equivalent about $\frac{3}{4}, v, 0$) involves both the hydrogen bonds of the terminal carboxyl $O_3C_5O_4$ and both the hydrogen bonds of the central carboxyl group $O_5C_6O_6$. The two equivalent pairs of spirals are tied together in the *a* direction by a pair of centrosymmetrically related molecules. The second family of spirals about the screw axes at $\frac{1}{4}, v, \frac{1}{2}$ and $\frac{3}{4}, v, \frac{1}{2}$ involve the bonds O_3–O_6 which formed part of the first spirals and the dimer type pair of O_1–O_2 bonds. The successive turns of the second type of spiral are linked by the O_1–O_7 hydrogen bonds.

The rigidity imparted to the crystal by this highly interlocked hydrogen bond system is evidenced by the low value of the temperature factor *B*. The intermolecular distances not involved in the hydrogen bonding are well in accord with the accepted van der Waals radii for structures of this type.

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X-ray Crystal Analysis of the Substrates of Aconitase.*

III. Crystallization, Cell Constants, and Space Groups of Some Alkali Citrates

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Cell dimensions and space groups have been determined for twelve alkali citrates and are listed with five others determined previously. The *p*H of the dissolved crystal is used in each case as a check on the ionic content of each crystal type.

The cell constants and space groups of the alkali citrates listed in Table 1 have been determined as part of a study of the structure of the substrates of the enzyme aconitase (Nordman, Weldon & Patterson, 1960*a*, *b*). In this paper the alkali citrates are represented by symbolic formulae of the type M_nH_{3-n}cit in which '*M*' stands for the metal and 'cit' stands for the tri-ionized citrate ion

$$^{-}OOC.CH_2.C(OH)(COO^{-}).CH_2.COO^{-}.$$

Crystallization

The method of crystallization used in each case is given in Table 1. Aqueous salt solutions were made by allowing 1·0*M* citric acid to react with weighed amounts of the appropriate alkali carbonate. In some cases slow evaporation to dryness led to usable crystals. In other cases crystals were grown from an aqueous citrate solution layered under either ethanol or acetone, i.e., under hydrophilic solvents in which citrate salts are nearly insoluble (cf. King, Magdoff, Adelman & Harker, 1956). Portions of the solution 2 c.c. in volume, were layered under 10–20 c.c. of the organic solvent in 16 × 150 mm. test tubes. Crystals grew in a week or two in stoppered tubes.

Using lithium, sodium, potassium, rubidium, and

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Table 1. *Cell constants for some alkali citrates*

Standard errors

Axial lengths: < 0·13% except* < 0·20%. Axial angles: < 0·10° except* < 0·25°

Cell volumes and calculated densities < 0·22% except* < 0·27%. Observed densities reproducible to 1%

Substance	a (Å)	b (Å)	c (Å)	β (°)	Probable space group	ϱ_o	ϱ_c	n	V (Å^3)	pH	Technique
$LiH_2cit.H_2O$	10·873	17·334	9·186		$Pbca$	1·651	1·660	8	1729·7	3·64	dried 30 °C.
LiH_2cit	9·143	11·354	7·475	107·75	$P2_1/a$	1·783	1·791	4	734·8	3·52	dried 90 °C.
NaH_2cit	9·648	11·680	7·481	105·25	$P2_1/a$	1·747	1·749	4	813·4	3·70	dried 70 °C.
KH_2cit (1)	12·981	14·970	9·442	α = 91·60 β = 93·35 γ = 110·00	$P\bar{1}$	1·777	1·780	8	1719·0	3·80	layer, dried 25 °C.
RbH_2cit (2)	19·145	9·710	14·924	108·63	$P2_1/c$	2·064	2·098	12	2628·5	3·50	dried 25 °C.
$(NH_4)H_2cit$	7·492	10·539	6·150	α = 102·42 β = 105·57 γ = 104·67	$P\bar{1}$	1·612	1·575*	2	441·3*	3·75	layer, dried 25 °C.
$Na_2Hcit.H_2O$	15·841	5·319	10·795	101·27	$P2_1$ or $P2$	1·831	1·893	4	892·2	5·04	layer
K_2Hcit	10·734	18·877	9·623		$B2mb$ or $Bm2_1b$	1·816	1·829	8	1949·9	4·96	layer
$(NH_4)_2Hcit$	10·767*	14·736*	6·165*		$Pn2b$	1·527	1·537*	4	978·1*	5·05	layer
$(NH_4)_{\frac{5}{4}}Rb_{\frac{3}{4}}Hcit$	10·760	14·690	6·141*		$Pn2_1m$ or $Pnm2$	1·887	1·895*	4	970·7*	5·12	layer
$Li(NH_4)Hcit.H_2O$	23·161	6·423	6·480	99·03	$P2_1/a$	1·617	1·627	4	952·1	5·02	layer
$LiRbHcit.H_2O$	23·148	6·485	6·481	99·70	$P2_1/a$	2·070	2·082	4	959·0	4·90	layer
$Li_3cit.2\,H_2O$	12·361	9·002	8·984*	95·48	$P2_1/c$	1·638	1·642	4	995·1	7·43	layer
$Na_3cit.2\,H_2O$ (3)	15·709	12·471*	11·266*	103·68	$C2/c$	1·819	1·823*	8	2144·5*	7·65	layer
$Na_3cit.5\,H_2O$ (4)	16·36	26·31	6·41		$Pmcn$			8			
$K_3cit.H_2O$ (5)	13·69	11·72	7·06	112	$P2_1/a$	1·991	2·052	4	1050·3	7·30	product of Merck & Co.
$Rb_3cit.H_2O$	14·373*	11·781	7·386*	112·83	$P2_1/a$	2·613	2·672*	4	1152·3*	8·03	dried 25 °C.

