validity of the intensity measurement. It was highest for well-defined lines measured with the densitometer and diffractometer and lowest for the broader and weaker lines which were visually estimated. Scale and temperature factors were obtained from the least-squares solution of the semilog plot of G_i^2(obsd.)/G_i^2 (calcd.) *vs.* $\sin^2\theta/\lambda^2$. The value 5.43 Å.^{2} was ultimately obtained for *B*.

Thirty-one observational equations were used and reduced in the usual way to two normal equations which were solved for x_1 and x_2. The 331 and 800 lines were omitted because of uncertainty in the signs of their structure factors. Atom form factors were taken from "Internationale Tabellen."[7] The form factor for cerium(IV) was approximated by the expression

$$f_{\mathrm{Ce(IV)}} = \frac{54}{58} f_{\mathrm{Ce}}$$

The final values for the parameters are

$$x_1 = 0.1951 \pm 0.0008$$
$$x_2 = 0.3119 \pm 0.0014$$

The uncertainties are standard deviations calculated according to Wittaker and Robinson.[10] The interatomic distances are therefore

$$\text{Ce–Cl} = 2.55 \pm 0.01 \text{ Å.}$$
$$\text{C–N} = 1.40 \pm 0.03 \text{ Å.}$$
$$\text{CH}_3\text{–Cl} = 3.79 \pm 0.05 \text{ Å.}$$

The error given here is believed to be somewhat low since no account of systematic errors has been taken in the statistical treatment.

Subtracting 0.99 Å., the covalent radius of chlorine, from the cerium–chlorine distance gives the value 1.56 Å. for the octahedral radius of cerium.[11] The carbon–nitrogen distance is significantly shorter than 1.47 Å., the sum of the covalent radii.[11] A shortening of this bond is expected because of the positive charge on the nitrogen atom. In any event, short carbon–nitrogen bonds are by no means unusual.[12] The sum of the van der Waals radii for chlorine and a methyl group is 3.80 Å.,[11] in excellent agreement with the value given above for the distance from methyl group to chlorine atom.

Observed and calculated values of G_i^2 are given in Table I. The discrepancy factor, $R = \Sigma\,|\Delta G_i^2|\,/\,\Sigma\,|G_i^2(\text{obsd.})|$, is 21%. If computed on the basis of structure factors, as is usually done, *R* would be about half as great.[9]

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(10) E. Wittaker and G. Robinson, "The Calculus of Observations," 4th Edition, Blackie and Son, London, 1944, Chapter 9.

(11) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948.

(12) C. Brown, *Acta Cryst.*, **2**, 228 (1949).

LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC AND STRUCTURAL CHEMISTRY, UNIVERSITY OF LEEDS, ENGLAND]

The Crystal Structure of Sodium Oxalate

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RECEIVED MARCH 29, 1954

Sodium oxalate has a simple type of ionic structure with a distorted octahedral coördination of oxygen atoms around the sodium ions. The space group is $P2_1/a$ with two $Na_2(COO)_2$ in a unit cell of dimensions a = 10.35, b = 5.26, c = 3.46 Å., all ±0.02 Å., β = 92°54 ± 6′. The crystal structure was determined from the (*h*0*l*) and (*hk*0) intensities and the atomic parameters were refined by Fourier projections and difference syntheses on (010) and (001). The dimensions of the oxalate ion, C–C = 1.54 Å., C–O = 1.23 Å., C–C–O 121° and 115°, O–C–O 124°, are in good agreement within experimental errors with those determined in ammonium oxalate hydrate. The oxalate ion in the sodium salt is planar, in contrast to that in the ammonium oxalate hydrate, and it is concluded that this difference in stereochemistry is a consequence of the hydrogen bond structure in the latter.

