

STUDIES ON THE CRYSTALS SEPARATING FROM AQUEOUS LITHIUM  
NITRATE SOLUTION

G. ARAVAMUDAN\* AND S. RAMASESHAN

Systematic studies (1, 2, 3, 4) on lithium nitrate-water systems have established the existence of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ . In fact Campbell and Bailey (3c) have not only isolated this salt but have succeeded in recording its X-ray powder diagram. During the course of some investigations on  $\text{LiNO}_3\text{-H}_2\text{O}$  systems in this Institute (5) very good single crystals of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  were obtained. This note reports the determination of its space group as well as some morphological studies of anhydrous  $\text{LiNO}_3$  crystals separating from aqueous solution at various temperatures.

When an aqueous  $\text{LiNO}_3$  solution corresponding to the composition of the trihydrate (56.11%  $\text{LiNO}_3$  by weight) is cooled to  $-5^\circ\text{C}$  spontaneous crystallization occurs with the deposition of a mass of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  crystals. If one of these tiny crystals is used to inoculate a more dilute solution (50%  $\text{LiNO}_3$ ) and the temperature maintained constant (say at  $25^\circ\text{C}$ ), extremely well defined euhedral crystals, sometimes as large as  $6\text{ cm} \times 2\text{ cm} \times 1.5\text{ cm}$ , could be grown during the course of 2 days.

The crystals appeared to belong to the orthorhombic system and the peculiar distribution of the faces suggested a hemimorphic form lacking a center of symmetry (point group  $mm2$ ). The  $a$  and  $b$  faces were well developed while the  $c$  face (perpendicular to the axis of elongation) could be recognized only in rare cases. Two prominent faces which made respectively  $28^\circ$  and  $46^\circ$  with the  $b$  face were later identified as the (110) and (120) planes. These angles were measured with a contact goniometer because of the inherent difficulty of mounting these excessively hygroscopic, low-melting crystals on a two-circle goniometer.

Using a few flawless crystals the density was determined by the flotation method (bromoform + xylene mixture) to be 1.55.

Rotation and Weissenberg photographs about the  $c$  axis were taken with a single crystal enclosed in a Lindemann glass tube. The crystal belongs to the orthorhombic symmetry with unit cell dimensions  $a = 6.82\text{ \AA}$ ,  $b = 12.78\text{ \AA}$ , and  $c = 6.05\text{ \AA}$ . The observed density gave four molecules in the unit cell.

From  $hk0$ ,  $hk1$ , and  $hk2$  Weissenberg photographs it was found that the constraining condition for the appearance of  $hkl$  reflections was  $h+k = 2n$ , while that for the  $h0l$  reflections was ( $h = 2n$ ),  $l = 2n$ . All the other reflections like  $hk0$ ,  $0kl$ ,  $h00$ ,  $0k0$ , and  $00l$  were also governed by these two conditions. The only space groups consistent with these conditions are (6):

centrosymmetric space group	$Cmcm-D_{2h}^{17}$ (No. 63)
or	
non-centrosymmetric space groups	$Cmc2-C_{2v}^{16}$ (No. 40)
	$Cmc2_1-C_{2v}^{12}$ (No. 36).

\*Present address: Department of Chemistry, Indian Institute of Technology, Madras, S. India.

If any weight could be given to the cursory morphological examination mentioned earlier, the crystal should belong to one of the latter two non-centrosymmetric space groups. The crystal structure analysis of this substance is in progress.

