JOURNAL OF SOLID STATE CHEMISTRY **133,** 21–24 (1997)
ARTICLE NO. SC977310

Li_2Pd_3B and Li_2Pt_3B: Ternary Lithium Borides of Palladium and Platinum with Boron in Octahedral Coordination[1]

U. Eibenstein and W. Jung

Institut für Anorganische Chemie der Universität Köln, Greinstr. 6, D-50939 Cologne, Germany

Received January 21, 1997; accepted February 6, 1997

The new isotypic compounds Li_2Pd_3B (cubic, $P4_332$, $Z = 4$, $a = 675.34(3)$ pm, 196 F values, $R = 0.029$) and Li_2Pt_3B (cubic, $P4_332$, $Z = 4$, $a = 675.52(5)$ pm, 119 F values, $R = 0.046$) were synthesized by reaction of the elements (900°C, 48 h). Both compounds are sensitive to moisture. The structure contains isolated boron atoms in a distorted octahedral coordination. By the BPd_6 and BPt_6 octahedra respectively a new type of three-dimensional framework of all vertex sharing octahedra is formed. © 1997 Academic Press

1. INTRODUCTION

In metal-rich borides the triangular prism is by far the most common coordination polyhedron of the boron atoms. Compared to this there are only a few compounds with octahedrally coordinated boron atoms. Most of them are perovskites like $RERh_3B_{1-x}$ prepared by Holleck (1) and Rogl and DeLong (2), AM_3B (A = Zr, Hf; M = Rh, Ir) or $REPd_3B$ reported by Rogl (3) and by Dhar *et al.* (4), respectively. New examples of ternary platinum metal borides with structures derived from perovskites are the tin platinum metal borides $SnRh_3B_{1-x}$ and Sn_4Rh_6B (5). The ternary borides Li_2Pd_3B and Li_2Pt_3B reported here crystallize with a new structure type containing boron in a distorted octahedral coordination. Li_2Pd_3B had already been detected in the course of a former investigation using X-ray powder methods but was ascribed the composition LiPdB (6). Now the correct composition could be determined by a structure determination based on single crystals. In the system Li/Pt/B only one ternary compound, $LiPt_3B$, has been known so far (7).

[1] Paper presented at the 12th International Symposium on Boron, Borides and Related Compounds, Baden, Austria, August 25–30, 1996.

2. SAMPLE PREPARATION AND LATTICE CONSTANTS

Li_2Pd_3B and Li_2Pt_3B were prepared by reaction of the elements in sealed tantalum tubes under an atmosphere of argon (lithium, 99.97%, Chemetall; palladium, 99.9%, powder, Degussa; platinum, 99.9%, powder, Degussa; boron, 99.9%, pieces, Aldrich). Mixtures of the elements were heated to 900°C for 48 h. The samples obtained were grey powders containing single crystals of irregular shape. Li_2Pt_3B and especially Li_2Pt_3B are extremely sensitive to moisture.

Guinier powder diagrams of Li_2Pt_3B were recorded using Cu$K\alpha_1$ radiation and Si as an internal standard. In the case of Li_2Pd_3B the powder pattern was recorded with a Straumanis camera. The lattice constants (Table 1) were obtained by least-square fits of the powder data.

3. STRUCTURE DETERMINATION

Single-crystal X-ray diffraction intensity data were collected with a four-circle diffractometer (CAD-4, Enraf–Nonius, Delft, Netherlands) using graphite-monochromated Mo$K\alpha$ radiation. Inspection of the data revealed the diffraction symbol $m3mP4_1$-- and thus led to the enantiomorphic pair of space groups $P4_132$ and $P4_332$. The structures of both compounds could be solved in space group $P4_332$ using direct methods in the XTAL program system (8). In the case of Li_2Pd_3B the space group $P4_132$ could be excluded by a final R value which was significantly higher than that in $P4_332$. The data set of Li_2Pt_3B, however, was not good enough for a distinction between the two space groups.

