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Cobalt Lithium Orthoborate, LiCoBO3

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Abstract

The title compound has been synthesized by a solid state reaction. Its structure is isotypic with those o LiMgBO3, LiMnBO3 and LiZnBO3. Co^{II} occupies sta tistically two close positions within the CoO5 trigo nal bipyramids. These polyhedra share edges to form chains running along the [$\bar{1}$01] axis and are linked to gether, *via* corner sharing, by BO3 planar groups. The Li atoms occupy statistically the center of two face-sharing tetrahedra. Such pairs of tetrahedra share edges to form chains running along the *c* axis.

Comment

Several M^{II} lithium orthoborates, LiM^{II}BO3, have already been identified for M = Mg, Mn, Co, Zn and

Cd. For some of them, single-crystal structure determinations have been reported, allowing the identification of three structure types. However, other types of cells have also been proposed on the basis of powder data. The overall structural information can be summarized as follows:

(i) LiMgBO3 (Norrestam, 1989), LiZnBO3 and LiMnBO3 (Bondareva *et al.*, 1978) exhibit isotypic monoclinic structures (*C*2/*c* space group).

(ii) LiCdBO3 crystallizes in three forms, two of which are clearly established, *i.e.* LiCdBO3-I, with a triclinic structure ($P\bar{1}$ space group; Sokolova *et al.*, 1979), and a hexagonal form ($P\bar{6}$ space group) for LiCdBO3-II (Kasanskaja *et al.*, 1978; Sokolova *et al.*, 1980). A third form, with a monoclinic cell, has been proposed (Wei *et al.*, 1990), but the structure is not yet known.

(iii) A new monoclinic form of LiZnBO3 has recently been identified (Belkébir *et al.*, 1996) and on account of the cell parameters, its structure is very likely to be a more symmetrical version of the LiCdBO3-I triclinic form mentioned above.

(iv) Based on X-ray powder data, a monoclinic cell and the $P2_1/c$ space group have recently been proposed for LiMgBO3 (Belkébir *et al.*, 1996), however, all the lines of the powder pattern are also compatible with the $A2/a$ space group (*C*2/*c* if one inverts the *a* and *c* parameters) and, accordingly, the structure of this compound is very likely to be that already mentioned above (Norrestam, 1989). Similarly, all lines [except a weak one, ($\bar{3}$43)] of the powder pattern of LiCoBO3 (Belkébir *et al.*, 1996) are also compatible with the $A2/a$ space group and the present paper shows that the crystal structure of this compound is isotypic with those of LiMgBO3, LiZnBO3 and LiMnBO3.

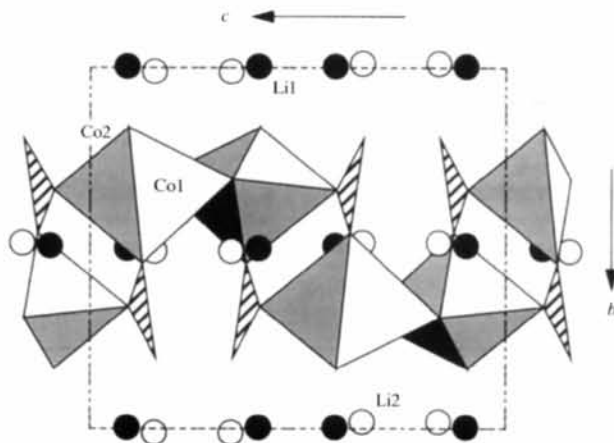In LiCoBO3, the Co^{II} cation occupies statistically two close positions [Co1–Co2 0.199 (4) Å] within the

Fig. 1. View of the title structure along [100] showing edge-sharing CoO5 trigonal bipyramids (shaded), triangular BO3 groups (dashed), and pairs of Li1 (black circles) and Li2 (open circles) sites (half occupied).

CoO$_5$ trigonal bipyramids, above and below the central plane. Similar positions are observed in LiZnBO$_3$ and LiMnBO$_3$, whereas in LiMgBO$_3$, the Mg atom is located at the center of such bipyramids. For the refinement of their occupancy, the Co-atom positions were attributed the same isotropic atomic displacement parameter (ADP). Within experimental error, these occupancies were found to be almost identical (50%). Occupancies of the Li-atom positions were refined in the same fashion and were also found to be identical (50%). The O-atom positions were refined with the use of anisotropic ADPs. Within the [CoBO$_3$]$^-$ framework, the M—O bonds are mainly covalent, thus rendering the Li—O bonds more ionic. As has been observed in other such cases, the ADPs for lithium are rather large.

Experimental

Single crystals of LiCoBO$_3$ were grown by heating Co$_3$O$_4$ in a large excess of LiBO$_2$ (1:10) in air at 1273 K for 24 h.

