[6(*c*)]. Samples of composition $FeCrGaSe_4$ could nevertheless possess a non-centrosymmetric $ZnIn_2S_4$-(III*a*) structure with an ordered cation distribution. A similar centrosymmetric polytype of the $ZnIn_2S_4$-(III*a*) structure has been reported very recently for layered $MnIn_2Se_4$ (Range, Klement, Döll, Bucher & Baumann, 1991). However, whereas the stacking of the Se layers in $MnIn_2Se_4$ is $(hM^tcM^ocM^th)_3$, as is common in the case of layered chalcogenides, that of the selenide under study is $(cM^thM^ohM^tc)_3$. The reason for this unusual stacking, which does not enable a 4 + 1 coordination of the tetrahedrally coordinated metal atoms, is not yet known. The similar $FeGa_2S_4$ structure type is $(hM^thM^ohM^th)_1$ with sole hexagonal stacking and only one sandwich in the unit cell.

### References

B. A. Frenz & Associates, Inc. (1982). *SDP Structure Determination Package*. College Station, Texas, USA.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Range, K.-J., Klement, U., Döll, G., Bucher, E. & Baumann, J. R. (1991). *Z. Naturforsch. Teil B*, **46**, 1122–1124.

Razzetti, C., Lottici, P. P. & Zanotti, L. (1984). *Mater. Chem. Phys.* **11**, 65–83.

Siwert, H. & Lutz, H. D. (1987). *J. Solid State Chem.* **69**, 215–218.

Stingl, Th. (1991). Thesis. Univ. of Siegen, Germany.

---

*Acta Cryst.* (1993). C**49**, 209–211

# Structure of Lithium Copper Pyrophosphate

By M. R. Spirlet* and J. Rebizant

*Commission of the European Communities, JRC, Institute for Transuranium Elements, Postfach* 2340, *D*7500 *Karlsruhe, Germany*

and M. Liegeois-Duyckaerts

*Laboratoire de Chimie Inorganique, B*6, *Université de Liège au Sart Tilman, B*4000, *Liège, Belgium*

(*Received* 8 *February* 1992; *accepted* 29 *April* 1992)

**Abstract.** $Li_2CuP_2O_7$, $M_r = 251.37$, monoclinic, $I2/a$, $a = 14.068\ (2)$, $b = 4.8600\ (8)$, $c = 8.604\ (1)$ Å, $\beta = 98.97\ (1)^\circ$, $V = 581.1\ (3)$ Å$^3$, $Z = 4$, $D_x = 2.873$ Mg m$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 4.2911$ mm$^{-1}$, $F(000) = 484$, $T = 295\ (1)$ K, $R = 0.048$ for 414 observed reflections $[I > 2\sigma(I)]$. The pyrophosphate anion is known to adopt varied conformations in different environments. In the present structure analysis, the bridge P—O—P angle is 121.5 (5)°, the P—O(bridge) bond length is 1.618 (4) Å and the P—O(terminal) bond lengths vary between 1.483 (5) and 1.530 (5) Å. The Cu and Li cations are tetracoordinated with Cu—O distances ranging from 1.923 (5) to 1.926 (5) Å and Li—O distances ranging from 1.87 (1) to 1.94 (1) Å.

**Introduction.** Few investigations of the structure of double pyrophosphate compounds of the type $M^I_2$-$M^{II}P_2O_7$ are reported in the literature. Complete structural data exist only for $K_2CdP_2O_7$ (Faggiani & Calvo, 1976) and $Na_2CaP_2O_7.4H_2O$ ($\alpha$ and $\beta$) (Cheng, Pritzker & Nyburg, 1980). The title compound, $Li_2CuP_2O_7$, was first analysed by powder X-ray diffraction and the pattern was indexed in a monoclinic unit cell with the following dimensions: $a = 14.050\ (2)$, $b = 4.868\ (1)$, $c = 8.608\ (2)$ Å, $\beta = 98.84\ (2)^\circ$. Its complete structure analysis, by single-crystal X-ray diffraction, is presented here.

**Experimental.** To obtain single crystals of $Li_2CuP_2O_7$, a stoichiometric mixture of $Li_2CO_3$, $CuCO_3.Cu(OH)_2$ and $NH_4H_2PO_4$ was progressively heated to about 1038 K in a platinum crucible; the mixture must be partly fused. After 4 h at this temperature, the mixture was cooled to 873 K and the furnace switched off. The sample was treated with hot water to isolate the crystals. The blue crystals are made up of parallel layers that cleave easily. This made the selection of single crystals suitable for X-ray analysis very difficult, the chosen samples often being twinned. The specimen finally selected was of approximate dimensions 0.2 × 0.2 × 0.05 mm. X-ray diffraction data were measured with an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation using $\theta$–$2\theta$ scans. The unit-cell dimensions were redetermined from 25

---

* On leave from the University of Liège, Belgium.

