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Robust packing in cyclopalladated primary amines: isomorphous crystal structures of four complexes with varying substitution patterns

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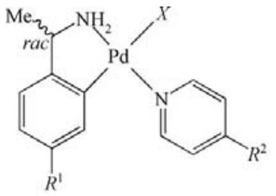
The crystal structures of (*SP*-4-4)-[*rac*-2-(1-aminoethyl)phenyl-κ^2C^1,N]chlorido(pyridine-κN)palladium(II), $[Pd(C_8H_{10}N)Cl(C_5H_5N)]$, (I), (*SP*-4-4)-[*rac*-2-(1-aminoethyl)phenyl-κ^2C^1,N]bromido(pyridine-κN)palladium(II), $[PdBr(C_8H_{10}N)(C_5H_5N)]$, (II), (*SP*-4-4)-[*rac*-2-(1-aminoethyl)-5-bromophenyl-κ^2C^1,N]bromido(4-methylpyridine-κN)palladium(II), $[PdBr(C_8H_9BrN)(C_6H_7N)]$, (III), and (*SP*-4-4)-[*rac*-2-(1-aminoethyl)-5-bromophenyl-κ^2C^1,N]iodido(4-methylpyridine-κN)palladium(II), $[Pd(C_8H_9BrN)I(C_6H_7N)]$, (IV), are reported. The latter is the first iodide complex in this class of compounds. All four complexes crystallize in the same space group, *viz*. $I4_1/a$, with very similar lattice parameters *a* and more flexible lattice parameters *c*. Their packing corresponds to that of their enantiomerically pure congeners, which crystallize in the *t*2 subgroup $I4_1$.

Comment

Orthopalladation was first reported by Cope & Friedrich (1968) and was originally restricted to activated tertiary amines. Contributions by Dunina *et al.* (1999), Fuchita and co-workers (Fuchita & Tsuchiya, 1993; Fuchita *et al.*, 1995, 1997) and Vicente *et al.* (1993, 1995, 1997, 2003) paved the way towards more general substrates. We have structurally characterized reaction products and intermediates (Calmuschi & Englert, 2002; Calmuschi, Jonas & Englert, 2004; Calmuschi-Cula *et al.*, 2005) and have used the target molecules in crystal engineering (Calmuschi, Alesi & Englert, 2004; Calmuschi & Englert, 2005). In this context, we previously reported (Calmuschi & Englert, 2002) pronounced pseudosymmetry in the crystal structure of the enantiomerically pure complex (*SP*-4-4)-[(*R*)-2-(1-aminoethyl)phenyl-κ^2-C^1,*N*]chlorido(pyridine-κN)palladium(II), *R*-(I). Complex (I) crystallizes in the space group $I4_1$, and we suggested that the centrosymmetric supergroup $I4_1/a$ might be the appropriate space group in the case of the racemate of this compound, *rac*-(I). In the present contribution, we confirm our earlier assumption: *rac*-(I) indeed crystallizes in $I4_1/a$, with lattice parameters very similar to those of the pure enantiomers. The results of a seeding experiment underline the similarity in the molecular arrangements of *R*-(I) and *rac*-(I). A crystal of the former was immerged in a saturated solution of the latter and allowed to grow under slow stirring while the temperature was gradually reduced from 292 to 282 K over a period of three months. IR spectroscopy on small peripheric fragments of the resulting large object revealed that the racemic solid grew on top of the enantiomerically pure seeded crystal. The IR spectra (KBr pellets) of *rac*-(I) show one strong and one much weaker band, while those of *R*-(I) exhibit two bands of equal intensity around 1600 cm^{-1}.



