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Key indicators

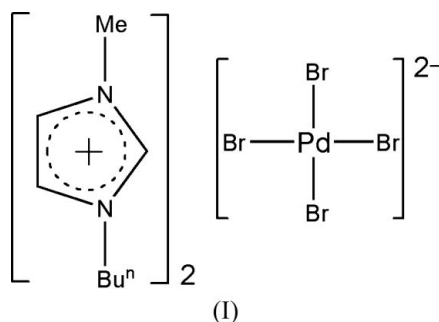
Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
 R factor = 0.026
 wR factor = 0.053
Data-to-parameter ratio = 25.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Bis(1-*n*-butyl-3-methylimidazolium) tetrabromopalladate(II)

In the title ionic compound, $(\text{C}_8\text{H}_{15}\text{N}_2)_2[\text{PdBr}_4]$, the asymmetric unit consists of one square-planar $[\text{PdBr}_4]^{2-}$ anion and two 1-*n*-butyl-3-methylimidazolium, $[\text{Bmim}]^+$, cations, where the imidazolium rings are planar and the β C atoms of the butyl substitutes are bent away from the ring planes at angles of 111.9 (3) and 112.3 (4)°. One methyl H atom and three ring H atoms of one of the two $[\text{Bmim}]^+$ cations form C—H...Br hydrogen bonds (2.81–2.92 Å and 157–165°), whereas the other cation is only involved in one hydrogen bond. Br atoms involved in hydrogen bonds are *trans* in the $[\text{PdBr}_4]^{2-}$ ion.

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Comment

Ionic liquids based on the 1-butyl-3-methylimidazolium cation are important alternatives to water as solvents for two phase catalytic oligomerization, hydrogenation and hydroformylation of olefins by transition metal complexes (Einloft *et al.*, 1996; Chauvin *et al.*, 1996). It has been shown that $[\text{Bmim}]_2[\text{PdCl}_4]$ in $[\text{Bmim}]\text{BF}_4$ (Bmim is 1-*n*-butyl-3-methylimidazolium) is a selective catalyst precursor for hydrodimerization of 1,3-butadiene (Dullius *et al.*, 1998). Crystallographic studies of Pd^{2+} -containing ionic liquids based on the widely used $[\text{Bmim}]^+$ cation are helpful for elucidating the local ordered structure around the Pd centres of catalytic systems in ionic liquids. The present paper reports the synthesis and crystal structure determination of the title compound, $[\text{Bmim}]_2[\text{PdBr}_4]$, (I).



The asymmetric unit of (I) (Fig. 1) consists of two imidazolium cations and one $[\text{PdBr}_4]^{2-}$ counter-ion. The tetrabromopalladate anion is essentially square planar, with the bond angles at Pd in the range 89.51 (2)–178.62 (2)°, and Pd—Br bond distances ranging from 2.4285 (5) to 2.4415 (5) Å, which are comparable with those found for other $[\text{PdBr}_4]^{2-}$ -containing compounds (Neve *et al.*, 1998). The imidazolium rings of the two cations are planar, and bond distances and angles are found to be almost the same as those in $[\text{Bmim}]_2[\text{PdCl}_4]$ (Dullius *et al.*, 1998). The β C atoms of the

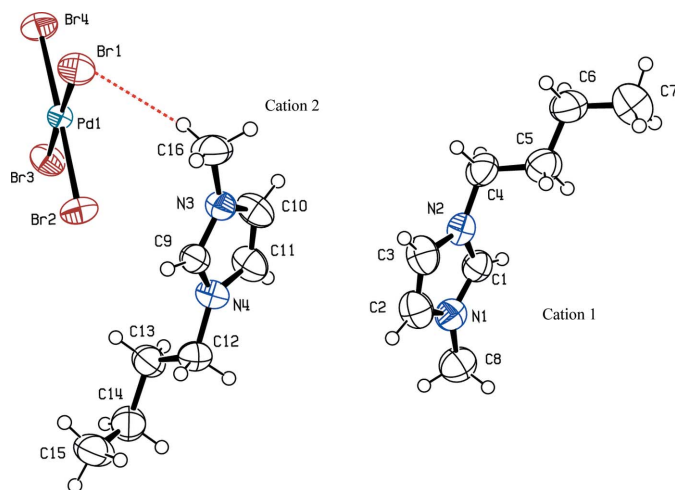


Figure 1
The molecular structure of (I), with 50% probability ellipsoids (arbitrary spheres for H atoms), showing the atom-labelling scheme. The dashed line indicates the C—H...Br hydrogen bond. The two [Bmim] cations are labeled as 1 and 2.

