**trans-Diacetonitriledibromopalladium(II)**

In the title compound, \([\text{PdBr}_2(\text{C}_2\text{H}_3\text{N})_2]\), the square-planar Pd\(\text{II}\) atom, on an inversion centre, has *trans* arrangements of the MeCN and of the bromo ligands. The molecules pack with weak C—H···Br interactions supporting a three-dimensional network.

**Comment**

Square-planar Pd\(\text{II}\) and Pt\(\text{II}\) complexes of the type \([\text{MX}_2(\text{NCR})_2]\) (\(M = \text{Pd or Pt; } X = \text{Cl, Br or I; } R = \text{alkyl or aryl}\)) are widely used as starting materials in coordination chemistry. The synthesis of \([\text{PdCl}_2(\text{NCPh})_2]\) was first reported by Kharasch *et al.* (1938) and this method of preparation has subsequently been adopted for a range of related complexes (Doyle *et al.*, 1960). Recently, we have had cause to use \([\text{PdX}_2(\text{NCMe})_2]\) complexes, and during these studies we obtained crystals of the title compound, *trans*-\([\text{PdBr}_2(\text{NCMe})_2]\), (I). Although complexes of the form \([\text{MX}_2(\text{NCMe})_2]\) (\(M = \text{Pd or Pt; } X = \text{Cl, Br or I}\)) are well documented synthetically, a search of the Cambridge Structural Database (CSD, Version 5.27; Allen, 2002) revealed little structural information (Edwards *et al.*, 1998; Kritzenberger *et al.*, 1994; Newkome *et al.*, 1986; Rochon *et al.*, 1984).

![Structure of (I)](image)

Fig. 1 shows the structure of a molecule of (I), together with the numbering scheme adopted. Atom Pd1 lies on an inversion centre. The square-planar coordination is as expected for Pd\(\text{II}\) and exact planarity is imposed by crystallographic symmetry requirements. All bond distances and angles are unexceptional (Table 1).

There are only two other structures of *trans*-\([\text{MX}_2(\text{NCMe})_2]\) in the CSD: \(M = \text{Pd, } X = \text{Cl}\) (Edwards *et al.*, 1998) and \(M = \text{Pt, } X = \text{Cl}\) (Kritzenberger *et al.*, 1994). These complexes and (I) crystallize in the space group \(P2_1/c\) and cell dimensions for all three complexes are similar.

A discussion of the packing is instructive. Of the previously reported analogues, the structure of *trans*-\([\text{PdCl}_2(\text{NCMe})_2]\) (Edwards *et al.*, 1998) is deposited in the CSD as a private communication, while for *trans*-\([\text{PtCl}_2(\text{NCMe})_2]\) (Kritzenberger *et al.*, 1994), no H-atom positions are included. Fig. 2
trans of an acetonitrile solution of the complex. In vacuo washed and dried added to precipitate the product. This was collected by filtration, the solution was reduced to half under vacuum, and then Et2O while hot and the filtrate cooled to room temperature. The volume of heated at reflux overnight. The resultng orange solution was filtered unlabelled atoms: $-x, -y, -z$.)

shows a view of the packing for (I). The molecules are aligned so as to optimize short intermolecular C—H⋯Br contacts (Table 2). These intermolecular interactions support a three-dimensional network. However, we note that the formation of C—H⋯Br—Pd hydrogen bonds between a weak donor and a strong acceptor is not surprising in the light of detailed analyses of halide ions and M⋯X ($X =$ halogen) behaving as hydrogen-bond acceptors (Aullón et al., 1998; Brammer et al., 1999; Brammer et al., 2001; Steiner, 1998).

**Experimental**

A mixture of PdBr$_2$ (200 mg, 0.75 mmol) in MeCN (10 ml) was heated at reflux overnight. The resulting orange solution was filtered while hot and the filtrate cooled to room temperature. The volume of the solution was reduced to half under vacuum, and then Et$_2$O was added to precipitate the product. This was collected by filtration, washed and dried in vacuo. Crystals were grown by slow evaporation of an acetonitrile solution of the complex, trans-[PdBr$_2$(NCMe)$_3$] was isolated as a dark-orange powder (yield 166 mg, 63.6%). Analysis, found for C$_{16}$H$_8$Br$_2$N$_2$Pd·1.5H$_2$O: C 12.8, H 2.4, N 7.4%; calculated: C 12.8, H 2.4, N 7.5%.

**Crystal data**

<table>
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<tr>
<th>Compound</th>
<th>Chemical formula</th>
<th>M$_r$</th>
<th>Density</th>
<th>Space group</th>
<th>$Z$</th>
<th>$D_a$</th>
<th>Radiation</th>
<th>Temperature</th>
<th>$T$</th>
<th>Crystal size</th>
<th>$I_{	ext{min}}$</th>
<th>$I_{	ext{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdBr$_2$(C$_2$H$_3$N)$_2$</td>
<td>[PdBr$_2$(C$_2$H$_3$N)$_2$]</td>
<td>548.31</td>
<td>2.607</td>
<td>P2$_1$/c</td>
<td>2</td>
<td>11.02</td>
<td>Mo Kα</td>
<td>173</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Data collection**

| Nonius KappaCCD area-detector | Otwinowski & Minor, 1997 |
| ϕ and ω scans | $T_{	ext{min}} = 0.10, T_{	ext{max}} = 0.19$ |
| Absorption correction: multi-scan | 4797 measured reflections |
| (DENZO/SCALEPACK) | 1291 independent reflections |
| | 1003 reflections with $I > 3σ(I)$ |
| $R_{	ext{int}} = 0.032$ | $θ_{	ext{max}} = 30.1^\circ$ |

**Refinement**

Refinement on $F$

$R[F > 2σ(F)] = 0.021$

$wR(F^2) = 0.025$

$S = 1.03$

1003 reflections

43 parameters

H-atom parameters constrained

$w = [1 – (F_c/F_s)^2]^{1/2}$/

$[0.577T_d(x) + 0.221T_t(x)]$

**Table 1**

| Pd1—Br1 | 2.4203 (3) |
| Pd1—N1 | 1.966 (2) |
| Br1—Pd1—N1 | 89.93 (7) |
| C2—Cl—N1 | 179.6 (3) |
| Pd1—N1—Cl | 1.452 (4) |
| Pd1—N1—Cl | 1.136 (4) |

**Table 2**

<table>
<thead>
<tr>
<th>D—H⋯A</th>
<th>D—H</th>
<th>H⋯A</th>
<th>D⋯A</th>
<th>D—H⋯A</th>
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<td>3.05</td>
<td>3.718 (3)</td>
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<tr>
<td>C2—H22⋯Br1</td>
<td>0.97</td>
<td>3.09</td>
<td>3.698 (3)</td>
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<tr>
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<td>0.98</td>
<td>2.89</td>
<td>3.794 (3)</td>
<td>157</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x, y, z + 1; (ii) x + 1, y, z + 1; (iii) x, y, z + 1.

H atoms were found in a difference map and initially refined with appropriate restraints, with a target C—H of 0.96 Å and $U_{	ext{iso}}(H) = 1.2U_{	ext{eq}}(C)$. They were then treated as riding.

Data collection: COLLECT (Nonius, 2001); cell refinement: DENZO/SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO/SCALEPACK; program(s) used to solve structure: SIR92 (Altomare et al., 1994); program(s) used to refine structure: CRYSTALS (Betteridge et al., 2003); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: CRYSTALS.

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References


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