(I) R^1 = H, R^2 = H, X = Cl
(II) R^1 = H, R^2 = H, X = Br
(III) R^1 = Br, R^2 = Me, X = Br
(IV) R^1 = Br, R^2 = Me, X = I

The remaining three complexes, (II)–(IV), represented in the scheme, albeit different with respect to the metal-bonded halogen ligands *X* and the substituents both on the chelating ligand (R^1) and on the pyridine ring (R^2), also crystallize in the space group $I4_1/a$, with very similar packing and closely related lattice parameters *a*. Their unit-cell parameters *c*, however, cover a much wider range, between 15.5123 (14) and

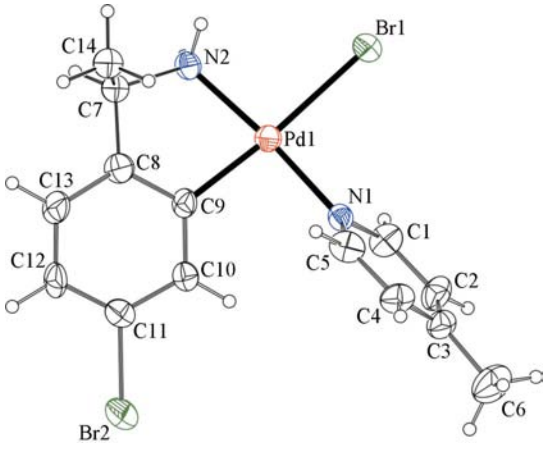


Figure 1
A displacement ellipsoid plot (at the 30% probability level) for (III). Atoms belonging to the minor conformer have been omitted for clarity. H atoms are shown as spheres of arbitrary radii. The same atomic numbering scheme has been used for all structures.

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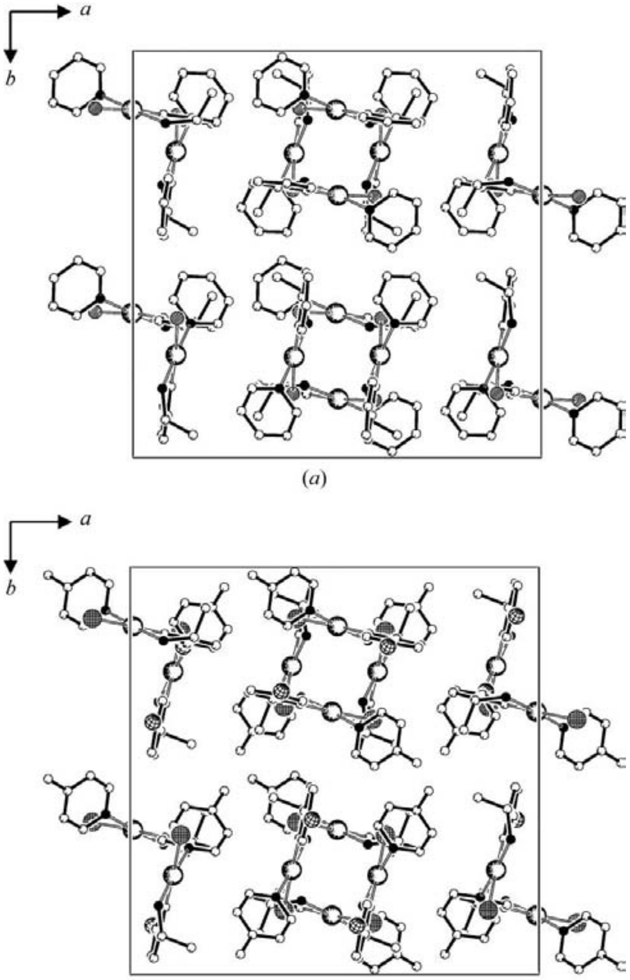
18.3193 (17) Å, according to the space filling requirements of the substituents. The molecular structure of (III) is illustrated in Fig. 1.