Anisotropic displacement parameters were used only for the heavy atoms. Final difference Fourier syntheses revealed no significant residual peaks (Li_2Pd_3B, $+0.204/-0.17$ e/Å^3; Li_2Pt_3B, $+0.713/-0.559$ e/Å^3). Crystallographic data, the pycnometrically determined density, and details of the data collection are summarized in Table 1. The structural parameters obtained after full matrix refinement are listed in Table 2. The interatomic distances are listed in Table 3.

0022-4596/97 $25.00

TABLE 1
Crystallographic Data and Details of the Data Collection of Li_2Pd_3B and Li_2Pt_3B

	Li_2Pd_3B	Li_2Pt_3B
Crystal system	Cubic	Cubic
Lattice constant (pm)	675.34(3)	675.52(5)
Space group	$P4_332$	$P4_332$
Formular units per cell	4	4
$D_{pyc.}$ (g cm^{-3})	7.49	—
$D_{X\ ray.}$ (g cm^{-3})	7.449	13.206
Crystal size (mm^3)	$0.02 \times 0.018 \times 0.015$	$0.031 \times 0.025 \times 0.02$
Absorption correction	According to crystal size	—
Measurement limits	$2\theta \leq 40^\circ$	$2\theta \leq 35^\circ$
Scan width (θ–2θ, +25% background)	0.9°	0.8°
Maximum measuring time per reflection (s)	60	180
Number of measured reflections	3918	2602
Number of independent reflections	230	169
Number of reflections with $I > 3\sigma_I$	196	119
Internal R (on F values) of equivalent reflections	0.062(4)	0.14(9)
Final value of R	0.029	0.046
Final value of R_W	0.018	0.029
Number of variable parameters	10	10

TABLE 3
Interatomic Distances up to 400 pm

	Li_2Pd_3B
Pd	(Pd, $4 \times 278.43(4)$, $2 \times 295.98(5)$, $2 \times 352.68(4)$; Li, $2 \times 272.9(6)$, $2 \times 282.1(6)$, $2 \times 284.1(6)$; B, $2 \times 212.86(3)$)
B	(6 Pd; Li, $6 \times 319.6(6)$; $2 \times 371.3(6)$)
Li	(9 Pd; 4 B; Li, $3 \times 255.4(8)$)
	Li_2Pt_3B
Pt	(Pt, $4 \times 276.1(1)$, $2 \times 302.1(1)$, $2 \times 354.80(6)$; Li, $2 \times 263(5)$, $2 \times 283(5)$, $2 \times 293(5)$; B, $2 \times 213.74(6)$)
B	(6 Pt; Li, $6 \times 309(5)$; $2 \times 388(5)$)
Li	(9 Pt; 4 B; Li, $3 \times 263(5)$)

4. DISCUSSION

The structure of Li_2Pd_3B and the isotypic compound Li_2Pt_3B is of a new type shown as a stereoplot in Fig. 1. The characteristic building elements are distorted Pd_6 octahedra centered by boron atoms (Fig. 2). The octahedra share all vertices to form a unique three-dimensional framework. Several three-dimensional frameworks formed by all vertex sharing octahedra are known (9). Besides the pyrochlore structure and the tungsten bronzes, that of the ReO_3 type forming the basis of the cubic perovskites is the most common one. In the ReO_3 structure the 12 edges of every octahedron are bridged by rings of four octahedra. In the Li_2Pd_3B structure every octahedron takes part in three rings of three octahedra and nine rings of five octahedra bridging the 12 edges. Thus six-membered Pd_3B_3 rings and ten-membered Pd_5B_5 rings are formed. Their arrangement is shown as a stereoplot in Fig. 3. While the ten-membered rings are corrugated, the six-membered rings are planar. As Fig. 4 shows, the three Pd_3B_3 rings surrounding one central octahedron are in approximately rectangular orientation. By the large Pd_5B_5 rings a system of interpenetrating tunnels is formed accommodating the lithium atoms. Figure 5 shows the lithium partial structure in which every atom has three neighbors at a distance of 255 pm. This distance is about 50 pm shorter than in lithium metal indicating an electron transfer from lithium to the Pd/B framework. The whole neighborhood of lithium is shown in Fig. 6. In addition to the three lithium atoms there are nine palladium atoms with distances of 3×273, 3×282, and 3×284 pm, which are all shorter than the sum of the metallic radii (292 pm for CN 12). There are no close contacts between the lithium and the boron atoms. Figure 7 gives the

