

{2,6-Bis[(dimethylamino- κN)methyl]-phenyl- κC]iodopalladium(II) bis(diiodine)}

Allison M. Mills,^{a*} Johannus A. M. van Beek,^b Gerard van Koten^b and Anthony L. Spek^a

^aBijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and

^bDebye Institute, Department of Metal-Mediated Synthesis, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Correspondence e-mail: a.m.mills@chem.uu.nl

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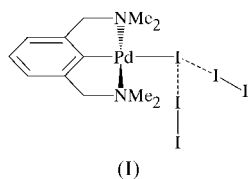
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The distorted square-planar coordination environment of the palladium(II) centre in [Pd(NCN)I]·2I₂ {NCN is 2,6-bis[(dimethylamino)methyl]phenyl, C₁₂H₁₉N₂} is defined by the monoanionic terdentate NCN ligand and one iodide anion. Two neutral I₂ molecules interact with the coordinated iodide anion at distances of ~3.3 Å, suggesting an alternative description of the title compound as a palladium penta-iodide complex, *i.e.* [Pd(NCN)I₅]. Weaker interactions of ~3.6 Å between the I₅⁻ anions link the complexes into a two-dimensional network.

Comment

In its terdentate coordination mode, the monoanionic aryldiamine ligand 2,6-bis[(dimethylamino)methyl]phenyl (NCN) acts as a rigid backbone with strong electron-donating ability (Albrecht & van Koten, 2001; Rietveld *et al.*, 1997). The unique properties of this pincer ligand allowed the preparation of the first complex containing an end-on coordinated I₂ molecule, [Pt(NCN)I(η¹-I₂)] (van Beek *et al.*, 1986; Gossage *et al.*, 1999). A number of similar five-coordinate η¹-I₂-Pt complexes with aryldiamine pincer ligands have subsequently



been reported (van Beek *et al.*, 1990; Gossage *et al.*, 1999). More recently, the unusual octahedral complex *trans*-[Pt(dmpe)₂I(η¹-I₂)]₃ [dmpe is 1,2-bis(dimethylphosphino)ethane] has been synthesized (Makiura *et al.*, 2001). These compounds have been proposed as models for the initial stage of the oxidative addition of dihalides to *d*⁸ transition metal complexes. An attempt to prepare an analogous palladium

complex, [Pd(NCN)I(η¹-I₂)], by reaction of [Pd(NCN)I] with I₂ led to the isolation of purple crystals with the stoichiometry [Pd(NCN)I₅] (Gossage *et al.*, 1999). In the title compound, [Pd(NCN)I]·2I₂, (I), two neutral I₂ molecules have been incorporated per [Pd(NCN)I] molecule, but neither interacts strongly with the metal atom. Selected geometric parameters for (I) are presented in Table 1.

As shown in Fig. 1, the coordination environment of the palladium(II) centre in (I) is defined by the monoanionic NCN pincer ligand and one iodide anion. The terdentate NCN ligand is coordinated to the metal *via* the anionic C1 [Pd—C 1.920 (8) Å] and the two amine N atoms [Pd—N 2.111 (7) and 2.126 (7) Å] at distances comparable to those in other NCN—Pd complexes, such as [(NCN)Pd(μ-Cl)Pd(NCN)]BF₄ [Terheijden *et al.*, 1987; Pd—C 1.909 (4)/1.929 (4) Å and Pd—N 2.094 (3)—2.105 (3) Å]. The iodide anion is coordinated *trans* to C1, an *sp*² donor with a large *trans* influence, at a Pd—I distance of 2.7731 (10) Å, which is somewhat longer than the distance observed in *trans*-[Pd{η¹, κC -(3,5-NCN)}(PPh₃)₂I] [3,5-NCN is 3,5-bis[(dimethylamino)methyl]phenyl; Spee *et al.*, 2000; Pd—I 2.6968 (4) Å]. The small bite angles of the NCN ligand [80.2 (3) and 81.3 (3)°] result in a distorted square-planar geometry at the metal atom; although the *cis* angles sum to 360.0 (5)°, they deviate by up to 13° from the ideal values of 90°. The two five-membered PdC₃N chelate rings adopt envelope conformations, but are puckered in opposite directions, with the *N*-donors mutually *trans*. Thus, the PdCN₂I coordination plane is tilted by 13.7 (4)° with respect to the plane of the aryl ring. The meridional coordination mode of the NCN ligand observed in (I) is typical of most square-planar NCN—metal complexes, including [Pt(NCN)I] (Smeets *et al.*, 1987), and results in approximate (non-crystallographic) C₂ symmetry for [Pd(NCN)I].

