

Dilithium Cadmium Orthosilicate

BY C. RIEKEL

Institut Max von Laue–Paul Langevin, BP 156 X, 38042 Grenoble CEDEX, France

(Received 23 March 1977; accepted 24 March 1977)

Abstract. $\text{Li}_2\text{CdSiO}_4$, $Pmnb$, $a = 6.479(1)$, $b = 10.715(2)$, $c = 5.119(1)$ Å, $Z = 4$, $D_c = 4.08$ g cm $^{-3}$. Li, Si and Cd occupy the tetrahedral position of the wurzite structure in an ordered way.

Introduction. Colourless crystals were grown from a LiCl melt containing CdO and SiO $_2$. Unit-cell and intensity data were measured on a Siemens four-circle diffractometer with Mo $K\alpha$ radiation and the θ – 2θ scan technique. Unit-cell parameters were refined from 30 high-order reflexions. 1336 unique reflexions were obtained from a crystal 0.2 × 0.1 × 0.1 mm. Reflexions were classified as observed only when the ratio (background intensity)/(total intensity + 1) was smaller than 0.5. 1103 reflexions remained for structure refinement. An empirical weighting scheme was applied by plotting mean $|AF|$ versus $|F_o|$ for groups of

reflexions of similar magnitudes and taking the weights for any F as proportional to $1/|AF|^2$ (Stout & Jensen, 1970).

The structure was solved from a Patterson map based on the Cd atom, which gave the positions of the Si and O atoms. The Li atom was localized from a difference Fourier map. Least-squares refinement of the atomic and anisotropic thermal parameters, including a dispersion correction for Cd, resulted in a final R ($= \sum |F_o| - |F_c| / \sum |F_o|$) for 1103 reflexions of 0.06. Atomic scattering factors for Cd $^{2+}$, Si $^{4+}$, O $^{2-}$ and Li $^+$,

Table 1. Fractional atomic coordinates and their standard deviations

	<i>x</i>	<i>y</i>	<i>z</i>
Cd(1)	0.25 (0)	0.16269 (4)	0.1745 (1)
Si(1)	0.25 (0)	0.3727 (2)	0.6676 (4)
O(1)	0.25 (0)	0.3535 (5)	0.3505 (1)
O(2)	–0.0466 (4)	0.0896 (3)	0.2890 (7)
O(3)	0.25 (0)	0.1929 (4)	0.7451 (8)
Li(1)	0.499 (1)	0.910 (1)	0.327 (3)

Table 2. Bond distances (Å) and angles (°)

Cd(1)–O(1)	2.234 (5)	O(2)–Cd(1)–O(3)	108.8 (1)
Cd(1)–O(2)	2.156 (3)	O(1)–Si(1)–O(2)	109.9 (2)
Cd(1)–O(3)	2.222 (6)	O(1)–Si(1)–O(3)	107.9 (3)
Si(1)–O(1)	1.627 (6)	O(2)–Si(1)–O(2)	108.2 (3)
Si(1)–O(2)	1.627 (3)	O(2)–Si(1)–O(3)	109.9 (2)
Si(1)–O(3)	1.654 (4)	Cd(1)–O(1)–Si(1)	109.7 (3)
O(1)–O(2)	2.673 (6)	Cd(1)–O(1)–O(2)	123.2 (2)
O(1)–O(3)	2.654 (7)	Cd(1)–O(1)–O(3)	73.3 (2)
O(2)–O(3)	2.686 (4)	Cd(1)–O(1)–Li(1)	95.6 (6)
Li(1)–O(1)	1.95 (1)	Si(1)–O(1)–Li(1)	119.1 (6)
Li(1)–O(2)	1.99 (2)	O(2)–O(1)–Li(1)	136.7 (6)
Li(1)–O(3)	2.00 (1)	O(2)–O(1)–Li(1)	84.9 (6)
		O(3)–O(1)–Li(1)	123.8 (4)
O(1)–Cd(1)–O(2)	102.9 (1)	Li(1)–O(1)–Li(1)	111.8 (9)
O(1)–Cd(1)–O(3)	105.4 (2)	Cd(1)–O(2)–Si(1)	117.2 (1)
O(2)–Cd(1)–O(2)	126.1 (2)	Cd(1)–O(2)–O(1)	97.4 (3)

