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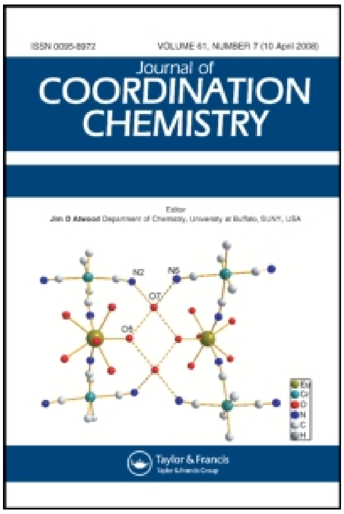

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
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THE CRYSTAL STRUCTURE OF DIBROMO (PHENYL-2-PYRIDYL DIMETHYLHYDRAZONE)PALLADIUM(II)

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To cite this Article Kovala-Demertzi, Dimitra , Domopoulou, Asimina , Nicholls, David , Michaelides, Adonis and Aubry, André(1993) 'THE CRYSTAL STRUCTURE OF DIBROMO (PHENYL-2-PYRIDYL DIMETHYLHYDRAZONE)PALLADIUM(II)', Journal of Coordination Chemistry, 30: 3, 265 — 271

To link to this Article: DOI: 10.1080/00958979308022759

URL: http://dx.doi.org/10.1080/00958979308022759

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J. Coord. Chem., 1993, Vol 30, pp. 265–271
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NOTE

THE CRYSTAL STRUCTURE OF DIBROMO (PHENYL-2-PYRIDYL DIMETHYLHYDRAZONE)PALLADIUM(II)

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KEYWORDS: Pd(II), hydrazones, x-ray structure

Nitrogen-containing heterocyclic compounds play an important role in several biological processes. Furthermore, their biological activity seems often to depend upon interaction with a metal ion. Interest in the study of hydrazones and their metal complexes has been growing because of their physiological activity, coordination capability and application in analytical chemistry.[1,2] Many hydrazones and their metallic derivatives show very interesting biological activity, *e.g.*, as antitumour or anticonvulsant agents, and behave as cytotoxic compounds toward tumour cells.[3] During the past few years, in addition to platinum compounds, coordination compounds of palladium(II) and (IV) seem to be promising in cancer chemotherapy.[4] Due to the biological activity of heterocyclic hydrazones and in continuing our systematic investigations of the platinum group metals with hydrazones and generally with heterocyclic nitrogen donor ligands,[5-10] we report here the crystal structure of dibromo(phenyl-2-pyridyldimethylhydrazone) palladium(II).

Template condensation of phenyl 2-pyridylketone with dimethylhydrazine in the presence of Li_2PdBr_4 in methanol solution results in the formation of two adducts. Crystals of each compound could be easily separated owing to their different colours. The yellow product is the *trans* complex PdL_2Br_2 where L = phenyl-2-pyridylketone. The crystal structure of this complex has been described elsewhere.[10] The red product is the complex $Pd(PPDH)Br_2$ where PPDH = dimethylhydrazone of phenyl-2-pyridylketone.

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Steric effects involving the *N*-dimethyl group in combination with the presence of a bulky phenyl group, inhibit the formation of the hydrazone adduct in this case and a mixture of two product PdL_2Br_2 and $Pd(PPDH)Br_2$ is obtained.

EXPERIMENTAL

Synthesis

A mixture of the solid $PdCl_2$ (0.425 g, 2.4 mmol) in methanol and concentrated hydrobromic acid (48%, 1.08 cm^3, 9.6 mmol) in methanol (1:4 molar ratio, metal salt to acid) was refluxed for 2 h. The resulting solution of Li_2PdBr_4, after filtration, was mixed with a solution of phenyl-2-pyridylketone (0.366 g, 2.0 mmol) and dimethylhydrazine (0.1 cm^3, 2.34 mmol) in methanol. The reaction mixture was stirred for 24 h at room temperature, during which time it slowly lightened in colour, then it was left in the refrigerator for one day. The resulting yellow powder was washed with methanol and ether and dried under vacuum. The red-orange filtrate was left for slow evaporation. Two different types of crystals formed, yellow plates together with red needles. The crystals were separated manually. The yellow powder and crystals were identified by I.R. spectroscopy and single crystal X-ray diffraction methods as PdL_2Br_2 (where L = phenyl-2-pyridylketone)[10] and the red needles as $Pd(PPDH)Br_2$)where PPDH = dimethylhydrazone of phenyl-2-pyridylketone).