Crystal data

LiCoBO$_3$
$M_r = 124.68$
Monoclinic
$C2/c$
$a = 5.129\,(1)$ Å
$b = 8.840\,(2)$ Å
$c = 10.100\,(2)$ Å
$\beta = 91.36\,(3)°$
$V = 457.8\,(2)$ Å^3
$Z = 8$
$D_x = 3.618$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22
    reflections
$\theta = 4.60–12.32°$
$\mu = 7.194$ mm^{-1}
$T = 293\,(2)$ K
Elongated parallelepiped
$0.090 \times 0.016 \times 0.010$ mm
Blue

Data collection

Enraf–Nonius CAD-4
    diffractometer
ω scans
Absorption correction:
    by integration (Sheldrick,
    1995)
    $T_{min} = 0.879$, $T_{max} = 0.930$
1477 measured reflections
661 independent reflections

425 reflections with
    $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 29.95°$
$h = -7 \rightarrow 7$
$k = -12 \rightarrow 12$
$l = -1 \rightarrow 14$
3 standard reflections
    frequency: 60 min
    intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.069$
$S = 0.977$
661 reflections
50 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0249P)^2]$
    where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.016$
$\Delta\rho_{max} = 0.655$ e Å^{-3}
$\Delta\rho_{min} = -0.707$ e Å^{-3}
Extinction correction: none
Scattering factors from
    *International Tables for
    Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co1†	0.1657 (6)	0.1673 (4)	0.1325 (9)	0.0066 (2)
Co2‡	0.1547 (8)	0.1645 (5)	0.1136 (9)	0.0066 (2)
Li1§	0.661 (3)	0.003 (3)	0.088 (3)	0.017 (2)
Li2¶	0.663 (3)	−0.005 (3)	0.157 (2)	0.017 (2)
B1	0.1642 (9)	−0.1684 (8)	0.1258 (5)	0.0073 (7)
O1	0.4026 (5)	0.3356 (4)	0.0913 (3)	0.0087 (6)
O2	−0.2167 (5)	0.1944 (3)	0.1587 (3)	0.0076 (7)
O3	0.3088 (6)	−0.0389 (3)	0.1266 (4)	0.0176 (8)

† Site occupancy = 0.56 (5).   ‡ Site occupancy = 0.44 (5).   § Site occupancy = 0.48 (2).   ¶ Site occupancy = 0.52 (2).

Table 2. *Selected geometric parameters (Å, °)*

Co1—O3	1.967 (4)	Li1—O1^{iii}	1.93 (2)
Co1—O1	1.971 (4)	Li1—O2^{iv}	1.94 (2)
Co1—O2	1.999 (3)	Li1—O3^v	2.20 (3)
Co1—O2^i	2.13 (1)	Li2—O3	1.86 (2)
Co1—O1^{ii}	2.28 (1)	Li2—O2^{iv}	1.87 (2)
Co2—O3	1.967 (5)	Li2—O1^{iii}	1.99 (2)
Co2—O2	1.986 (3)	Li2—O3^{vi}	2.21 (3)
Co2—O1	1.992 (5)	B1—O3	1.364 (7)
Co2—O1^{ii}	2.08 (1)	B1—O1^{vii}	1.379 (5)
Co2—O2^i	2.33 (1)	B1—O2^{iii}	1.395 (7)
Li1—O3	1.89 (2)		
O3—Co1—O1	117.4 (2)	O2—Co2—O1	122.9 (2)
O3—Co1—O2	118.9 (2)	O3—Co2—O1^{ii}	96.5 (4)
O1—Co1—O2	123.3 (2)	O2—Co2—O1^{ii}	96.6 (4)
O3—Co1—O2^i	95.6 (3)	O1—Co2—O1^{ii}	87.9 (3)
O1—Co1—O2^i	93.6 (4)	O3—Co2—O2^i	89.6 (4)
O2—Co1—O2^i	87.3 (3)	O2—Co2—O2^i	82.4 (4)
O3—Co1—O1^{ii}	90.5 (4)	O1—Co2—O2^i	87.3 (4)
O1—Co1—O1^{ii}	83.1 (3)	O1^{ii}—Co2—O2^i	173.5 (2)
O2—Co1—O1^{ii}	90.3 (3)	O3—B1—O1^{vii}	120.4 (5)
O2^i—Co1—O1^{ii}	173.9 (2)	O3—B1—O2^{iii}	119.6 (4)
O3—Co2—O2	119.5 (2)	O1^{vii}—B1—O2^{iii}	120.0 (5)
O3—Co2—O1	116.4 (2)		

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

Data collection: *CAD-4 Manual* (Schagen *et al.*, 1989). Cell refinement: *CAD-4 Manual*. Data reduction: *XPREP* in *SHELXTL* (Sheldrick, 1995). Program(s) used to solve structure: *XS* in *SHELXTL*. Program(s) used to refine structure: *XL* in *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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