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Key indicators

Single-crystal X-ray study
 $T = 173$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.021
 wR factor = 0.025
Data-to-parameter ratio = 23.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.*trans*-Diacetonitriledibromopalladium(II)

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

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Comment

Square-planar Pd^{II} and Pt^{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 $[\text{PdCl}_2(\text{NPh})_2]$ 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).

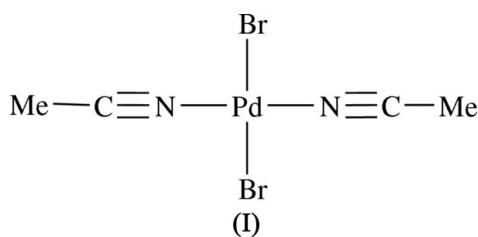


Fig. 1 shows the structure of a molecule of (I), together with the numbering scheme adopted. Atom Pd1 lies on an inversion centre. The square-planar coordination is as expected for Pd^{II} and exact planarity is imposed by crystallographic symmetry requirements. All bond distances and angles are unexceptional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

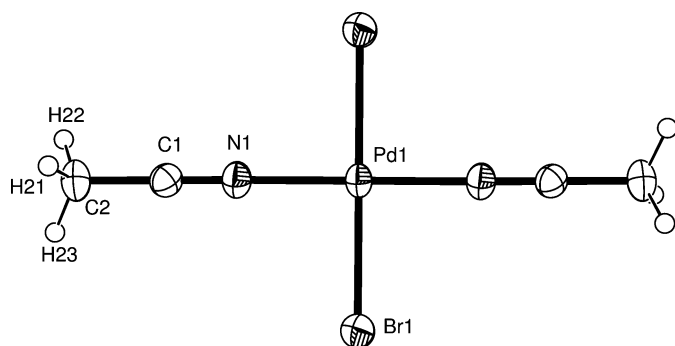


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. (Symmetry code for unlabelled atoms: $-x, -y, -z$.)

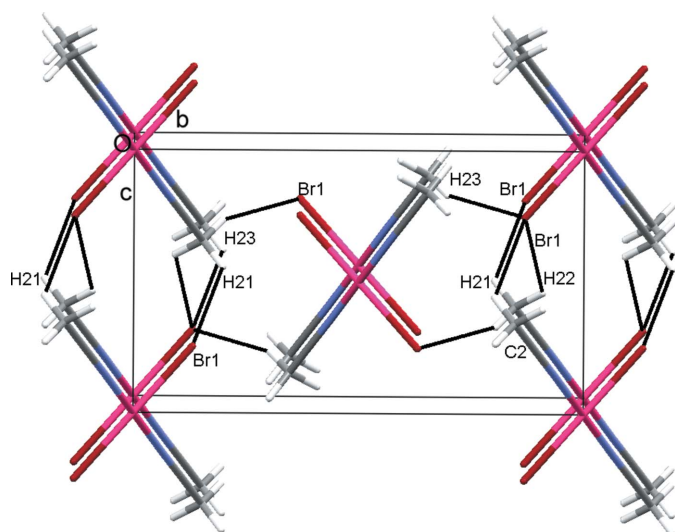


Figure 2
The packing of (I), viewed approximately down the a axis, showing the intermolecular C—H...Br interactions (black lines).

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 $M-X$ ($X = \text{halogen}$) 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_2O 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*- $[\text{PdBr}_2(\text{NCMe})_2]$ was isolated as a dark-orange powder (yield 166 mg, 63.6%). Analysis,

found for $\text{C}_4\text{H}_6\text{Br}_2\text{N}_2\text{Pd}\cdot 1.5\text{H}_2\text{O}$: C 12.8, H 2.4, N 7.4%; calculated: C 12.8, H 2.4, N 7.5%.

Crystal data

$[\text{PdBr}_2(\text{C}_2\text{H}_3\text{N})_2]$
 $M_r = 348.31$
Monoclinic, $P2_1/c$
 $a = 5.1979(3) \text{ \AA}$
 $b = 12.0686(7) \text{ \AA}$
 $c = 7.0740(3) \text{ \AA}$
 $\beta = 90.327(3)^\circ$
 $V = 443.75(4) \text{ \AA}^3$

$Z = 2$
 $D_x = 2.607 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
 $\mu = 11.02 \text{ mm}^{-1}$
 $T = 173 \text{ K}$
Block, dark orange
 $0.24 \times 0.19 \times 0.15 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (*DENZO/SCALEPACK*;

Otwinowski & Minor, 1997)
 $T_{\min} = 0.10$, $T_{\max} = 0.19$
4797 measured reflections
1291 independent reflections
1003 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\text{max}} = 30.1^\circ$

Refinement

Refinement on F
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.025$
 $S = 1.03$
1003 reflections
43 parameters
H-atom parameters constrained
 $w = [1 - (F_o - F_c)^2/36\sigma^2(F)]^2 / [0.377T_0(x) + 0.221T_1(x) +$

$0.171T_2(x)]$
where T_i are Chebyshev polynomials and $x = F_o/F_{\text{max}}$ (Prince, 1982; Watkin, 1994)
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.53 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.67 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Pd1—Br1	2.4203 (3)	C1—C2	1.452 (4)
Pd1—N1	1.966 (2)	C1—N1	1.136 (4)
Br1—Pd1—N1	89.93 (7)	Pd1—N1—C1	178.7 (2)
C2—C1—N1	179.6 (3)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H21...Br1 ⁱ	0.96	3.05	3.718 (3)	128
C2—H22...Br1 ⁱⁱ	0.97	3.09	3.698 (3)	122
C2—H23...Br1 ⁱⁱⁱ	0.96	2.89	3.794 (3)	157

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

H atoms were found in a difference map and initially refined with appropriate restraints, with a target C—H of 0.96 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. 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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