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Crystal data and structure solution

Weissenberg photographs were used for investigating space group and approximate unit-cell dimensions. X-ray data were collected at room temperature in the $\omega/2\theta$ scan mode ($\theta < 27°$) on an Enraf-Nonius CAD-4 diffractometer with (Mo Kα) graphite-monochromatised Mo Kα radiation. Accurate lattice parameters were derived from the setting angle of 25 reflections ($6 < \theta < 15$). Crystal data are summarised in Table 1.

Table 1 Crystal data for $Pd(PPDH)Br_2$

Formula	$PdBr_2N_3C_{14}H_{15}$
M	491.52
a (Å)	17.170(2)
b (Å)	9.090(3)
c (Å)	10.080(3)
V(Å^3)	1573
Z	4
Dx (gcm^{-3})	2.011
Space group	$P2_12_12_1$
Total reflections	1597
Used reflections with $I > \sigma(I)$	1144
Weighting scheme	$w = 1/[\sigma^2(F) + 0.0159F^2]$
R	0 = .087
R_W	0.097
GOF	1.09

Data reduction was performed by using the SDP package.[11] Intensities were corrected for Lorentz and polarization effects. No absorption corrections were applied (cryst. max. dim. 0.2 mm). The Pd position was determined by direct methods with MULTAN-80.[12] The remaining atoms were located from difference Fourier maps, using SHELX-76.[13] No hydrogen atoms could be located. Anisotropic refinement was possible only by using a damping factor (with SHELX-76). Data collection with another crystal and using Ag Kα radiation gave the same results.

Geometric calculations were performed with ORFFE[14] and BONDLA of the XTAL 3.0 package;[15;18] MOLDRAW[16] and SCHAKAL[17] were used for plotting of the structure. Final coordinates and *Beq* values are listed in Table. 2.

RESULTS AND DISCUSSION

A drawing of the complex [Pd(PPDH)Br_2] with the atom numbering scheme is shown in Figure 1. Tables 3 and 4 list selected bond distances and angles, respectively. The Pd(II) atom is four coordinated and is surrounded in a planar fashion by two *cis* nitrogen atoms of the bidentate chelate ligand PPDH and two *cis* bromide atoms. The four atoms are nearly coplanar (to within 0.18 Å) and the Pd(II) atom is displaced 0.004 Å from the least-squares plane. The Pd-N_2 (pyridine) distance is 2.03(2) Å, whereas Pd-N_1 (azomethine) is 2.05(2) Å. This very small difference could be due to subtle constraints in the geometry of the ligand or could be explained in terms of hard and soft acid and base concepts.[19] Pd(II) is known

Table 2 Positional parameters and estimated standard deviations.

Atom	*x/a*	*y/b*	*z/c*	*B*(Å2)
Pd	0.2354(1)	0.1515(2)	0.1337(2)	2.55(3)
Br1	0.3134(3)	0.3634(6)	0.1340(6)	7.8(1)
Br2	0.3289(3)	0.0388(9)	0.2663(6)	8.5(1)
N1	0.153(1)	-0.012(2)	0.136(2)	2.7(2)
N2	0.153(1)	0.249(2)	0.019(2)	2.8(2)
C1	0.160(2)	0.370(3)	-0.040(3)	4.5(2)
C2	0.084(2)	0.431(3)	-0.115(3)	4.5(2)
C3	0.027(2)	0.356(3)	-0.121(3)	3.5(2)
C4	0.024(2)	0.229(3)	-0.054(3)	3.2(2)
C5	0.084(1)	0.170(3)	0.012(2)	2.9(2)
C6	0.090(1)	0.028(3)	0.080(2)	2.6(2)
C7	0.017(2)	-0.063(3)	0.082(3)	3.4(2)
C8	-0.049(2)	-0.019(3)	0.168(3)	3.6(2)
C9	-0.116(2)	-0.102(3)	0.181(3)	4.1(2)
C10	-0.126(3)	-0.229(4)	0.091(3)	6.3(2)
C11	-0.069(2)	-0.261(3)	0.007(3)	5.4(2)
C12	0.013(2)	-0.184(3)	-0.011(3)	4.6(2)
N3	0.151(1)	-0.152(3)	0.198(2)	3.3(2)
C13	0.156(2)	-0.151(3)	0.331(3)	4.9(2)
C14	0.212(2)	-0.247(3)	0.141(3)	4.3(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a^2 * *B*(1, 1) + b^2 * *B*(2, 2) + c^2 * *B*(3, 3) + *ab*(cos gamma) * *B*(1, 2) + *ac*(cos beta) * *B*(1, 3) + *bc*(cos alpha) * *B*(2, 3)].