TABLE 2
Structural Parameters of Li_2Pd_3B and Li_2Pt_3B

Atom	Equipoint	x	U_{11} (pm^2)	$U_{22} = U_{33}$ (pm^2)	$U_{12} = U_{13}$ (pm^2)	U_{23} (pm^2)
			Li_2Pd_3B			
12 Pd	12*d* (1/8, *x*, 1/4 − *x*)	0.30417(5)	146(2)	137(2)	31(1)	−7(2)
8 Li	8*c* (*x*, *x*, *x*)	0.3072(9)	174(21)			
4 B	4*b* (7/8, 3/8, 1/8)		145(169)			
			Li_2Pt_3B			
12 Pt	12*d* (1/8, *x*, 1/4 − *x*)	0.3079(2)	107(7)	136(5)	31(4)	−47(5)
8 Li	8*c* (*x*, *x*, *x*)	0.293(7)	238(170)			
4 B	4*b* (7/8, 3/8, 1/8)		167(116)			

Note. The anisotropic displacement factor exponent takes the form $-2\pi^2 (h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \ldots + 2klb^*c^*U_{23})$.

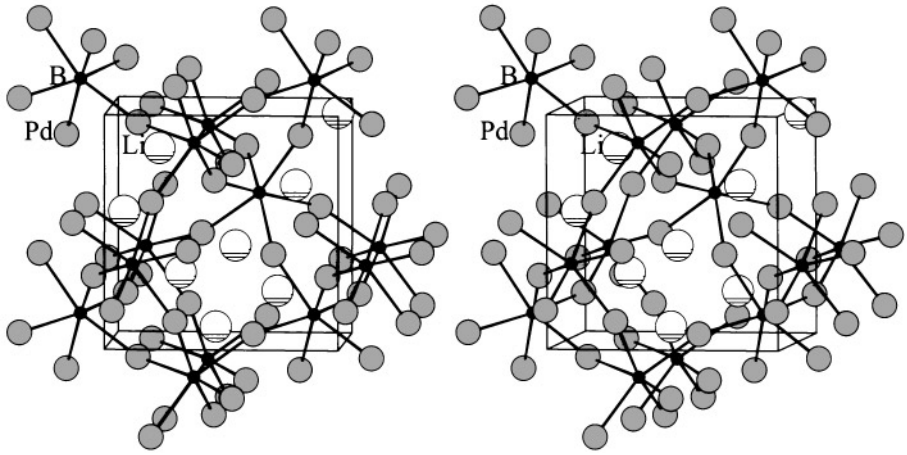

FIG. 1. Stereoplot of the Li_2Pd_3B structure.

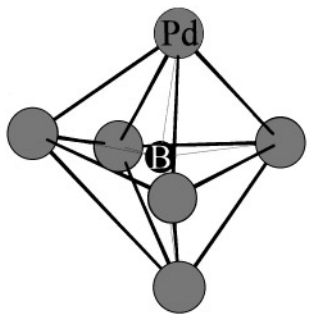

FIG. 2. Distorted Pd_6B octahedron in the structure of Li_2Pd_3B.

environment of the palladium atoms. As every palladium atom forms the common vertex of two Pd_6 octahedra, there are eight neighboring palladium atoms. Their distances (named a, b, c in Fig. 7) are 2×278.43, 2×295.98, and 2×352.68 pm. While the first two values are only slightly larger than in metallic palladium, the third is too large for binding interactions, and the two corresponding palladium atoms are outside of the first coordination sphere. The Pd–B distance of 213 pm is short and may be attributed to strong covalent bonds. Together with the six neighboring lithium atoms the coordination number of palladium sums up to 14 (six Pd, two B, six Li).

