefore only reflexions with general indices hkl , none of them zero, could show such an inequality. Reflexions of the type hll , occurring in the $[01\bar{1}]$ zone, were therefore chosen for study. These could be conveniently measured, using a thin crystal plate ground parallel to (100).

From the symmetry of the point group $T-23$, it follows that $I_{hll} = I_{\bar{h}\bar{l}l}$, $I_{\bar{h}ll} = I_{h\bar{l}l}$ for reflexions in the zone $[01\bar{1}]$. But $I_{hll} \neq I_{\bar{h}\bar{l}l}$, since Friedel's law does not hold for these. Thus, for a particular reflexion with $h = 5$ and $l = 1$, two pairs of reflexions can be studied, namely, 511 , $\bar{5}\bar{1}\bar{1}$ and $\bar{5}11$, $5\bar{1}\bar{1}$. Further, two settings are possible for the Geiger counter (used for recording the reflexions) for each reflexion, namely at an angle of 2θ on either side of the X-ray beam. Thus, in all, eight observations are possible for each reflexion, giving four measurements of the Bijvoet inequality.

4. Experimental details

Cu $K\alpha$ radiation was used in the present study and, since the Bijvoet inequality was expected to be small, accurate intensity measurements were made with a Unicam single-crystal goniometer with its accessories for Geiger-counter attachment. The speed of rotation of the standard apparatus was too fast, about 10° per min. Therefore a tangent screw arrangement, driven by a synchronous motor, was provided, giving a speed of rotation of 1° in 4 min. The Geiger counter was Amperex Type 153C, with argon and halogen filling. The recording equipment consisted of a counting rate

meter for initial adjustment of the crystal and a scale-of-128 circuit for the measurement of the integrated intensities of the reflexions. These were built in the laboratory, following standard models (Elmore & Sands, 1949). The X-ray tube was Philips PW 1009, which had filament stabilization, and it was found that measurements were generally reproducible to about 3%.

Initial measurements showed an appreciable anomalous dispersion effect for several reflexions. It was, however, very large for 511 and 611 , and these two were measured in all the eight settings.

The measurements made with a dextro-rotatory crystal are summarized in Table 1. All reflexions with $h < 6$ and $l < 3$, covering a range of Bragg angles from 10° to 55° are listed there. A few reflexions like 311 and 422 , where the X-ray beam was either at grazing incidence or emergence from the crystal, were not measured. The calculated values of $|F|^2$, as well as the magnitude of the Bijvoet inequality to be expected expressed as a percentage of the mean value of $|F|^2$, are also given in the table. The calculations were made using Viervoll & Ögrim's (1949) data for the structure A , whose atomic positions are given in § 1. The corrections to the real and imaginary parts of the scattering of the chlorine atom were obtained from James's book (1948) to be $\Delta f' = 0.23$, $\Delta f'' = 0.66$. The contribution of the sodium and oxygen atoms to the anomalous dispersion effect was negligible and was omitted.

It is seen from Table 1 that there is good agreement between the sense of the calculated Bijvoet inequality and that measured. The only exception is 111 , which is a strong reflexion likely to be affected by extinction and therefore highly texture sensitive. The difference of 3% observed is not significant.

Table 1. *Measurements of hll reflexions with a dextro-rotatory crystal*

Calculated values of $|F|^2$ are for the structure A . Measured values are of integrated intensity in arbitrary units, with Cu $K\alpha$ radiation. $\Delta|F|^2$ is positive if $|F(hll)|^2 > |F(\bar{h}\bar{l}l)|^2$, and similarly for ΔI .

hll	$ F ^2$ neglecting anomalous dispersion	Calculated values with anomalous dispersion			Measured intensity		
		$ F(hll) ^2$	$ F(\bar{h}\bar{l}l) ^2$	$\Delta F ^2$ (%)	$I(hll)$	$I(\bar{h}\bar{l}l)$	ΔI (%)
111	843	852	890	-4.5	1495	1450	3
211	877	959	852	12	64.4	60.7	6
311	504	538	490	9.5	Grazing conditions		
411	114	143	108	30	1191	1125	6
511	64.5	56	100	-68	406	603	-40
611	61	83	48	57	704	570	20
711	124	150	147	2.4	673	647	4
122	992	897	838	5.9	296	267	10
222	211	258	223	16	100	91	10
322	417	460	365	22	30.6	26	12
422	95	112	121	-9.4	Grazing conditions		
522	512	498	568	-13	1210	1297	-7
622	92	107	91	17	347	316	9
133	875	962	853	12	116	109	6
233	115	115	114.5	0.4	25.5	25.5	0
333	2471	2595	2636	-1.6	103	114	-10
433	111	111	111	0	Grazing conditions		
533	823	845	884	-4.7	1635	1635	0