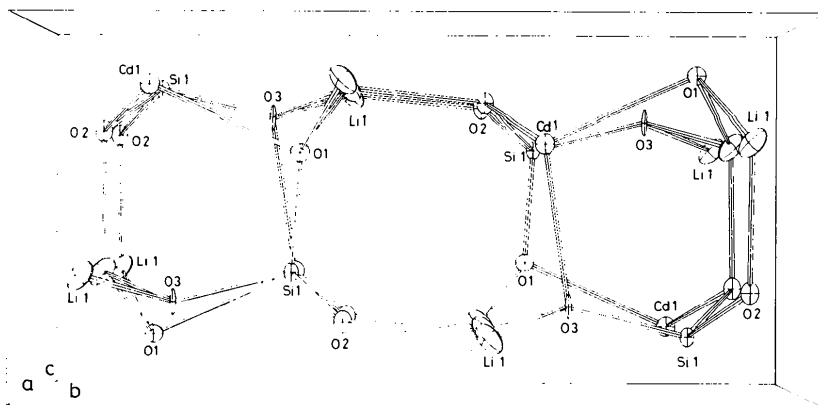


Fig. 1. The unit cell of $\text{Li}_2\text{CdSiO}_4$. The atoms are represented by 50% probability ellipsoids.

and the dispersion correction for Cd were taken from *International Tables for X-ray Crystallography* (1959, 1962). All Fourier and refinement calculations were carried out with the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) on the DEC10 computer of the Institut Laue-Langevin. Final positional parameters are listed in Table 1. Interatomic bond lengths and bond angles are given in Table 2; the unit cell is depicted in Fig. 1.*

Discussion. The structure of $\text{Li}_2\text{CdSiO}_4$ is related to the wurzite structure. The metal atoms occupy the cation sites in an ordered way. Of special interest is the ordering of Li atoms in chains parallel to the a axis, with a distance of 3.24 Å between two neighbouring Li

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32589 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

atoms in a chain. The SiO_4 tetrahedra are less distorted than they are in synthetic (Riekel, 1973) or natural (Birle, Gibbs, Moore & Smith, 1968) olivines. This distortion is also evident in the infrared spectrum of $\text{Li}_2\text{CdSiO}_4$ as the peak attributed to the ν_3 vibration of the SiO_4 tetrahedron is split because of the reduced site symmetry.

References

- BIRLE, J. D., GIBBS, G. V., MOORE, P. P. & SMITH, J. B. (1968). *Amer. Min.* **53**, 807.
International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 RIEKEL, C. (1973). PhD Thesis, Univ. of Munich.
 STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
 STOUT, G. H. & JENSEN, L. H. (1970). *X-ray Structure Determination*. London: Macmillan.

Acta Cryst. (1977). **B33**, 2657–2659

(3-Pyrida-3-[2,6])(6-benza-6-[1,4;2,5])(9-pyrida-9-[2,6])spiro[5.5]undecaphane-1,4,7,10-tetraene

BY A. W. HANSON

Division of Biological Sciences, National Research Council of Canada, Ottawa, Canada K1A 0R6

(Received 14 February 1977; accepted 5 April 1977)

Abstract. $\text{C}_{24}\text{H}_{16}\text{N}_2$, FW 332.4; monoclinic, $P2_1/c$, $a = 9.233$ (9), $b = 8.801$ (9), $c = 22.29$ (2) Å, $\beta = 107.08$ (5)° at 20°C, $\lambda(\text{Cu } K\alpha_1) = 1.54050$ Å; $V = 1731.3$ Å³; $D_m = 1.29$, $Z = 4$, $D_x = 1.28$ g cm⁻³. The molecule has non-crystallographic twofold rotation symmetry. The pyridine rings are inclined at 75° to the central benzene nucleus, which is distorted to a twist-boat conformation.

Introduction. The crystals supplied were amber in colour and wedge-shaped, with prominent forms {110}, {011} and {001}. The space group was determined from single-crystal photographs (absent reflexions: $h0l$ for l odd; $0k0$ for k odd). The specimen used for intensity measurements was of nominal dimensions $0.23 \times 0.23 \times 0.17$ mm and was mounted about c^* . The intensities of the 2938 independent reflexions within the limiting sphere $2\theta = 130^\circ$ were measured with a four-circle diffractometer, using Ni-filtered Cu $K\alpha$ radiation and a scintillation counter. The θ - 2θ scan

mode was used, with scans of 2° for $2\theta < 100^\circ$, and 3° otherwise. Background counts were accumulated for 10 s at the end of each scan. For 594 reflexions the net count was less than either 60, or 10% of the corresponding background; these were considered to be unobserved, and were not used in the analysis. No corrections were made for absorption ($\mu = 5.9$ cm⁻¹).

The structure was determined uneventfully by symbolic addition procedures. Refinement was by block-diagonal least squares, minimizing $\sum w(\Delta F)^2$. The H atoms were placed in chemically reasonable positions, and were included in the refinement. The 33 most intense reflexions were corrected for extinction in the manner described by Pinnock, Taylor & Lipson (1956), the largest correction being 10% of F_o . The weighting scheme used in the final stages was $w = w_1 w_2$ where $w_1 = F_o/6$ for $F_o < 6$, = 1 otherwise, and $w_2 = 2.5 \sin^2 \theta$ for $\sin^2 \theta < 0.4$, = 1 otherwise. This weighting scheme was effective in ensuring that there was no obvious systematic dependence of the weighted