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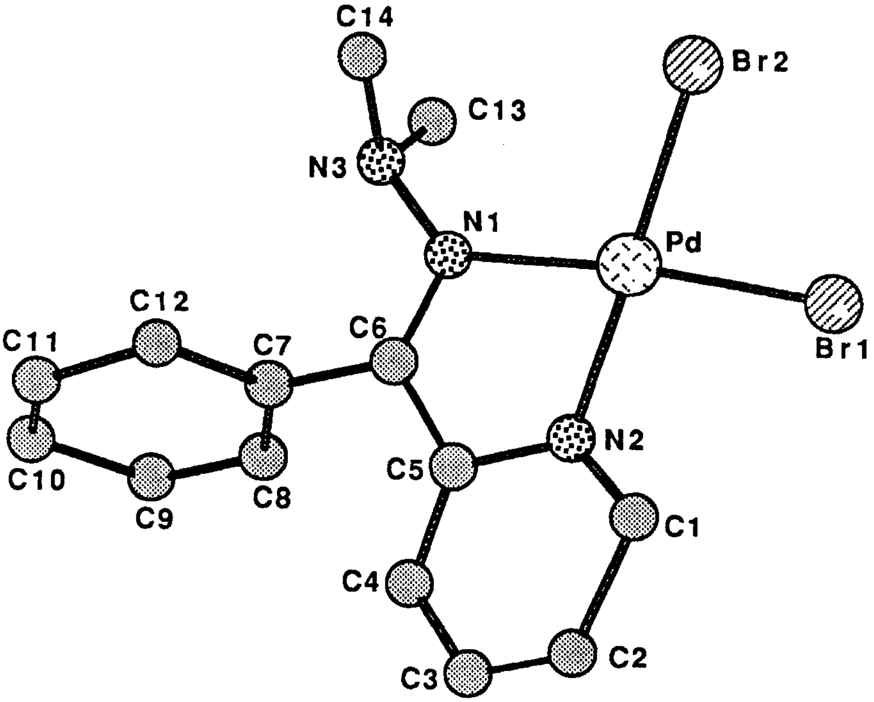

Figure 1 Atom numbering scheme for the complex molecule.

Table 3 Selected bond distances (Angstroms)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
PD	BR1	2.347(6)	C1	C2	1.60(4)	C8	C9	1.38(4)
PD	BR2	2.327(6)	C2	C3	1.20(4)	C9	C10	1.48(4)
PD	N1	2.05(2)	C3	C4	1.34(4)	C10	C11	1.33(5)
PD	N2	2.03(2)	C4	C5	1.34(4)	C11	C12	1.59(5)
N1	C6	1.28(3)	C5	C6	1.47(4)	N3	C13	1.34(4)
N1	N3	1.42(3)	C6	C7	1.49(4)	N3	C14	1.48(4)
N2	C1	1.26(4)	C7	C8	1.48(4)			
N2	C5	1.38(3)	C7	C12	1.44(4)			

Numbers in parentheses are estimated standard deviations.

to make preferentially strong bonds with easily polarizable soft bases. As the extended π-congugated system makes pyridine of higher polarizability than the imino group, this fact could rationalize the observed trend in Pd-N bond distances. It seems that a stronger coordination occurs between N_2 and Pd than between N_1 and Pd 2.03(2)/2.05(2) Å.[20] The external N_3 atom is tetrahedral while N_1 and N_2 of the chelate ring are planar.[21] The distances of N_3, C_6, C_7 and C_5 from the

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Table 4 Selected bond angles (degrees).