The difference in configuration between the nonplanar oxalate ion found in $(NH_4)_2(COO)_2{\cdot}H_2O$[3] and the planar acid molecule in α-$(COOH)_2$,[4] β-$(COOH)_2$,[5] $(COOH)_2{\cdot}2H_2O$,[6] raises the question as to whether this is a characteristic difference between the ion and the acid molecules or a consequence of interionic or intermolecular forces in the crystal structures. An examination of the reported data on oxalate structure does not provide a conclusive answer. The crystal structures of the isomorphous $K_2(COO)_2{\cdot}H_2O$ and $Rb_2(COO)_2{\cdot}H_2O$ were studied by Hendricks,[5] who reported the crystallographic data included in Table I. If the space group of these compounds in C2/c, the oxalate ion must be centrosymmetrical and with the assumption of planar trigonal carbon valences, the whole ion must be planar. However the space group C2/c is not uniquely determined and the alternative Cc symmetry must be eliminated by the results of the structure analysis. Hendricks' early analysis was based on qualitative intensity estimations of 37 reflections, and it would appear from the published record that not very good agreement was obtained between observed and calculated intensities. The dimensions found for the oxalate ion, C–C = 1.60 Å., and unequal C–O bonds 1.14 Å., and 1.30 Å., suggest ill-defined atom positions, at least for the anions. Although the cations may be approximately arranged according to the space group C2/c, there is no evidence that this is necessarily true for the oxalate ions and water molecules and the space group assignment must be regarded as inconclusive.

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(1) Department of Chemistry, University of Pittsburgh.

(2) Scaife Foundation Fellow, University of Pittsburgh.

(3) G. A. Jeffrey and G. S. Parry, *J. Chem. Soc.*, 4864 (1952); S. Hendricks and M. E. Jefferson, *J. Chem. Phys.*, **4**, 102 (1936).

(4) E. G. Cox, M. W. Dougill and G. A. Jeffrey, *J. Chem. Soc.*, 4854 (1952).

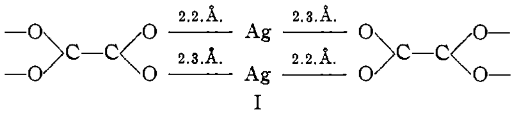
(5) S. Hendricks, *Z. Krist.*, **91**, 48 (1935).

(6) D. W. J. Cruickshank and F. R. Ahmed, *Acta Cryst.*, **6**, 385 (1953).

Table I

Salt	Space group	No. of moles in cell	Oxalate ion symm.	Cell dimensions *a*	*b*	*c*	*β*	Density Obs.	Calcd.
$K_2C_2O_4.H_2O$	C2/c	4	$\bar{1}$	9.32	6.17	10.65	110° 58′	2.154	2.139
$Rb_2C_2O_4.H_2O$	C2/c	4	$\bar{1}$	9.66	6.38	11.20	110° 30′	2.763	2.845
$Ag_2C_2O_4$	$P2_1/a$	2	$\bar{1}$	9.47	6.16	3.46	104°	5.029	5.151
$Na_2C_2O_4$	$P2_1/a$	2	$\bar{1}$	10.35	5.26	3.46	92° 54′	2.34	2.365

The crystal structure of silver oxalate has been studied in more detail.[7] It is not truly an ionic structure for the principal feature is the existence of chain molecules of composition $(Ag_2C_2O_4)_x$ with strong bonds between silver and oxygen atoms along the length of the chain, I. In this respect it resembles the structure of *β*-oxalic acid II. By space group requirements the oxalate group is centrosymmetrical, but it is reported to be non-planar in that the carbon atoms are displaced to opposite sides of the plane determined by the oxygen atoms. This may well be an error in the atomic positions for the light atoms, for the agreement between the observed and calculated structure factors is better for structure factors calculated from the silver atoms alone than for those which include the scattering contributions from the atoms of the oxalate ion.



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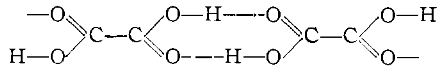

II

Apart from cell dimensions and optical data on the hydrated calcium oxalates, no other crystal data are reported for the neutral oxalate salts. Sodium oxalate was selected as an appropriate means for studying this problem by structure analysis because, in the absence of water of crystallization, it would most likely provide an example of the oxalate ion in a normal ionic environment, in direct contrast to the hydrogen-bonded ammonium oxalate hydrate. The only previous reference to the crystal structure which could be found was by E. Langyel[8] who commented that the crystals might be triclinic.

