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The crystal structure of dithio-oxamide.

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The molecular structure of dithio-oxamide (rubeanic acid), $(CS.NH_2)_2$, has been determined by an X-ray diffraction study of single crystals. The crystals are triclinic with

$a = 5{\cdot}857$ Å, $b = 10{\cdot}690$ Å, $c = 3{\cdot}933$ Å,
$\alpha = 90°31'$, $\beta = 102°47'$, $\gamma = 92°24'$.

The space group is $P\bar{1}$ and the unit cell contains two planar molecules, each lying on a centre of symmetry. The structure was refined by successive three-dimensional differential syntheses, performed on the Manchester University electronic computer. The bond lengths are

	Molecule 1	Molecule 2
C–C	1·544 Å	1·534 Å
C–N	1·308	1·285
C–S	1·663	1·662

A detailed discussion of this analysis and of the results will be presented later, but it is of interest to note that the C–C distance is that of a single bond, in agreement with recent work on α-anhydrous oxalic acid (Cox, Dougill & Jeffrey, 1952) and on oxalic acid dihydrate (Ahmed & Cruickshank, 1953). A preliminary value of 1·49 Å has been published for the corresponding bond in oxamide (Romers, 1953).

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On the relation among the results of various structure investigations on potassium bicarbonate, $KHCO_3$.

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Table 1. *The cell dimensions determined by several investigators*

	a	b	c	β
(i)	15·01	5·69	3·68 Å	104° 30′
(ii)	15·01±0·04	5·50±0·02	3·67±0·01 kX.	104° 30′
(iii)	15·11	5·67	3·71 Å	103° 45′
(iv)	15·176±0·003	5·630±0·002	3·708±0·002 Å	104° 31′±5′
	a'	b	c'	β'
(v)	15·129	5·630±0·002	3·708±0·002 Å	103° 49′

(i): Dahr (1937); (ii): Herpin (1952); (iii): our previous values (1952); (iv): our revised values; (v): our [102] axis = a' axis

Since we reported in a short communication to this journal on the crystal structure of potassium bicarbonate (Nitta, Tomiie & Koo, 1952), there has appeared another similar report by Herpin (1952). Though the atomic parameters obtained by Herpin are not as accurate as ours, her results agree approximately with ours. As to the cell dimensions, there exist slight differences among the values reported by various X-ray investigators (Dahr, 1937; Nitta *et al.*, 1952; Herpin, 1952). We have therefore re-examined the cell dimensions by the back-reflexion method using (18,2,0), (470), (404), (40$\bar{4}$), (204) and (20$\bar{4}$) spectra with the rocksalt Debye–Scherrer lines as reference. The values thus obtained are listed in the fourth row of Table 1. The calculated density is $\varrho_c = 2{\cdot}1846$ g.cm.$^{-3}$, which is closer to the values obtained by direct measurements (Groth, 1906–19). For comparison, all the previously reported values of the cell dimensions are given in Table 1.

Couture-Mathieu (1950) has examined the Raman effect of single crystals of $KHCO_3$ and has determined the orientation of the carbonate ions in them. She proposed an atomic arrangement in the unit cell using her results and Dahr's X-ray data (1937), assuming that the carbonate ions are linked by hydrogen bonds in the same manner as those existing in $NaHCO_3$ (Zachariasen, 1933). However, we had thought that Couture-Mathieu's proposed structure did not agree with ours, in respect of the orientation of the carbonate ions, if her axes were the same as ours.