The underlying packing pattern of both the racemic and the enantiomerically pure palladium complexes is particularly robust and extends to a recently published series of chiral platinum derivatives (Calmuschi-Cula & Englert, 2008). Their racemic counterparts have not yet been structurally characterized but will most likely also crystallize in the *t*2 supergroup $I4_1/a$. We note that chemically related compounds with different substituents in the periphery do not generally show the same packing in the solid, in particular when more than one modification is made to a given structure. Comparisons of packing patterns on a sound statistical basis are not very popular because they usually imply extensive manual intervention in addition to database searches. However, van der Streek & Motherwell (2005) have recently published the GRX search algorithm and applied it to the question of isomorphism between chloro- and methyl-substituted compounds. They found that approximately 25% of their crystal structures are isostructural. Our complexes (I) and (IV) share the same packing pattern, although they differ in three positions, with an iodide replacing a chloride ligand at the metal, a Br substituent instead of a H atom in the cyclopalladated amine, and a methyl group rather than a H atom on the coordinated pyridine ring. Fig. 2 shows this similarity with respect to the packing.



(*a*)

(*b*)

Figure 2
Projections of the unit cells of (*a*) (I) and (*b*) (IV), showing the closely related packing. The compounds differ at the molecular level. In the *para* position of the primary amine, (I) features a H and (IV) a Br (globe pattern) substituent. In the *para* position of the pyridine ring, (IV) carries an extra methyl substituent. Compound (I) is a chloride (diagonal hatched) and (IV) an iodide (crosshatched) complex.

Complexes (I)–(IV) all exhibit classical intermolecular hydrogen bonds between the only relevant donors, namely the amine H atoms and the halide ligands of neighboring molecules. A summary of these interactions is provided in Table 1. Comparison with the Cambridge Structural Database (CSD; Allen, 2002) confirms that these hydrogen bonds are not exceptional. We searched the CSD for intermolecular contacts between NH donors and halogen-atom acceptors bonded to any other atom. The search was restricted to contacts with donor–hydrogen–acceptor angles greater than or equal to 140° and to error-free entries without disorder, and resulted in the following mean hydrogen–acceptor distances: $H\cdots Cl = 2.460$ Å, 5555 observations; $H\cdots Br = 2.639$ Å, 1053 observations; $H\cdots I = 2.843$ Å, 530 observations. The compounds described here are typical molecular crystals. Their packing coefficient – defined as the ratio between the filled volume, based on the van der Waals radii for all atoms, and the total volume of the unit cell – ranges from 68.6% for (IV) to 71.9% for (I). According to Kitaigorodsky (1973), 'the overwhelming majority of crystals' have packing coefficients between 65 and 77%.

Experimental

Complexes (I)–(IV) were prepared according to the procedures of Fuchita & Tsuchiya (1993) and/or Vicente *et al.* (1995). Light-yellow or colorless rods or blocks suitable for single-crystal X-ray diffraction were obtained by crystallization from methanol/water mixtures at room temperature. Crystals of (II) were covered with small crystallites of the same compound; as a result, an unusual second parameter in the weighting scheme, less satisfactory agreement factors and a clearly inferior $R_{\rm int}$ value were encountered.

Compound (I)

Crystal data

$[Pd(C_8H_{10}N)Cl(C_5H_5N)]$
$M_r = 341.12$
Tetragonal, $I4_1/a$
$a = 18.3310$ (8) Å
$c = 15.5123$ (14) Å
$V = 5212.5$ (6) Å^3

$Z = 16$
Mo $K\alpha$ radiation
$\mu = 1.61$ mm^{-1}
$T = 100$ (2) K
$0.23 \times 0.08 \times 0.04$ mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{\rm min} = 0.709$, $T_{\rm max} = 0.939$

33317 measured reflections
2990 independent reflections
2544 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.074$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.073$
$S = 1.11$
2990 reflections
153 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.50$ e Å^{-3}

Compound (II)

Crystal data

[PdBr($C_8H_{10}N$)(C_5H_5N)]
$M_r = 385.58$
Tetragonal, $I4_1/a$
$a = 18.5197$ (9) Å
$c = 15.7281$ (16) Å
$V = 5394.4$ (7) Å^3
$Z = 16$
Mo $K\alpha$ radiation
$\mu = 4.32$ mm^{-1}
$T = 110$ (2) K
0.17 × 0.05 × 0.03 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{\min} = 0.527$, $T_{\max} = 0.881$
29977 measured reflections
2519 independent reflections
1839 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.173$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.141$
$S = 1.11$
2519 reflections
153 parameters
15 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.73$ e Å^{-3}
$\Delta\rho_{\min} = -1.34$ e Å^{-3}

