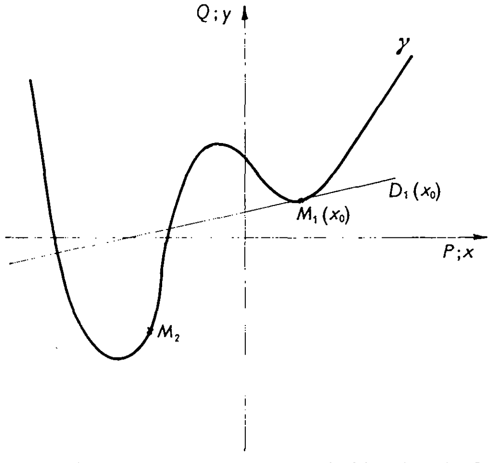

Fig. 3. La droite $D_1(x_0)$ ne peut servir à délimiter le domaine d'existence car le point $x_0$ n'est pas un minimum absolu de la fonction $g(x)$.

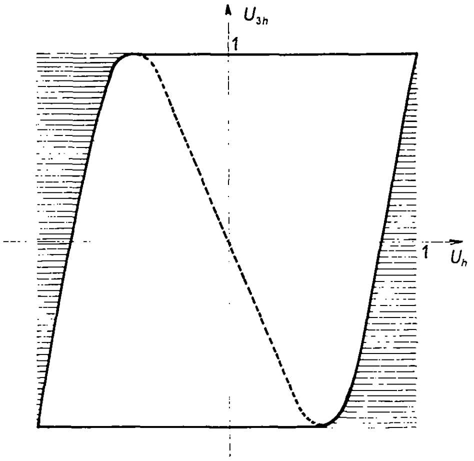

Fig. 4. Le point représentatif: $U_h$, $U_{3h}$ se trouve dans la région non hachurée.

les droites $D_1(x_0)$ (Fig. 3), l'existence de points tels que $M_2$ infirmant la condition (4).

## Application

(1) *Cristal centrosymétrique*

Prenons:

$$p(x) = \cos 2\pi hx \qquad P = U_h$$
$$q(x) = \cos 2\pi kx \qquad Q = U_k \, .$$

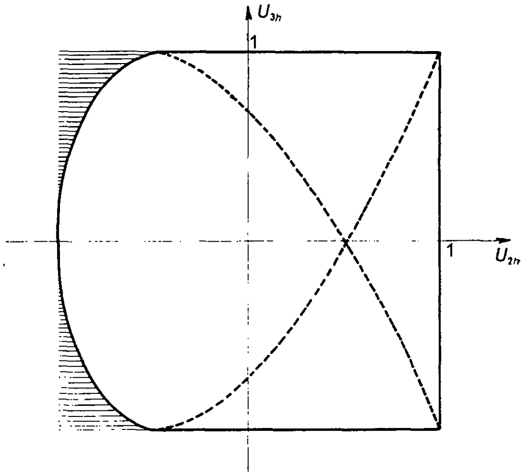

Fig. 5. Le point représentatif: $U_{3h}$, $U_{2h}$ se trouve dans la région non hachurée.

$\Gamma$ est une courbe de Lissajous et on trouve ainsi une inégalité entre $U_h$ et $U_k$ (cette inégalité n'est pas généralement susceptible d'une représentation algébrique simple).

Par exemple pour $U_h$ et $U_{3h}$, $U_{2h}$ et $U_{3h}$ on a les Figs. (4 et 5).

Pour $U_h$ et $U_{2h}$ on retrouve la parabole de Harker & Kasper.

(2) *Cristal non centrosymétrique*

Si on écrit $U_h = A_h + iB_h$ la méthode permet de trouver des inégalités entre $B_h$ et $B_k$, $B_h$ et $A_k$; il suffit de choisir correctement $p(x)$ et $q(x)$.

Cette méthode peut-être généralisée; en prenant:

$$g(x) = 1 + ap(x) + bq(x) + cr(x)$$

on délimite un volume permis dans un espace à trois dimensions convenablement choisi; appliquée à $U_1, U_2, U_3$ on trouve un volume compris entre les deux cônes d'équations.

$$U_1^2 + U_2^2 \pm 2U_1U_2 - (1 \pm U_1)(1 \pm U_3) = 0 \, .$$

On reconnaît là certaines des inégalités de Harker & Kasper.