Table 2. *Measurements in eight settings of 511 and 611 reflexions for a dextro-rotatory crystal*

Values within brackets in the last column are for an error of 1° in grinding

Reflexion	Incidence condition	Measured intensity for		Anomalous dispersion effect \bar{I}/I	Measured intensity for		Anomalous dispersion effect \bar{I}/I	Asymmetry effect I_2/I_1 (calc.)
		hll	$\bar{h}\bar{l}\bar{l}$		$h\bar{l}\bar{l}$	$\bar{h}ll$		
$hkl = 511$ $\theta = 37^\circ 31'$ $\varepsilon = 15^\circ 45'$	$I_1 (i = \theta + \varepsilon)$	221	320	1.45	203	292	1.44	—
	$I_2 (i = \theta - \varepsilon)$	420	603	1.43	399	572	1.43	—
	I_2/I_1 (obs.)	1.90	1.88	—	1.93	1.95	—	2.16 (2.04)
$hkl = 611$ $\theta = 46^\circ 16'$ $\varepsilon = 13^\circ 15'$	$I_1 (i = \theta + \varepsilon)$	503	342	1.47	468	342	1.38	—
	$I_2 (i = \theta - \varepsilon)$	750	540	1.39	704	530	1.32	—
	I_2/I_1 (obs.)	1.50	1.57	—	1.50	1.55	—	1.53 (1.52)

Table 3. *Measurements with a laevo-rotatory crystal*

Values within brackets are for the dextro-rotatory crystal of Table 2

hkl	Condition of incidence	Intensities observed, I				Average I/\bar{I}	Average I_2/I_1
		hll	$\bar{h}\bar{l}\bar{l}$	$h\bar{l}\bar{l}$	$\bar{h}ll$		
511	$I_1 (i = \theta + \varepsilon)$	216	153	218	149	1.44 (1.44)	1.98 (1.92)
	$I_2 (i = \theta + \varepsilon)$	423	279	450	315		
611	$I_1 (i = \theta + \varepsilon)$	109	146	112	154	1.38 (1.39)	1.53 (1.53)
	$I_2 (i = \theta - \varepsilon)$	171	234	180	252		

Table 4. *Calculations with atomic scattering factors for ionized and unionized atoms*

Zachariassen's values (1929, denoted by Zach.) are for ionized atoms at room temperature. Viervoll & Ögrim's data (1949, denoted by V. & Ö.) are for unionized atoms. For chlorine, the corrections to the scattering factor owing to anomalous dispersion have been included

hkl	$\frac{\sin \theta}{\lambda}$	Ref.	Atomic scattering factors			$ F ^2$ calc.		Ratio	Measured ratio
			Na	Cl	O	hll	$\bar{h}\bar{l}\bar{l}$		
511	0.395	{ Zach. V. & Ö.	4.1	$6.64 + 0.66i$	1.3	68	98	1.44	1.44
			5.45	$8.44 + 0.66i$	2.9	56	100	1.96	
611	0.469	{ Zach. V. & Ö.	3.2	$5.80 + 0.66i$	0.8	41	32	1.28	1.39
			4.6	$7.80 + 0.66i$	2.4	83	48	1.73	

5. More detailed measurements

The above measurements indicate that the absolute configuration of a dextro-rotatory crystal is the structure *A*. Further confirmation of this was obtained by making a more detailed study of the reflexions 511 and 611, which gave large values for the Bijvoet inequality, the observed differences being nearly 40%. For these, accurate measurements of the intensity ratio of the inverse reflexions were made in all the eight settings.