0108-2701/93/020209-03$06.00

Table 1. *Fractional atomic coordinates and temperature factors* (Å$^2$) *with e.s.d.'s in parentheses*

The Cu, Li, P and O(1) atoms were refined anisotropically using the anisotropic displacement parameter of the form: $\exp\{-[B(1,1)*h^2 + B(2,2)*k^2 + B(3,3)*l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl]\}$.

| | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| Cu | 0.2500 | −0.2500 | 0.2500 | 0.83 (3) |
| Li | 0.060 (1) | −0.116 (3) | 0.616 (2) | 1.0 (3) |
| P | 0.1486 (2) | 0.1172 (5) | −0.0367 (2) | 0.61 (4) |
| O(1) | 0.2500 | 0.280 (2) | 0.000 | 0.7 (2) |
| O(2) | 0.1479 (4) | −0.022 (1) | −0.1962 (7) | 1.0 (1) |
| O(3) | 0.1517 (4) | −0.095 (1) | 0.0942 (7) | 1.1 (1) |
| O(4) | 0.0708 (4) | 0.324 (1) | −0.0400 (7) | 0.9 (1) |

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| P—O(1) | 1.618 (4) | Cu—O(2$^{\text{i}}$) | 1.926 (5) |
| P—O(2) | 1.530 (5) | Cu—O(2$^{\text{ii}}$) | 1.926 (5) |
| P—O(3) | 1.523 (5) | Cu—O(3) | 1.923 (5) |
| P—O(4) | 1.483 (5) | Cu—O(3$^{\text{iii}}$) | 1.923 (5) |
| Li—O(2$^{\text{iv}}$) | 1.93 (1) | Li—O(4$^{\text{v}}$) | 1.87 (1) |
| Li—O(3$^{\text{ii}}$) | 1.94 (1) | Li—O(4$^{\text{vi}}$) | 1.98 (1) |
| P—O(1)—P | 121.5 (5) | O(2$^{\text{i}}$)—Cu—O(3) | 95.2 (2) |
| O(1)—P—O(2) | 106.0 (2) | O(2$^{\text{i}}$)—Cu—O(3$^{\text{iii}}$) | 84.8 (2) |
| O(1)—P—O(3) | 105.3 (3) | O(2$^{\text{iv}}$)—Li—O(3$^{\text{ii}}$) | 84.4 (5) |
| O(1)—P—O(4) | 107.4 (3) | O(2$^{\text{iv}}$)—Li—O(4$^{\text{v}}$) | 142.4 (7) |
| O(2)—P—O(3) | 111.0 (3) | O(2$^{\text{iv}}$)—Li—O(4$^{\text{vi}}$) | 106.8 (6) |
| O(2)—P—O(4) | 112.4 (3) | O(3$^{\text{ii}}$)—Li—O(4$^{\text{v}}$) | 119.2 (7) |
| O(3)—P—O(4) | 114.1 (3) | O(3$^{\text{ii}}$)—Li—O(4$^{\text{vi}}$) | 109.5 (6) |
| O(2$^{\text{i}}$)—Cu—O(2$^{\text{ii}}$) | 180.0 | O(4$^{\text{v}}$)—Li—O(4$^{\text{vi}}$) | 93.0 (5) |
| O(3)—P···P$^{\text{i}}$—O(3$^{\text{i}}$) | 94.4 (3) | O(2)—P···P$^{\text{i}}$—O(2$^{\text{i}}$) | −127.3 (3) |
| O(3)—P···P$^{\text{i}}$—O(4$^{\text{i}}$) | −144.8 (3) | O(2)—P···P$^{\text{i}}$—O(3$^{\text{i}}$) | −16.4 (3) |
| O(4)—P···P$^{\text{i}}$—O(4$^{\text{i}}$) | −24.0 (4) | O(2)—P···P$^{\text{i}}$—O(4$^{\text{i}}$) | 104.4 (3) |