To obtain the relationship between Couture-Mathieu's Raman investigation and our X-ray one, we have re-investigated the problem, making optical extinction and goniometric measurements of the crystal. From our examination, we found that the a axis described in Groth's *Chemische Krystallographie*, and also adopted by Couture-Mathieu as the a axis, was not the a axis but the [102] axis, which has been chosen by all of the X-ray investigators. On the basis that her a axis is not the a axis of the X-ray investigators, it was found that Couture-Mathieu's conclusion for the orientation of the carbonate

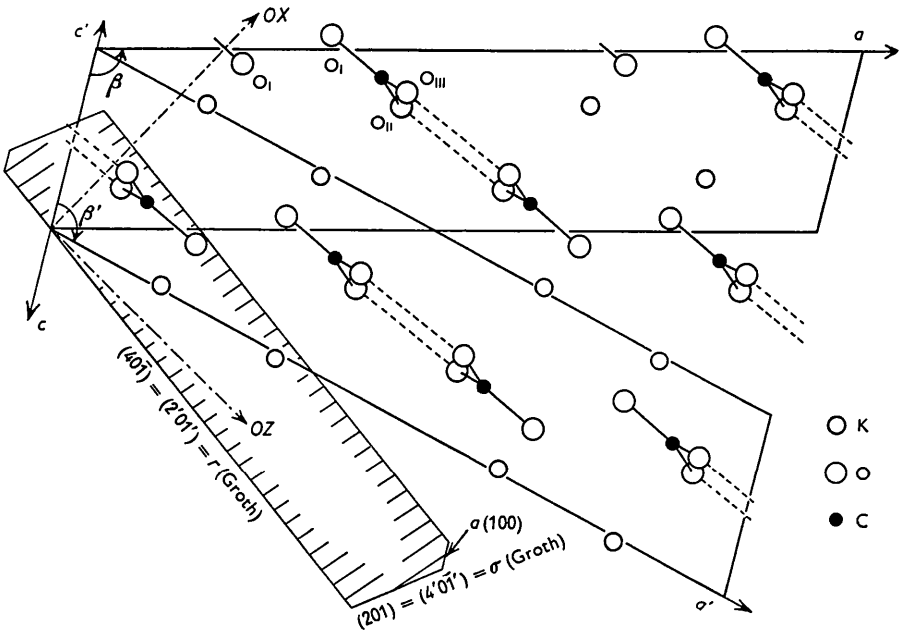

Fig. 1. The atomic arrangement projected on (010). The a, c axes and β represent the axial system of the X-ray investigators; the a', c' axes and β' represent that of Couture-Mathieu. The OX and OZ indicate the bisectors of the optical axes. The shaded section is the cross section of the actual crystal perpendicular to the (010) plane. The notations for planes, r, σ etc., are similar to Groth's.

ions is correct and her x and z atomic parameters agree approximately with ours when her choice of axes is transformed to ours. These relations are shown in Fig. 1. In either of these two axial systems, there is much similarity in the cell dimensions and the space group notation does not change. Our present cell dimensions, if based on the choice of the axes given in *Chemische Krystallographie*, are given in the fifth row of Table 1. The y parameters adopted by Couture-Mathieu, which were different from the X-ray values by approximately $\frac{1}{4}$, led to the incorrect structure. All the reported atomic parameters are listed in Table 2. The parameters reported by Couture-Mathieu are transformed to our axial system.

Thus in the present case of the crystal structure of potassium bicarbonate care must be taken in the choice of axial system.

Table 2. *Various atomic parameters*

		x	y	z
K	(1)	$0{\cdot}163_3$	0·021	0·301
	(2)	0·168	0·777	0·265
	(3)	0·166	0·025	0·3
O_I	(1)	$0{\cdot}196_0$	0·541	0·078
	(2)	0·190	0·270	0·125
	(3)	0·195	0·525	0·090
O_{II}	(1)	$0{\cdot}081_3$	0·725	−0·317
	(2)	0·075	0·483	−0·252
	(3)	0·082	0·725	−0·285
O_{III}	(1)	$0{\cdot}078_9$	0·320	−0·233
	(2)	0·070	0·084	−0·268
	(3)	0·082	0·325	−0·285
C	(1)	$0{\cdot}117_7$	0·529	−0·150
	(2)	0·112	0·279	−0·129
	(3)	0·122	0·525	−0·160

(1): Ours; (2): Couture-Mathieu; (3): Herpin.

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