Two neutral I₂ molecules are positioned 3.2720 (11) and 3.2886 (11) Å from the coordinated iodide anion. These contacts are somewhat shorter than the weakly bonding

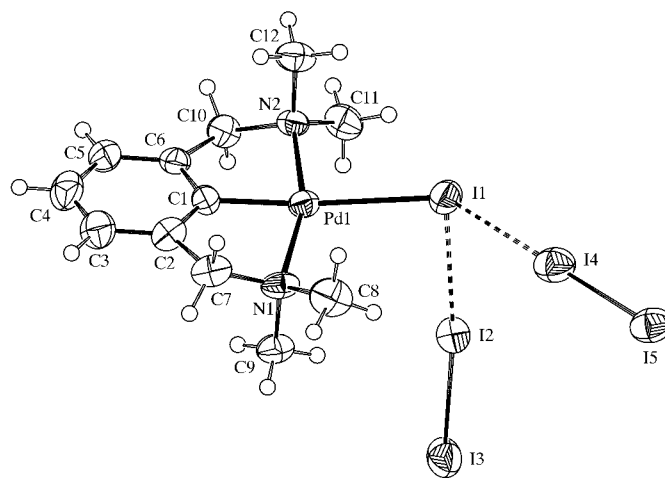
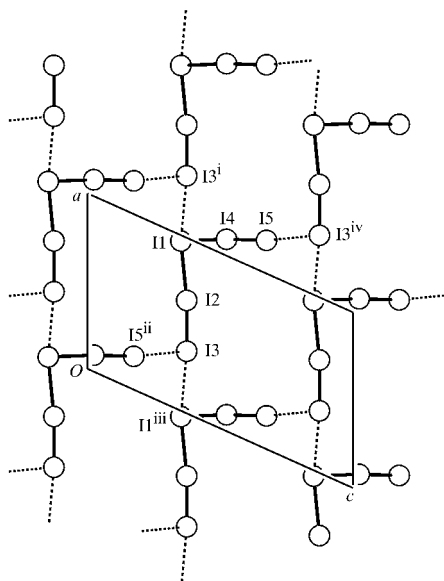


Figure 1
PLATON/ORTEP representation (Spek, 2002) of (I) with displacement ellipsoids at the 50% probability level. The dashed lines indicate intermediate I—I distances of ~3.3 Å between the coordinated iodide anion and the neutral I₂ molecules.

**Figure 2**

View down the b axis of the kinked two-dimensional $[I_5^-]$ net in (I). The I_5^- anions are connected by weak $I \cdots I$ contacts of ~ 3.6 Å, which are represented by dashed lines [symmetry codes: (i) $1 + x, y, z$; (ii) $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $x - 1, y, z$; (iv) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$].

intermolecular distance of 3.496 (6) Å in the crystal structure of iodine. The bond lengths within the perturbed I_2 molecules [$I-I$ 2.7477 (11) and 2.7729 (11) Å], on the other hand, are slightly elongated compared to the intramolecular distance of 2.715 (6) Å in elemental iodine (van Bolhuis *et al.*, 1967). These considerations suggest an alternative description of the title compound as a palladium penta-iodide complex, *i.e.* $[Pd(NCN)I_5]$, in which the I_5^- anion is an adduct of the type $[I \cdot 2I_2]$. The coordinated I_5^- anion is L-shaped, with inner and outer angles of 90.37 (2) and 172.42 (3)/175.53 (3)°, respectively, and is oriented such that one I_2 component is nearly perpendicular to the NCN aryl-ring plane [83.5 (4)°]. The observed values of both the $I-I-I$ angles and $I-I$ distances in the coordinated ion fall within the range reported for free I_5^- anions (Cambridge Structural Database, Version 5.22 of October 2001; Allen & Kennard, 1993).