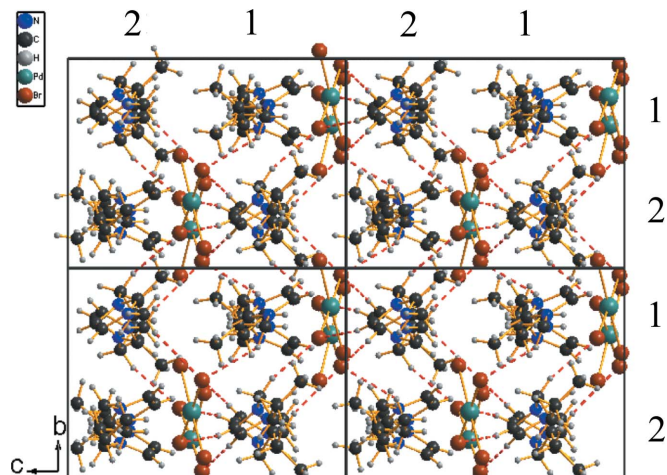


Figure 2
A packing diagram of (I), viewed along the *a* axis. Dashed lines indicate C—H...Br hydrogen bonds.

butyl chains are twisted out of the planes of the imidazolium rings at angles of 112.3 (4) and 111.9 (3)°. The conformational features of the cations that differentiate them are the torsion angles around C5—C6 [176.9 (5)°] and C13—C14 [68.2 (5)°] (Table 1). The all-*gauche* conformation at the C13—C14 bond of cation 2 is in contrast with the *anti* conformations at all the C—C bonds of the alkyl chain of cation 1, which projects the chain away from the imidazolium ring. The conformation of cation 1 is the same as in monoclinic polymorph II of [Bmim]Cl (Holbrey *et al.*, 2003).

The different conformations of the cations result in different hydrogen-bonding patterns. In cation 1, there is only one hydrogen bond (C4—H4B...Br1; see Table 2 for details). However, there are four hydrogen bonds in cation 2, involving three ring H atoms and one methyl H atom. The hydrogen-bonding patterns are similar to those observed in [Bmim]₂[CoCl₄] (Zhong *et al.*, 2006). The hydrogen bonds between cation 2 and [PdBr₄]²⁻ link them together, forming a three-

dimensional network (Fig. 2), with the weakly hydrogen-bonded cations 1 lying in between the mesh.

Experimental

The title compound was synthesized by refluxing a mixture of [Bmim]Br (0.38 mmol, 83 mg) and PdBr₂ (0.188 mmol, 50 mg) in acetonitrile (5 ml) in a Schlenk tube for 24 h. The resulting red solution was then filtered and the filtrate was concentrated and left to crystallize at 283 K, with the addition of diethyl ether. Suitable crystals were obtained by recrystallization from dichloromethane-diethyl ether (1:1) at room temperature (m.p. 396.5–397.3 K). Elemental analysis, calculated for C₁₆H₃₀Br₄N₄Pd: C 27.28, H 4.29, N 7.95%; found: C 27.15, H 4.37, N 7.90%.

Crystal data

(C₈H₁₅N₂)₂[PdBr₄]
M_r = 704.46
 Orthorhombic, *Pna*2₁
a = 21.6041 (8) Å
b = 9.1708 (3) Å
c = 12.1753 (4) Å
V = 2412.25 (14) Å³

Z = 4
D_x = 1.940 Mg m⁻³
 Mo *K*α radiation
 μ = 7.40 mm⁻¹
T = 294 (2) K
 Rod, purple-red
 0.20 × 0.20 × 0.18 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2005)
T_{min} = 0.230, *T_{max}* = 0.264

24651 measured reflections
 5993 independent reflections
 4817 reflections with *I* > 2σ(*I*)
R_{int} = 0.030
 θ_{max} = 28.3°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.026
wR(*F*²) = 0.053
S = 1.02
 5993 reflections
 231 parameters
 H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0383*P*)² + 1.1806*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.34 e Å⁻³
 Δρ_{min} = -0.38 e Å⁻³
 Absolute structure: Flack (1983),
 2851 Friedel pairs
 Flack parameter: 0.02 (2)

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------|-------------|-----------------|-------------|
| Pd1—Br3 | 2.4285 (5) | Pd1—Br2 | 2.4388 (4) |
| Pd1—Br1 | 2.4342 (4) | Pd1—Br4 | 2.4415 (5) |
| Br3—Pd1—Br1 | 178.62 (2) | Br1—Pd1—Br4 | 90.668 (16) |
| Br1—Pd1—Br2 | 89.738 (16) | | |
| N2—C4—C5—C6 | -179.6 (4) | N4—C12—C13—C14 | -177.0 (4) |
| C4—C5—C6—C7 | -176.9 (5) | C12—C13—C14—C15 | 68.2 (5) |

Table 2

Hydrogen-bond geometry (Å, °).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| C4—H4B...Br1 ⁱ | 0.97 | 2.88 | 3.678 (5) | 140 |
| C10—H10...Br1 ⁱⁱ | 0.93 | 2.86 | 3.755 (5) | 163 |
| C11—H11...Br3 ⁱⁱⁱ | 0.93 | 2.81 | 3.687 (5) | 157 |
| C12—H12A...Br3 ^{iv} | 0.97 | 2.81 | 3.730 (5) | 159 |
| C16—H16B...Br1 | 0.96 | 2.92 | 3.854 (5) | 165 |

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

The methyl H atoms were constrained to an ideal geometry, with C–H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, but the methyl group was allowed to rotate freely about its C–C bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.97–1.00 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 2005); cell refinement: *SAINTE* (Bruker, 2005); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

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