Compound (III)

Crystal data

[PdBr(C_8H_9BrN)(C_6H_7N)]
$M_r = 478.51$
Tetragonal, $I4_1/a$
$a = 18.5329$ (13) Å
$c = 18.071$ (3) Å
$V = 6206.8$ (12) Å^3
$Z = 16$
Mo $K\alpha$ radiation
$\mu = 6.33$ mm^{-1}
$T = 100$ (2) K
0.31 × 0.23 × 0.13 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{\min} = 0.244$, $T_{\max} = 0.493$ (expected range = 0.217–0.439)
13256 measured reflections
3374 independent reflections
1916 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.067$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.075$
$S = 1.00$
3374 reflections
172 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.69$ e Å^{-3}
$\Delta\rho_{\min} = -0.59$ e Å^{-3}

Compound (IV)

Crystal data

[Pd(C_8H_9BrN)I(C_6H_7N)]
$M_r = 525.50$
Tetragonal, $I4_1/a$
$a = 18.8243$ (9) Å
$c = 18.3193$ (17) Å
$V = 6491.5$ (7) Å^3
$Z = 16$
Mo $K\alpha$ radiation
$\mu = 5.50$ mm^{-1}
$T = 110$ (2) K
0.13 × 0.09 × 0.08 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*MULABS* as implemented in *PLATON*; Spek, 2003)
$T_{\min} = 0.535$, $T_{\max} = 0.668$
38236 measured reflections
3338 independent reflections
2302 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.088$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.059$
$S = 1.01$
3338 reflections
172 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.69$ e Å^{-3}
$\Delta\rho_{\min} = -0.52$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

Complex	D—H···A	D—H	H···A	D···A	D—H···A
(I)	N2—H2*A*···Cl1$^{\rm i}$	0.92	2.54	3.318 (3)	142
(I)	N2—H2*B*···Cl1$^{\rm ii}$	0.92	2.47	3.357 (3)	161
(II)	N2—H2*A*···Br1$^{\rm i}$	0.92	2.68	3.471 (8)	144
(II)	N2—H2*B*···Br1$^{\rm ii}$	0.92	2.59	3.494 (8)	166
(III)	N2—H2*A*···Br1$^{\rm i}$	0.92	2.80	3.568 (4)	142
(III)	N2—H2*B*···Br1$^{\rm ii}$	0.92	2.60	3.475 (4)	160
(IV)	N2—H2*A*—I1$^{\rm i}$	0.92	3.02	3.793 (4)	143
(IV)	N2—H2*B*—I1$^{\rm ii}$	0.92	2.81	3.696 (4)	162

Symmetry codes: (i) $-y+\frac{1}{4}, x+\frac{1}{4}, -z+\frac{1}{4}$; (ii) $-x, -y+\frac{1}{2}, z$.

After completion of the initial structure models, residual maxima were found with electron densities between 1.3 and 2.2 e Å^{-3}, and at distances between 1.3 and 1.4 Å from the corresponding chiral center (C7), indicating disorder for the attached methyl group (C14). A pronounced prolate anisotropic displacement parameter for the chiral C7 atom induced us to consider split positions for this atom also. The sum of the site-occupation factors of both conformations was constrained to unity, the disordered atoms were refined with isotropic displacement parameters and distance restraints were imposed on the bond lengths involved. Occupancies for disordered sites and interatomic distances for each structure are given in the supplementary material. H atoms were treated as riding on the corresponding C (C—H = 0.98 Å) or N atoms (N—H = 0.92 Å).

For all compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3003). Services for accessing these data are described at the back of the journal.

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