The Crystal Structure Analysis.[9]—The cell dimensions and uniquely determined Space Group are given in Table I. With two $Na_2(COO)_2$ molecules in the unit cell, the Na ions lie in general positions and the centers of symmetry of the oxalate ions are at (0, 0, 0) and (1/2, 1/2, 0).

Suitable crystals for intensity measurements were obtained by slow cooling of aqueous solutions; as no corrections were made for absorption, these errors were minimized by using small crystals of approximately uniform cross-section of 0.15 mm. (μ = 40.2 cm.$^{-1}$). The *hk*0 and *h*0*l* reflections were recorded on Weissenberg photographs by the multiple-film technique with Cu Kα radiation and their intensities were estimated visually. After correlation and correction for the Lorentz-polarization factors, 71 (*hk*0) and 47 (*h*0*l*) structure amplitudes were available for the determination of the twelve unknown atomic parameters.

The projection down the short *c*-axis was examined first. The phase problem was solved from the contour map of the Patterson projection (Fig. 1), whereon it was possible to identify the three Na–Na vector peaks, A, B, C, corresponding to the separations 0, $1/2 - 2y_{Na}$; $1/2 - 2x_{Na}$, 0; $2x_{Na}$, $2y_{Na}$. With the positions of the sodium atoms determined, the orientation of the oxalate ion about the symmetry center was selected so as to give reasonable coördination around the sodium ions and to satisfy the principal remaining features of the Patterson synthesis. This trial structure was refined by a Fourier synthesis (Fig. 2) which showed resolution of all the atomic peaks. After a further Fourier refinement and determination of more exact scale and temperature factors, the agreement index, *R*, was 0.21, which confirmed the structure solution in this projection. Further refinement was carried out by difference syntheses and re-

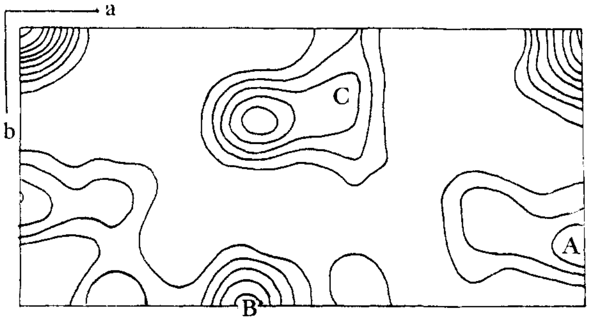

Fig. 1.

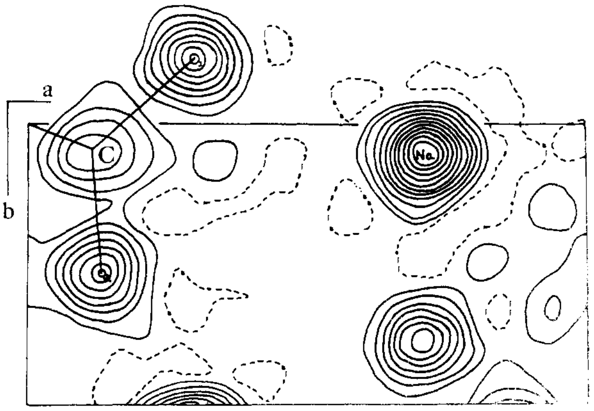

Fig. 2.

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[7] R. L. Griffith, *J. Chem. Phys.*, **11**, 499 (1943).

[8] E. Langyel, *Z. Krist.*, **97**, 67 (1937).