The (hll) planes are neither parallel nor perpendicular to the surface of the plate, and consequently the reflexion is asymmetric. The intensity measured would depend on the angle of incidence of the X-ray beam on the crystal surface. If ε is the angle between a reflecting plane (hll) and the surface of the crystal, the reflexion hll can be measured under two conditions in which the angles of incidence are $(\theta + \varepsilon)$ and $(\theta - \varepsilon)$; the corresponding angles of emergence would be $(\theta - \varepsilon)$ and $(\theta + \varepsilon)$ respectively. It can be shown that the ratio of the integrated intensities I_1 and I_2 , measured in the two settings, is given by $I_2/I_1 = \sin(\theta + \varepsilon)/\sin(\theta - \varepsilon)$. The four values for the asym-

metry effect I_2/I_1 and the four values of the anomalous dispersion effect $I_{hll}/I_{\bar{h}\bar{l}\bar{l}}$ have been calculated separately and are shown in Table 2. It is seen that the four measured values of I_2/I_1 are in reasonable agreement with the calculated value. The quantities within brackets in the last column of Table 2 represent the values of I_2/I_1 if ε is different by 1°, owing to an error of grinding.

As a further check, the 511 and 611 reflexions were measured in all the eight settings with a laevo-rotatory crystal. The data are presented in Table 3 and it is seen that the Bijvoet inequality shows an exactly inverse trend, which is to be expected for the two enantiomers.

Finally, the observed values were compared with those calculated using Zachariassen's values (1929) for the atomic scattering factors of the ionized atoms Na^+ , Cl^{+5} and O^{-2} at room temperature. These, together with those calculated from Viervoll & Ögrim's data (1949) for unionized atoms are given in Table 4. Although the measured data do not agree with either perfectly, they lie in between.

No attempt was made to convert the measured

integrated intensities into absolute values, as it was outside the scope of the present study. However, it will be appreciated that the ratio of the measured intensities of the inverse reflexions represents the ratio of the squares of the structure amplitudes, since absorption and other corrections are identical for both the measurements.

The detailed measurements thus confirm that the structure of a dextro-rotatory crystal is the structure *A*, whose atomic coordinates, with respect to a right-handed system of coordinates are those given in § 1. The measurements with the laevo-rotatory crystal showed an exactly inverse trend, and therefore its structure would be the inverse of the one described.

6. Comparison with optical-activity calculation

With the structure *A* (Fig. 1) and the atomic coordinates given in § 1, Ramachandran (1951*b*) has calculated the optical rotatory power (ρ) of the crystal from the known polarizability and optical anisotropy of the O_3 group. While he obtained the correct order of magnitude (ρ calculated is $30^\circ \text{ cm.}^{-1}$, ρ observed is $31.3^\circ \text{ cm.}^{-1}$, for 5893 \AA), we are particularly interested in the sign.

The parameter g (the value of the isotropic gyration tensor) was given as positive in the above paper. However, a recalculation made recently showed that it is negative for the structure *A*, and that the actual value is also slightly different, namely $38.8^\circ \text{ cm.}^{-1}$ for 5893 \AA . The negative sign is inherent even in the earlier calculations, but no stress was laid on the sign then.

Now, the polarizability theory of optical activity (Ramachandran, 1951*a*), on the basis of which the above calculations were made, demands that g and ρ are opposite in sign, if ρ is defined to be positive for a dextro-rotatory crystal. Consequently, it follows that a crystal with the absolute configuration corresponding to structure *A* must be dextro-rotatory, in agreement with direct X-ray determination.

It is thus gratifying to note that the polarizability theory of optical activity leads to the correct absolute

configuration and can therefore be used confidently in those cases where the more direct X-ray method is found to be difficult.

It was noticed that in a review article Wooster (1953) had arrived at an opposite conclusion regarding the sense of the optical activity for the structure *A*. However, he had based his observations on the work of Ramachandran (1951*b*) and on the wrong sign of g given there for sodium chlorate.

The Unicam single crystal goniometer was modified for Geiger-counter measurements, as mentioned in § 4, by Sri S. Raman, and we wish to thank him for making the instrument available to us. We are also grateful to Dr S. Ramaseshan and Sri S. Venkataraman for discussions on the theory of optical activity and to the referee for drawing our attention to an error in the first draft regarding the sign of the gyration tensor components.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

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Ein um das Zentralatom drehbares Tetraedermodell als Hilfsmittel bei der Bestimmung von Kristallstrukturen. VON F. LIEBAU, G. LINDEMANN UND S. NORDMEYER, *Institut für anorganische Chemie der Deutschen Akademie der Wissenschaften zu Berlin, Berlin-Adlershof, Deutschland*

(Eingegangen am 16. Juni 1957)

Bei der Strukturbestimmung einer kristallinen Substanz wird man in der Regel zuerst die Lagen der Atome mit

der höchsten Ordnungszahl und erst später die der leichteren Atome finden. Demzufolge werden in Kristallen