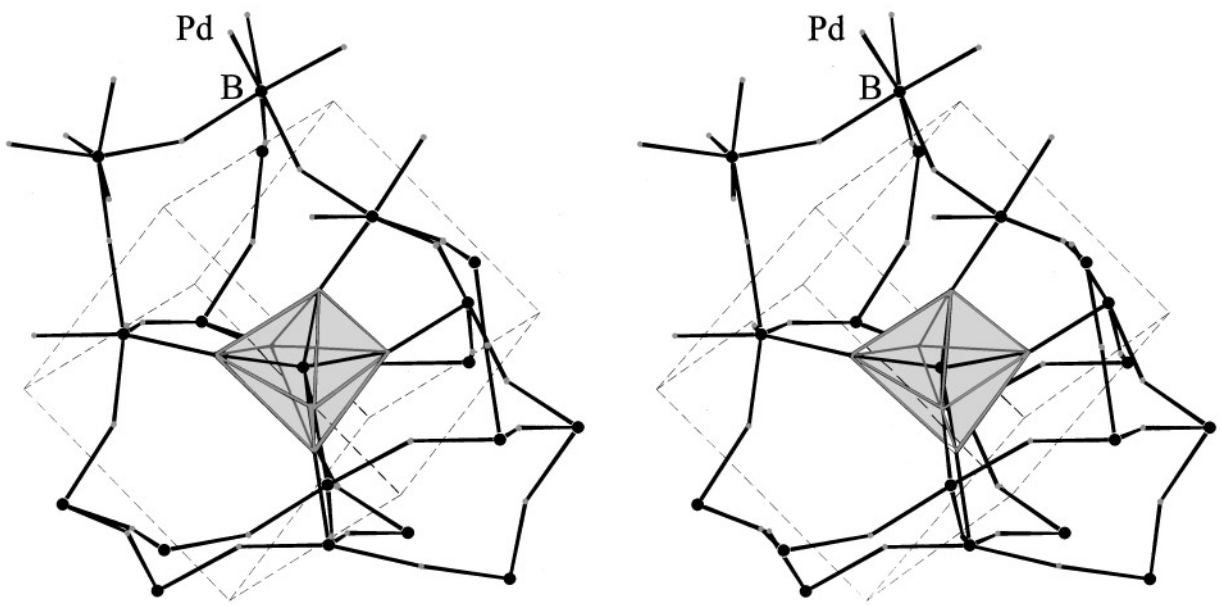

FIG. 3. Arrangement of the three planar Pd_3B_3 rings and the nine corrugated Pd_5B_5 rings around one central Pd_6B octahedron in the structure of Li_2Pd_3B. In one of the Pd_5B_5 rings the octahedral coordination of the boron atoms is completed. B, larger black circles; Pd, small gray circles.

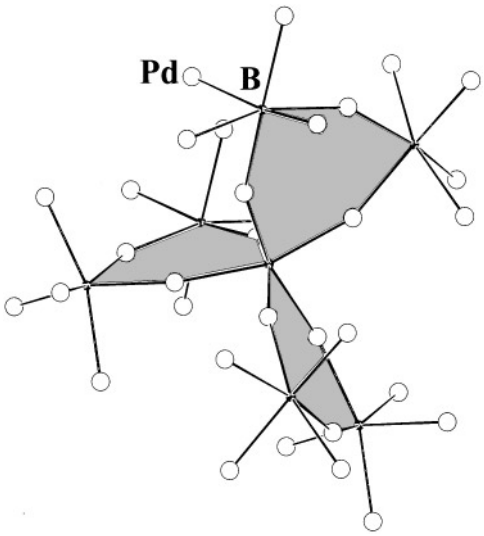

FIG. 4. Arrangement of the three planar Pd_3B_3 rings around one central Pd_6B octahedron.

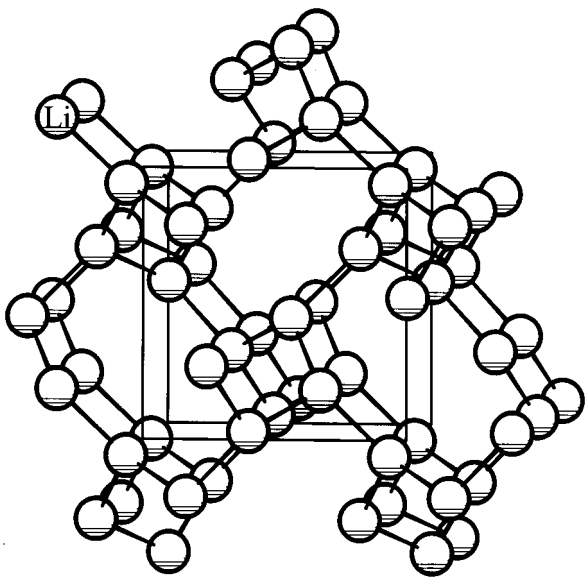

FIG. 5. Lithium partial structure.