[9] Material supplementary to this article has been deposited as Document number 4241 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints or $1.25 for 35 mm. microfilm by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

sulted in the x, y-coördinates given in Table II and an agreement index of 0.162. To obtain the z-parameters, the b-axis projection was examined. Of the 47 ($h0l$) intensities which were measured, six corresponded to unitary structure factors of greater than 0.6; consequently the phases of the majority of the structure factors could be determined by application of the inequality relationship $(U_H \pm U_{H'})^2 \leqq (1 \pm U_{H+H'})(1 \pm U_{H-H'})$. In the Fourier synthesis the Na ion and one oxygen atom were resolved, but the other oxygen and the carbon atom were superimposed. The agreement index at this stage of the analysis was 0.24. The atomic parameters were refined by difference syntheses to correct for termination of series errors and obtain more accurate positions for the unresolved atoms. The final agreement index was 0.139. The x coördinates common to both projections agreed within 0.02 Å.

TABLE II

	Atomic coördinates in fractions of monoclinic axes			Atomic coördinates in Å. (Z' is ⊥ to X and Y)		
	x	y	z	X	Y	Z'
Na	0.353	0.053	0.307	3.600	0.279	1.061
O^1	.152	− .114	.163	1.544	−0.600	0.563
O^2	.067	.260	.228	0.653	1.368	0.788
C	.064	.040	.107	0.643	0.210	0.370

The atomic coördinates are given in Table II both in fractions of the monoclinic cell edges and in Å. The interatomic distances and valence angles are given in Table III. The oxalate ion is planar to well within the limits of the experimental errors. The equation to the plane containing O and the origin is

$$x + 0.637y - 2.064z = 0$$

and C is 0.005 Å. out of that plane.

TABLE III

INTERATOMIC DISTANCES AND VALENCE ANGLES

The oxalate ion

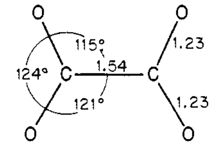
C–C	1.54 Å.	C–C–O^1	120.6°
C–O^1	1.23	C–C–O^2	115.3°
C–O^2	1.23	O^1–C–O^2	124.3°
O^1–O^2	2.18		
O^1–$O^{2'}$	2.69		

Interionic distances, Å.

Na (I) to	O^1 (I)	2.29 (I, x,y,z)
	O^1 (II′)	2.54 (II′, $^1/_2 - x$, $^1/_2 + y$, $1 - z$)
	O^1 (III′)	2.64 (III′, $^1/_2 - x$, $^1/_2 + y$, $-z$)
	O^2 (IV′)	2.35 (IV′, $^1/_2 - x$, $-^1/_2 + y$, $1 - z$)
	O^2 (V′)	2.58 (V′, $^1/_2 - x$, $-^1/_2 + y$, $-z$)
	O^2 (III)	2.45 (III, $^1/_2 + x$, $^1/_2 - y$, z)

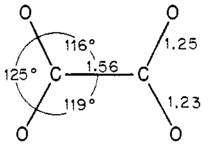
The standard deviation of the x,y-coördinates from the resolved projection estimated by Cruickshank's method[10] were: Na, 0.006; O, 0.008; C, 0.020 Å.

Discussion of the Structure.—In $Na_2(COO)_2$ the oxalate ion is planar, whereas in $(NH_4)_2(COO)_2 \cdot H_2O$ the two carboxyl groups are twisted about the central C–C bond so as to lie in planes inclined at 28°. With this exception the dimensions of the ions, III and IV, are identical within the limits of the experimental errors of the two analyses. This close agreement could be fortuitous for neither investigation was pursued to the degree of precision which is now possible for organic crystal structures,[11] and differences up to 0.07 Å. for example, could exist between the two C–C bond lengths. However the agreement between the C–O bond lengths and the correlation between these results and those from the α-oxalic acid[4] and the oxalic acid dihydrate[6] in which the C–C distances were 1.56 and 1.53 Å. suggests that this is unlikely. It would appear then that the difference in configuration of the two ions makes little difference to the C–C bond length and therefore also to the binding energy of the central carbon atoms. This supports the conclusion put forward in an earlier paper[4] that there is a relatively much smaller amount of π bond-character in the C–C bond in oxalic acid and the oxalate ion than in the situation where the carboxyl group is conjugated to a phenyl, for example, *cf.* the recent structure determinations of nicotinic acid[12] (V) and salicylic acid[13] (VI).