A powder photograph of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  was taken using a 9-cm Unicam powder camera. Since the specimen diameter was nearly 0.6 mm, high resolution could not be attained. Table I gives an approximate visual estimate of the intensity of each line, its spacing,

TABLE I  
Powder data of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$

No.	Intensity	$d$ , observed	Index	$d$ , calculated	$d$ , Campbell and Bailey
1	VW	6.40	020	6.395	6.13
2	W	6.01	110	6.015	
3	S	4.31	{ 021 111	{ 4.358 4.268	4.20
4	W	3.40	200	3.410	3.47
5	VW	3.10	{ 040 131	{ 3.198 3.102	
6	VS	3.01	{ 002 220	{ 3.025 3.007	2.99
7	W	2.85	041	2.838	2.79
8	M	2.70	{ 020 112 221	{ 2.734 2.702 2.693	2.68
9	S	2.34	{ 150 240 132	{ 2.392 2.332 2.320	2.37
10	S	2.13	{ 222 060	{ 2.133 2.130	2.13
11	VW	2.05	{ 061 330	{ 2.010 2.005	2.02
12	VW	1.88	{ 331 152	{ 1.904 1.878	1.90
13	M	1.80	212	1.800	1.80

its index, and spacing computed from the Weissenberg data as also the values reported by Campbell and Bailey. The present measurements are accurate to 1% only.

The work of Campbell and his co-workers has definitely disproved the existence of lithium nitrate hemihydrate ( $\text{LiNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) which Donnan and Burt (1) reported. According to these authors the anhydrous salt separating at higher temperatures (70 to 90° C) had a different crystal form from the "hemihydrate" crystals which they claimed were formed in their experiments at about 40° C. However, this suggested that the morphological study of crystals grown from concentrated aqueous solution by evaporation or by cooling at various temperatures from 0° C to 90° C would be of interest. These crystals were most carefully examined optically and goniometrically. A simple plastic attachment was made to the Unicam two-circle goniometer to completely prevent moist air from coming in contact with the hygroscopic crystals. Although the measurement of the angles were necessarily inaccurate (due to the intervening thin plastic cover) there was no doubt from the stereographic projections that all the crystals obtained were definitely the anhydrous rhombohedral  $\text{LiNO}_3$ . The crystals, however,

exhibited a profusion of faces and forms, the most prominent being  $c(0001)$ ,  $m(10\bar{1}0)$ ,  $r(10\bar{1}1)$ ,  $0(02\bar{2}1)$ ,  $e(01\bar{1}2)$ , and  $v(21\bar{3}1)$ . Measurement of the rhombohedral angle gave a value  $72^\circ 30'$  well in agreement with that computed from X-ray data (7) ( $72^\circ 42'$ ) for anhydrous  $\text{LiNO}_3$ .

It is perhaps worth while mentioning that it was impossible to separate out the trihydrate crystals from concentrated solutions of lithium nitrate even at temperatures as low as  $0^\circ \text{C}$ . Neither do these crystals form on the slow removal of water from saturated solution above  $-5^\circ \text{C}$ . This is due to the strong tendency of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  to supercool and it is precisely for this reason that seeding of the solution has to be resorted to for preparing the trihydrate crystals at ambient temperature ( $25^\circ \text{C}$ ).

The authors wish to thank Professor K. R. Krishnaswamy and Professor R. S. Krishnan for their kind interest in this work.

1. F. G. DONNAN and B. C. BURT. *J. Chem. Soc.* **83**, 335 (1903).
2. A. MASSINK. *Z. physik. Chem.* **92**, 351 (1918).
- 3(a). A. N. CAMPBELL. *J. Am. Chem. Soc.* **64**, 2680 (1942).
- 3(b). A. N. CAMPBELL and E. M. KARTZMARK. *Can. J. Chem.* **34**, 1404 (1956).
- 3(c). A. N. CAMPBELL and R. N. BAILEY. *Can. J. Chem.* **36**, 518 (1958).
4. G. ARAVAMUDAN. *Current Sci. (India)*, **26**, 49 (1957).
5. G. ARAVAMUDAN. Ph.D. Thesis, Mysore University, India, 1958.
6. INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY. Vol. 1. Kynoch Press, Birmingham.
7. W. H. ZACHARIASEN. In R. W. G. Wyckoff. *Crystal structures*. Vol. 1. Interscience, New York.

RECEIVED OCTOBER 3, 1960.  
INDIAN INSTITUTE OF SCIENCE,  
BANGALORE 12,  
SOUTH INDIA.