Symmetry code: (i) $\frac{1}{2}-x, y, -z$; (ii) $-1+x, -\frac{1}{2}-y, \frac{1}{2}+z$; (iii) $\frac{1}{2}-x, -\frac{1}{2}-y, \frac{1}{2}-z$; (iv) $x, y, 1+z$; (v) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vi) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

reflections in the range $4 < 2\theta < 40°$. These dimensions are in agreement with the values observed from powder data. From systematic absences the possible space groups could be *I*2, *Im*, *I*2/*m* or *Ia* and *I*2/*a* [all *h*0*l* reflections with *h*, *l* odd were weak but some had apparent intensities greater than $2\sigma(I)$, with a maximum of $5\sigma(I)$]. Intensity data were collected in the range $4 < 2\theta < 50°$, $h$ −16 to 16, $k$ 0 to 6, $l$ −11 to 11; 1160 observed reflections [$I > \sigma(I)$] were collected, corresponding to 583 unique reflections ($R_{\text{int}} = 0.023$). The intensities of three standard reflections were measured at 30 min intervals and anisotropic decay correction was applied to the data (total decay 6.24%). The intensities were corrected for Lorentz–polarization effects. An empirical absorption correction was made using $\psi$ scans for six reflections with $\chi$ near 90°; reflections were measured at 10° intervals from 0 to 360°. The relative transmission factors ranged from 84.56 to 99.58%. The structure was solved by direct methods in space group *I*2. The refinement of the structure by Fourier techniques and full-matrix least-squares refinement was first carried out in this space group. Nevertheless, the final atomic positions revealed that the structure could be described in space group *I*2/*a*. The reflections *h*0*l* with *h*,*l* odd were therefore omitted from the original collected data and the final refinement carried out in space group *I*2/*a*. The function minimized was $\sum(\Delta F)^2$. Unit weights were used. 414 reflections with $F^2 > 2\sigma(F^2)$ were used in the refinement. The atoms were treated anisotropically except for the pyrophosphate terminal O atoms which were refined isotropically. No extinction correction was applied. This made a total of 42 variables (including the scale factor) in the final least-squares cycles. The final agreement factors were $R = 0.048$, $wR = 0.058$, $S = 1.91$. The final $(\Delta/\sigma)_{\max}$ was less than 0.01. The maximum and minimum heights in the final difference Fourier map were 0.705 and $-0.397$ e Å$^{-3}$, respectively. Atomic factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The programs used were from the Enraf–Nonius (1986) *SDP* system.

**Discussion.** Final atomic coordinates are given in Table 1.* Corresponding distances and angles are listed in Table 2. The structure is illustrated in Fig. 1. The bridging O atom, O(1), of the pyrophosphate anion lies on a twofold axis with a P—O—P angle of 121.5 (5)° and P—O(bridge) bond length of 1.618 (4) Å. The P—O(terminal) bond lengths range from 1.483 (5) to 1.530 (5) Å. The average

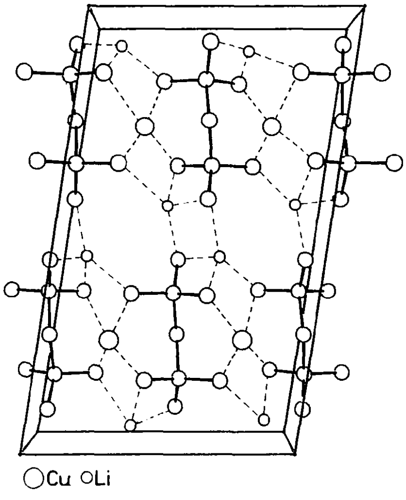

Fig. 1. The X-ray crystal structure of the title compound. The *a* axis is vertical and the *c* axis is horizontal from left to right (Johnson, 1976).

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55515 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

O(bridging)—P—O(terminal) bond angle is 106.2 (3)$^c$ and that of O(terminal)—P—O(terminal) is 112.5 (3)°. The $PO_3$ groups are approximately eclipsed as shown by the O(terminal)—P—P—O(terminal) torsion angles reported in Table 2. In the present instance, the variations in the P—O(terminal) bond distances do not appear to correlate with the number and strength of the Cu—O and Li—O interactions. The terminal O atoms are each bonded either to two Li cations or to one Li and one Cu cation (Table 2). The four close oxygen neighbours of the Cu ion [which lies on a centre of symmetry, 4(*c*)1] are at distances of 1.926 (5) and 1.923 (5) Å for O(2) and O(3), respectively, in a square-planar configuration. The Li ion is tetracoordinated in a distorted tetrahedral environment with Li—O distances ranging from 1.87 (1) to 1.98 (1) Å (Table 2).