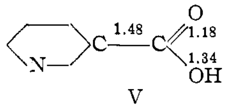
planar ion in $Na_2(COO)_2$

III

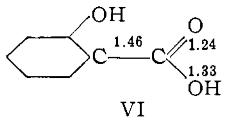


non-planar ion in $(NH_4)_2(COO)_2 \cdot H_2O$

IV



V



VI

The explanation of the difference in configuration of the two oxalate ions must therefore be sought in their respective environments. The essential features of the ionic structure of sodium oxalate are illustrated in Fig. 3, which shows the normal projection of the structure on (001). Two oxalate ions in adjacent unit cells in the c-axis direction are shown in order to illustrate the coördination

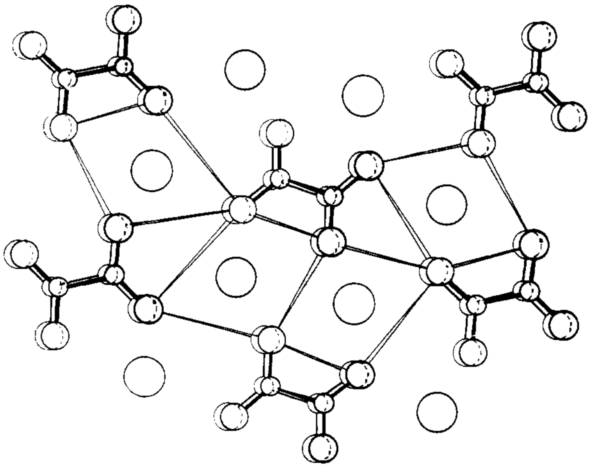


Fig. 3.—Structure of $Na_2(COO)_2$, showing octahedral coördination of sodium ions.

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(10) D. W. J. Cruickshank, *Acta Cryst.*, **2**, 65 (1949).

(11) G. A. Jeffrey, D. W. J. Cruickshank and E. G. Cox, *Quart. Revs.*, III, **4**, 335 (1953).

(12) W. B. Wright and G. S. D. King, *Acta Cryst.*, **6**, 305 (1953).

(13) W. Cochran, *ibid.*, **6**, 260 (1953).

around the sodium ions. The structure can be described as a packing of linear arrays of the respective ions parallel to the *c*-axis, so that each column of ions is surrounded by six others of opposite charge. The arrangement of these columns in respect to each other and the spacing in the *c*-axis direction is such as to give distorted octahedral coördination of oxygen atoms around each sodium ion. The degree of distortion is indicated by the Na...O distances listed in Table II and shown diagrammatically in Fig. 3.

In contrast to this comparatively simple ionic structure, that of the ammonium oxalate hydrate is complicated by hydrogen bonding between the water molecules and the oxalate and ammonium ions. The structure is shown in Fig. 4. The oxalate ions are hydrogen bonded through the water molecules into linear chains parallel to the *a* axis. The arrangement of the adjacent chains and of the ammonium ions is then governed by the requirement of a coördination of four oxygen atoms about the $(NH_4)^+$ and of two oxygens and two ammonium ions about the water molecule which is as close to tetrahedral as possible.