The $[Pd(NCN)I_5]$ complexes are linked by weaker $I \cdots I$ interactions (Table 2) that are nevertheless considerably shorter than the sum of the van der Waals radii (3.96 Å; Bondi, 1964). The central I1 atom of one I_5^- anion interacts with the terminal I3 atom of the next I_5^- anion [$I1 \cdots I3^i$ 3.5851 (13) Å; symmetry code: (i) $1 + x, y, z$], forming infinite one-dimensional chains that run along the a direction. Head-to-tail $I_5^- \cdots I_5^-$ contacts [$I3 \cdots I5^{ii}$ 3.6495 (13) Å; symmetry code: (ii) $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$] link the chains into a two-dimensional network. In the anionic $[I_5^-]$ substructure, kinked polyiodide nets composed of fused 12-membered rings, presented in Fig. 2, are stacked perpendicular to the b direction.

Experimental

The title compound was prepared by adding I_2 to a solution of $[Pd(NCN)I]$ in CH_2Cl_2 . Purple crystals suitable for X-ray analysis were obtained after recrystallization of the crude product from a CH_2Cl_2 /hexanes mixture (Gossage *et al.*, 1999).

Crystal data

$[Pd(C_{12}H_{19}N_2)I] \cdot 2I_2$
 $M_r = 932.19$
 Monoclinic, $P2_1/c$
 $a = 9.585$ (2) Å
 $b = 15.510$ (2) Å
 $c = 15.865$ (2) Å
 $\beta = 114.198$ (11)°
 $V = 2151.3$ (6) Å³
 $Z = 4$

$D_x = 2.878$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 11.3$ – 14.2 °
 $\mu = 8.03$ mm⁻¹
 $T = 294$ (2) K
 Needle, purple
 $1.45 \times 0.38 \times 0.30$ mm

Data collection

Enraf–Nonius CAD-4F diffractometer
 $\omega/2\theta$ scans
 Absorption correction: analytical (*ABSTOMPA* in *PLATON*; Spek, 2002)
 $T_{min} = 0.063$, $T_{max} = 0.140$
 4036 measured reflections
 3796 independent reflections

3296 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.038$
 $\theta_{max} = 25.0$ °
 $h = -11 \rightarrow 0$
 $k = -18 \rightarrow 0$
 $l = -17 \rightarrow 18$
 2 standard reflections
 frequency: 60 min
 intensity decay: 25%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.104$
 $S = 1.16$
 3796 reflections
 186 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 15.2774P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 1.45$ e Å⁻³
 $\Delta\rho_{min} = -0.93$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.00323 (15)

Table 1

Selected geometric parameters (Å, °).

I1–Pd1	2.7731 (10)	I4–I5	2.7477 (11)
I1–I2	3.2720 (11)	Pd1–C1	1.920 (8)
I1–I4	3.2886 (11)	Pd1–N1	2.111 (7)
I2–I3	2.7729 (11)	Pd1–N2	2.126 (7)
I2–I1–I4	90.37 (2)	N1–Pd1–N2	161.4 (3)
I3–I2–I1	172.42 (3)	C1–Pd1–I1	174.8 (2)
I5–I4–I1	175.53 (3)	N1–Pd1–I1	102.9 (2)
C1–Pd1–N1	80.2 (3)	N2–Pd1–I1	95.65 (19)
C1–Pd1–N2	81.3 (3)		

Table 2

Selected contact distances (Å).

$I1 \cdots I3^i$	3.5851 (13)	$I3 \cdots I5^{ii}$	3.6495 (13)
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Symmetry codes: (i) $1 + x, y, z$; (ii) $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$.

X-ray data were collected using Zr-filtered Mo $K\alpha$ radiation with a collimator broad enough to accommodate the larger than usual maximum crystal dimension of 1.45 mm (Alexander & Smith, 1962). The aromatic and methylene H atoms were placed in idealized positions and allowed to ride on their C atoms, with $C-H = 0.93$ and 0.97 Å, respectively, and $U_{iso}(H) = 1.2U_{eq}(C)$. The methyl H atoms were constrained to ideal geometries and allowed to rotate freely about their $C-C$ bonds, with $C-H = 0.96$ Å and $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: locally modified *CAD-4 Software* (de Boer & Duisenberg, 1984); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1107). Services for accessing these data are described at the back of the journal.

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