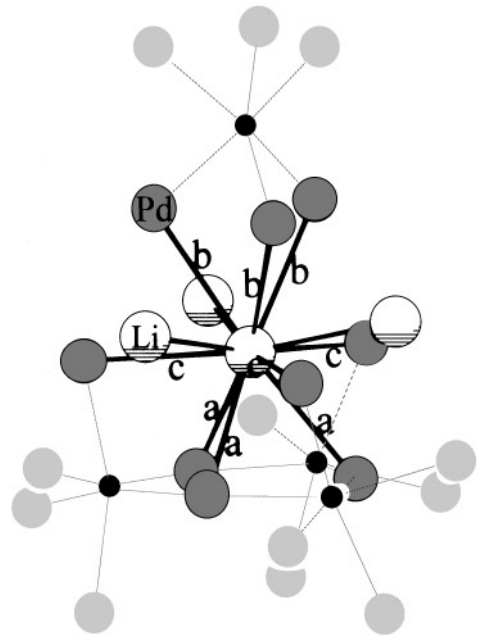

FIG. 6. Near neighbor environment of the lithium atoms. The distances are: Li–Pd, (a) 282.1(6) pm, (b) 272.9(6) pm, (c) 284.1(6) pm; Li–Li, $3 \times 255.4(8)$ pm.

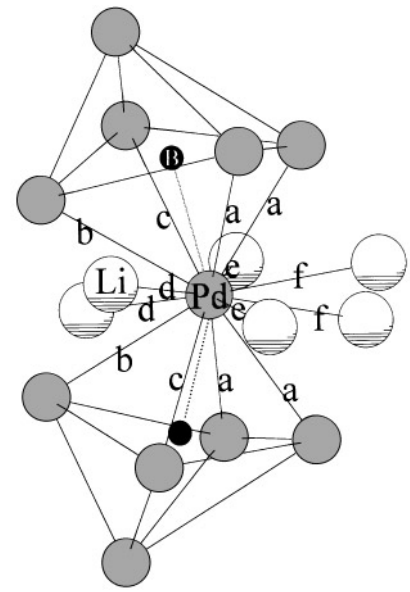

FIG. 7. Environment of the palladium atoms. The distances are: Pd–B, $2 \times 212.86(3)$ pm; Pd-Pd, (a) 278.43(4) pm, (b) 295.98(5) pm, (c) 352.68(4) pm; Pd–Li, (d) 272.9(6) pm, (e) 284.1(6) pm, (f) 282.1(6) pm.

ACKNOWLEDGMENT

Financial support from the Fonds der Chemischen Industrie is gratefully acknowledged.

REFERENCES

1. H. Holleck, *J. Less-Common Metals* **52,** 167 (1977).
2. P. Rogl and L. DeLong, *J. Less-Common Metals* **91,** 97 (1983).
3. P. Rogl and H. Nowotny, *J. Less-Common Metals* **67,** 41 (1979).
4. S. K. Malik, S. K. Dhar, and R. Vijayaraghavan, *Bull. Mater. Sci. India* **6**(2), 263 (1984).
5. W. Klünter and W. Jung, *Z. Anorg. Allg. Chem.* **622,** 2099 (1996).
6. W. Jung and B. Schmidt, *Naturwissenschaften* **12,** 583 (1974).
7. R. Mirgel and W. Jung, *J. Less-Common Metals* **144,** 87 (1988).
8. S. R. Hall and J. M. Steward, "XTAL 3.2," University of Western Australia and Maryland, 1989.
9. A. F. Wells, "Structural Inorganic Chemistry," 5th ed., Oxford Univ. Press., Oxford, 1984.