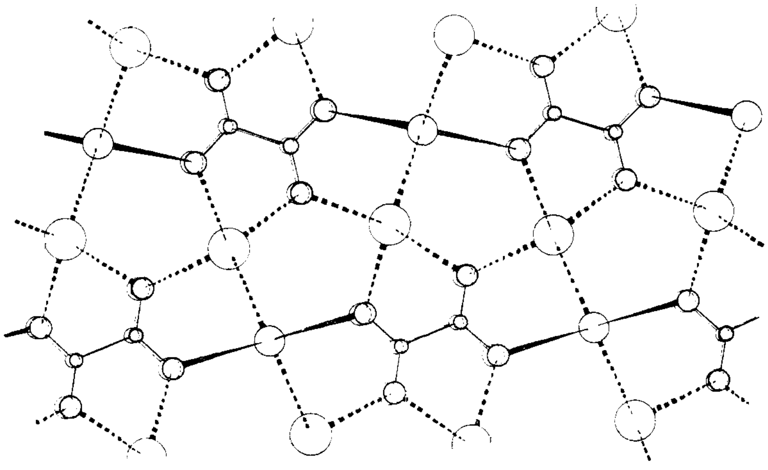

Fig. 4.—Structure of $(NH_4)(COO)_2H_2O$: full lines, O_1–H_2O 2.80 Å.; dotted lines, NH_4^+–H_2O, 2.88 Å., NH_4^+–O_1, 2.67 Å.; NH_4^+–O_2, 2.81, 2.85 Å.

In view of the well-established directional character of hydrogen bonding and the rather simple ionic pattern of the sodium oxalate structure, it is concluded that the normal configuration of the oxalate ion is planar and that the non-planar structure in the $NH_4(COO)_2 \cdot H_2O$ is a direct consequence of the hydrogen bonding in the crystalline state. It seems likely that, in the complete absence of bonding interaction between the π-electrons of the two carbonyl groups in an isolated ion, a non-planar configuration might be the more stable due to the repulsion of the oxygen poles. Consequently some consideration was given to calculating the possible influence of the $\overset{+}{C}$–$\overset{-}{O}$ dipoles on the configuration of minimum potential energy in respect to rotation about the central C–C bond. Calculations of the difference in the electrostatic energy between the planar and non-planar configurations[14] were based on two conventional models: (i) with a fractional electronic charge x_e on each oxygen atom, (ii) with dipoles oriented in the direction of the C–O bonds and situated at 0.70 Å. from the carbon atom centers.

With the geometry for the oxalate ion as determined in this analysis and $x_e = 0.5$ (μC–O = 3.0 *D*), the 90° staggered configuration was that of lowest potential energy in both calculations, with ΔU equal to 2.1 and 4.0 kcal./g. ion for (i) and (ii), respectively. For (ii), the difference was approximately 10% of the total dipole interaction energy. In addition to these classical repulsion forces between poles or dipoles, there will be energy differences due to exchange repulsion and dispersion forces (assuming that the oxygen atoms in different carboxyl groups can be regarded as isolated electronic systems). These forces are balanced at an average equilibrium distance which defines the van der Waals radius. A value of 1.4 Å. for oxygen atoms is given by Pauling,[15] but it appears from the results of the oxalic acid structure analysis that 1.6 Å. is more appropriate for carboxyl oxygen atoms in directions other than along hydrogen bonds. On this basis also, the staggered configurations for the ion would be favored, for the $O^1 \ldots O^{2'}$ and $O^1 \ldots O^{1'}$ distances of 2.7 and 3.4 Å. in the planar form become 3.1 Å. on 90° rotation of one of the carboxyl groups. Although there is some doubt as to the validity of arguments based on van der Waals radii when applied to atoms in the same molecule and in directions subtending angles less than a right angle with the primary bonds, it appears unlikely that the difference in the energy terms arising from dispersion and repulsion forces would exceed those due simply to the concentration of electron density over nuclear charge in the vicinity of the carboxyl oxygen atoms.

While more detailed calculations would be desirable, these would require a degree of detailed knowledge of the electron distribution in the ion which is not at present available. However, it is not unreasonable to assume that the results of these more accurate calculations would be in the same sense, although not necessarily of the same magnitude, as those for the models discussed in this paper. The interpretation of the rather unusual circumstance of the oxalate ion having a different stereochemistry in two different salts therefore appears to come from the balance between the opposing effects of the polar repulsions of the carboxyl oxygens and of the π electron configuration across the C–C bond. In the absence of any strong intermolecular forces, the conjugation effect is the greater and the ion is planar. In the case of the ammonium oxalate hydrate, the requirements of the pattern of hydrogen bonds in the crystal lattice are such that they, and not the intramolecular forces, determine the stereochemistry of the oxalate ion.

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[14] J. F. Böttcher, "Theory of Electric Polarisation," Elsevier Press, Houston, Texas, 1952.

[15] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.