## References

Cheng, P. T., Pritzker, K. P. H. & Nyburg, S. C. (1980). *Acta Cryst.* B**36**, 921–924.

Enraf–Nonius (1986). *Structure Determination Package*. Version 18. Enraf–Nonius, Delft, The Netherlands.

Faggiani, R. & Calvo, C. (1976). *Can. J. Chem.* **54**, 3319–3324.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

---

*Acta Cryst.* (1993). C**49**, 211–214

# Structure of Strontium Lithium Indium Pyroborate, $Sr_2LiInB_4O_{10}$

By Kathleen I. Schaffers and Douglas A. Keszler*

*Department of Chemistry and Center for Advanced Materials Research, Oregon State University,*
*Gilbert Hall* 153, *Corvallis, Oregon* 97330-4003, *USA*

(*Received* 30 *December* 1991; *accepted* 15 *June* 1992)

**Abstract.** Indium lithium distrontium decaoxotetraborate, $InLiSr_2B_4O_{10}$, $M_r = 500.23$, monoclinic, $P2_1/n$, $a = 12.637$ (1), $b = 5.251$ (1), $c = 13.748$ (1) Å, $\beta = 116.94$ (1)°, $V = 813.2$ (4) Å$^3$, $Z = 4$, $D_x = 4.085$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71069 Å, $\mu = 154.94$ cm$^{-1}$, $F(000) = 912$, $T = 298$ K, $R = 0.060$ for 1731 reflections having $F_o^2 \geq 3\sigma(F_o^2)$. The structure is composed of a three-dimensional $SrO_7$ polyhedral framework with hexacoordinated In and pentacoordinated Li atoms in interstitial sites. Marked deviations from orthogonality in the distorted octahedral $InO_6$ group include O3—In—O9, 80.8 (3), O1—In—O9, 80.8 (3), O1—In—O9, 84.6 (3) and O2—In—O9, 97.0 (3)°. Pyroborate groups form layers extending in the plane ($\bar{1}01$).

**Introduction.** While searching for a suitable lithium borate flux for crystal growth of the compound $Sr_3In(BO_3)_3$ (Cox, Schaffers & Keszler, 1992), we discovered an interaction of the In compound with the metaborate $LiBO_2$ to form the new material $Sr_2LiInB_4O_{10}$. Here, we describe the structure of this material which is a derivative of the Sc analog $Sr_2LiScB_4O_{10}$ (Thompson & Keszler, 1989).

**Experimental.** Crystals of the title compound were grown from a melt containing 40 mol % SrO made by heating $Sr(NO_3)_2$ (AESAR, ACS) in air, 6 mol % $In_2O_3$ (Alfa, ultrapure), 28 mol % $LiBO_2$ (AESAR, 99.9%), and 26 mol % $B_2O_3$ (Alfa, 99.98%). The sample was melted in a Pt crucible at 1303 K and slowly cooled at 10 K h$^{-1}$ to 1003 K then 88 K h$^{-1}$ to 300 K. The resulting crystals were washed in hot distilled water to remove any excess $LiBO_2$. A clear, colorless plate of dimensions 0.15 (1) × 0.07 (1) × 0.25 (1) mm was selected for X-ray structure analysis, and data were collected on a Rigaku AFC-6*R* single-crystal diffractmeter equipped with Mo $K\alpha$ radiation. Accurate unit-cell parameters were derived by automatic centering and least-squares analysis of 20 peaks collected in the range $30 \leq 2\theta \leq 36°$. The $\omega$–$2\theta$ scan technique was used to collect 2627 data in the range of indices $0 \leq h \leq 17$, $0 \leq k \leq 7$ and $-19 \leq l \leq 19$. From these measurements, 1731 unique reflections having $F_o^2 \geq 3\sigma(F_o^2)$ were obtained to $\sin\theta/\lambda = 1.36$ Å$^{-1}$. The intensities of three standard reflections measured after each segment of 200 data exhibited no significant decay during the collection.

The structure was refined with the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1989). All atomic coordinates were determined by comparison with the isostructural compound $Sr_2LiScB_4O_{10}$. Positional parameters and isotropic thermal factors were refined for each atom, followed by averaging the data ($R_{\text{int}} = 0.083$), correction for absorption (transmission coefficients = 0.74–

---

* Author to whom correspondence should be addressed.

0108-2701/93/020211-04$06.00