### Références

Harker, D. & Kasper, J. S. (1948). *Acta Cryst.* **1**, 70.
Karle, J. & Hauptman, H. (1950). *Acta Cryst.* **3**, 181.

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*Acta Cryst.* (1962). **15**, 89

## Unit cell and space group of $LiBrO_3$.

By John H. Burns, *Reactor Chemistry Division, Oak Ridge National Laboratory,* Oak Ridge, Tennessee, U.S.A.*

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The unit-cell dimensions and possible space groups for lithium bromate have been determined by single-crystal Weissenberg and precession methods. Specimens of anhydrous $LiBrO_3$ were obtained by recrystallization from an aqueous solution of $LiBrO_3.H_2O$ above 52 °C. It was necessary to protect the crystals from moisture during X-ray examination.

Lithium bromate is primitive orthorhombic and has the unit-cell dimensions given in Table 1. Systematic

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* Operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

absences indicate that the space group is *Pnma* or *Pn*$2_1$*a*. An approximate density of 3·62 g.cm.$^{-3}$, obtained by pycnometry, corresponds to four formula weights per unit cell (calculated density: 3·76 g.cm.$^{-3}$).

Table 1. *Unit-cell and space-group data*

| | $LiBrO_3$ | $NaIO_3$ |
|---|---|---|
| *a* | 5·99 ± 0·02 Å | 6·37 |
| *b* | 7·86 ± 0·02 | 8·11 |
| *c* | 5·06 ± 0·02 | 5·74 |
| *Z* | 4 | 4 |
| Space group | *Pnma* or *Pn*$2_1$*a* | *Pnma* |

The crystal structure of sodium iodate has been reported by MacGillavry & Van Eck (1943) and by Náray-Szabó & Neugebauer (1947). The unit-cell and space-group data for $NaIO_3$, taken from these papers, is included in Table 1 to indicate its similarity to $LiBrO_3$. For the purpose of this comparison the axes of $NaIO_3$ have been renamed, bringing them into the standard setting. Although the diffraction symmetry is the same for both compounds, the optical goniometric determination of the point group of $NaIO_3$ (Eakle, 1896) allowed a unique space-group assignment to be made. A survey of the reflections of $LiBrO_3$ reveals that the *hkl* intensities are generally weak if $h+l$ is odd or $k$ is odd, a relationship also observed in the case of $NaIO_3$. The two compounds are probably isomorphous.

The powder pattern of $LiBrO_3$, obtained with a Norelco diffractometer and Cu *K*α radiation, is presented along with the calculated spacings in Table 2.

The writer is grateful to G. E. Boyd for suggesting this problem and to D. E. LaValle for providing the samples.

## References

EAKLE, A. S. (1896). *Z. Kristallogr.* **26**, 558.

MACGILLAVRY, C. H. & VAN ECK, C. L. P. (1943). *Rec. Trav. Chim. Pays-Bas*, **62**, 729.

NÁRAY-SZABÓ, I. & NEUGEBAUER, J. (1947). *J. Amer. Chem. Soc.* **69**, 1280.