(1) Preliminary measurements were made by C. E. Nordman.

(2) Nordman, Weldon & Patterson (1960*a*).

(3) Our data agree reasonably with Burns & Iball (1954) who give

$$a = 11{\cdot}23 \pm 0{\cdot}05,\quad b = 12{\cdot}501 \pm 0{\cdot}002,\quad c = 15{\cdot}82 \pm 0{\cdot}08\ \text{Å};\quad \beta = 104°\ 22'.$$

(4) Burns & Iball (1954).

(5) Cell dimensions from Burns & Iball (1954), pH and observed density this paper.

ammonium ions, we attempted to make the five possible monovalent salts and the fifteen divalent salts, including mixed salts of the type lithium rubidium hydrogen citrate (LiRbHcit). We obtained crystals of all the monovalent salts, but only six of the possible divalent salts. Crystals were obtained of all the homogeneous trivalent salts except that of ammonium which is reported to be deliquescent. No attempt was made to crystallize any of the thirty possible mixed trivalent salts.

The ratio of alkali cations to citrate ions in a crystal was determined by measurement of the *p*H of an aqueous solution made from it. This procedure is justified for a case such as the citrates, in which the *p*K's are well separated, provided that the solutions are strong enough to insure adequate buffering (cf. Table 1).

The degree of hydration was calculated from the observed density and the known ionic content of the asymmetric unit.

In most cases the degree of ionization of the citrate ion in the crystals obtained corresponded to that in the solutions from which they were grown. However, when a solution of constitution Rb_2Hcit was evaporated, crystals of RbH_2cit grew from the resulting syrup. In layered preparations the following anomalies were observed:

Li_3cit grew from Li_2Hcit under acetone at 23°,
NaH_2cit grew from Na_2Hcit under butanol at 70°,
Na_2Hcit grew from NaH_2cit under ethanol at 23°,
$Na_3cit.2H_2O$ grew from Na_2Hcit under ethanol at 23°.

Cell dimensions and density

Cell dimensions were obtained from measurements of precession photographs taken with Cu *Kα* radiation. The procedure used in reducing the data and the analysis of the errors in the cell constants is described elsewhere (Patterson & Love, 1960).

Crystal density was measured by flotation in mixtures of $CHCl_3$ and CH_2I_2. The density of the flotation mixture was measured by weighing a known volume. This volume was determined by means of a 1 c.c. hypodermic syringe mounted in a holder with a fixed stop for the plunger. The syringe was calibrated by weighing the amount of water delivered by it. When weighings are carried out in stoppered bottles, they are reproducible to about ±0·05%.

Discussion

This survey has revealed four isomorphous pairs. They are:

LiH_2cit; NaH_2cit,
$Li(NH_4)Hcit.H_2O$; $LiRbHcit.H_2O$,
$(NH_4)_2Hcit$; $(NH_4)_{2-x}Rb_xHcit$ ($x \approx \frac{3}{4}$),
$K_3cit.H_2O$; $Rb_3cit.H_2O$.

The third pair are not isomorphous in the strict sense. The cell dimensions of the two salts are very similar but the space groups are not the same. They probably belong to continuous series of isomorphous salts but we have not attempted to prepare other salts of this type.

The collection of three-dimensional X-ray data for the structure analysis of the first pair (LiH_2cit and NaH_2cit) is in progress, and structural studies on the second and possibly the fourth pair are intended.

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