Table 2. *Powder pattern of* $LiBrO_3$

| *hkl* | *I* | $d_o$ (Å) | $d_c$ (Å) | *hkl* | *I* | $d_o$ (Å) | $d_c$ (Å) | *hkl* | *I* | $d_o$ (Å) | $d_c$ (Å) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 011 | 1 | 4·26 | 4·26 | 221 | 3 | 2·153 | 2·155 | 113 | 1 | 1·588 | 1·590 |
| 020 | 28 | 3·92 | 3·93 | 022 | 8 | 2·124 | 2·127 | 232 | 5 | 1·551 | 1·555 |
| 101 | 100 | 3·86 | 3·87 | 040 | 6 | 1·961 | 1·965 | 331 | 7 | 1·514 | 1·515 |
| 111 | 25 | 3·47 | 3·47 | 202 | 28 | 1·930 | 1·933 | 400 | 12 | 1·500 | 1·498 |
| 200 | 16 | 2·99 | 3·00 | 212 | 5 | 1·875 | 1·877 | 410 | 3 | 1·472 | 1·471 |
| 210 | 33 | 2·796 | 2·799 | 301 | 5 | 1·856 | 1·857 | 420 | 1 | 1·400 | 1·399 |
| 121 | 47 | 2·754 | 2·756 | 231 | 1 | 1·836 | 1·837 | 250 | 5 | 1·390 | 1·392 |
| 002 | 36 | 2·527 | 2·530 | 311 | 8 | 1·807 | 1·808 | 133 | 6 | 1·378 | 1·380 |
| 211 | 1 | 2·448 | 2·449 | 141 | 14 | 1·749 | 1·752 | 341 | 2 | 1·349 | 1·350 |
| 220 | 26 | 2·376 | 2·382 | 222 | 9 | 1·733 | 1·734 | 060 | 2 | 1·308 | 1·310 |
| 031 | 8 | 2·327 | 2·327 | 321 | 33 | 1·678 | 1·679 | 430 | 3 | 1·300 | 1·300 |
| 102 | | | 2·331 | 240 | 6 | 1·640 | 1·643 | 152 | | | 1·303 |
| 112 | 6 | 2·230 | 2·234 | 103 | 3 | 1·622 | 1·624 | 402 | 8 | 1·290 | 1·289 |

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## The crystal structure of hexacyanochromate(III) of divalent cations.

By ADOLFO FERRARI, MARIA ELENORA TANI and EMANUELE MORISI, *Institute of Chemistry, University of Parma, Italy*

(*Received* 26 *June* 1961)

The hexacyanochromates(III) of divalent cations with formula $Me_3^{II}[Cr(CN)_6]_2 . 6H_2O$ has been prepared and studied by X-ray powder analysis (Cu *K*α radiation, $\lambda = 1·5418$ Å), as a continuation of a programme of researches on complex hexacyanides.

These compounds are isostructural with the hexacyanoferrates(III), -cobaltates(III), -rhodiates(III) (Ferrari & Tani, 1960) and -iridates(III) (Ferrari, Tani & Morisi, 1961) of divalent cations (space group $O_h^5$-$Fm3m$ or $T_d^2$-$F\bar{4}3m$, $Z = 2$).

The unit-cell constants are:

$Mn_3[Cr(CN)_6]_2 . 6H_2O$, $a = 10·836 \pm 0·036$ Å, $d_c = 1·798$
$Fe_3\,[Cr(CN)_6]_2 . 6H_2O$, $a = 10·426 \pm 0·031$ Å, $d_c = 2·026$
$Co_3\,[Cr(CN)_6]_2 . 6H_2O$, $a = 10·362 \pm 0·012$ Å, $d_c = 2·092$
$Ni_3\,[Cr(CN)_6]_2 . 6H_2O$, $a = 10·352 \pm 0·014$ Å, $d_c = 2·096$
$Cu_3\,[Cr(CN)_6]_2 . 6H_2O$, $a = 10·325 \pm 0·020$ Å, $d_c = 2·156$
$Zn_3\,[Cr(CN)_6]_2 . 6H_2O$, $a = 10·601 \pm 0·047$ Å, $d_c = 2·007$
$Cd_3\,[Cr(CN)_6]_2 . 6H_2O$, $a = 10·953 \pm 0·030$ Å, $d_c = 2·176$

The unit-cell constants decrease from Mn to Cu, then increase as observed in the previous series.

The different numbers of molecules of water in the different series are accounted for by their zeolitic character; in all these compounds, water can be eliminated without any change in the structure.

The series of hexacyanomanganates(III) is now under study, but their preparation is rather difficult owing to their instability. Nevertheless it is possible to foresee that the size of the $[Mn(CN)_6]^{3-}$ ion is between that of $[Cr(CN)_6]^{3-}$ and $[Fe(CN)_6]^{3-}$, the size of these ions decreasing with increase of the atomic weight of the metal atom.

## References

FERRARI, A. & TANI, M. E. (1960). *Gazz. Chim. Ital.* **90**, 1565.

FERRARI, A., TANI, M. E. & MORISI, E. (1961). *Acta Cryst.* **14**, 695.