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N1	Pd	N2	80.9(7)	N1	C6	C7	123.(2)
N1	Pd	Br2	98.6(5)	C5	C6	C7	116.(2)
N2	Pd	Br1	92.3(5)	C6	C7	C8	120.(2)
Br1	Pd	Br2	88.1(2)	C6	C7	C12	117.(2)
C6	N1	N3	115.(2)	C8	C7	C12	123.(3)
C1	N2	C5	121.(2)	C7	C8	C9	123.(2)
N2	C1	C2	116.(2)	C8	C9	C10	118.(3)
C1	C2	C3	120.(3)	C9	C10	C11	118.(3)
C2	C3	C4	119.(3)	C10	C11	C12	129.(3)
C3	C4	C5	125.(3)	C7	C12	C11	108.(2)
N2	C5	C4	118.(2)	N1	N3	C13	116.(2)
N2	C5	C6	112.(2)	N1	N3	C14	109.(2)
C4	C5	C6	130.(2)	C13	N3	C14	110.(2)
N1	C6	C5	121.(2)				

Numbers in parentheses are estimated standard deviations.

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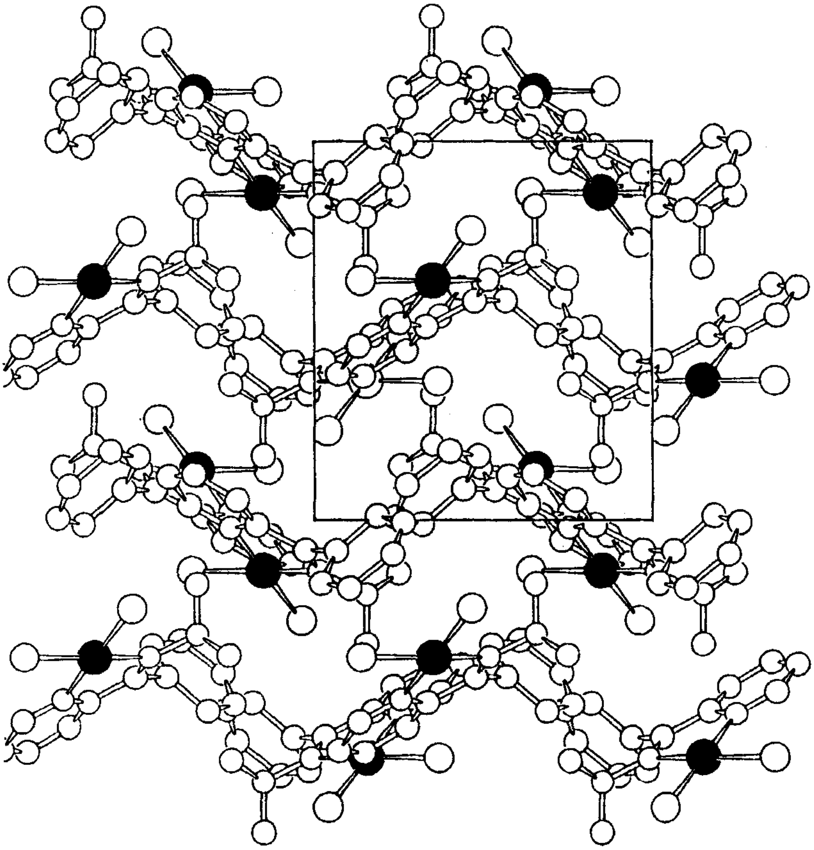

Figure 2 A SCHAKAL view of the crystal packing along the *a* axis.

coordination least-square plane are 0.29, 0.34, 0.67 and 0.26 Å, respectively, and the dihedral angle between the phenyl and pyridine rings is 79.6°.

An interesting feature of this structure is the possible existence of hydrogen bonding of the type C-H.....Br (C_{13}-Br_2 = 3.50 Å, C_{14}-Br_2 = 3.52 Å and C_1-Br_1 = 3.16 Å).[18] The Pd-N bond distances are comparable to those found in other square planar complexes of Pd(II).[10,20,21]

There are significant variations in the dimensions of the rings in the hydrazone ligand probably resulting from the weakness of many of the reflections used, and from the relatively limited number of reflections (Table 1). Additionally, the large displacement parameters of the two bromine atoms could also contribute to this deviation (Table 2).

The Pd-Br distances are slightly different, the shorter Pd-Br_2 bond (2.327(6) Å) is opposite the shorter Pd-N_2 (2.03(2) Å); in the other *trans* pair Pd-Br_1 (2.374(6) Å) is opposite Pd-N_1 (205(2) Å). The Pd-Br distances are similar to those found in other square planar palladium complexes.[10,22]

The essential characteristic of the crystal packing is the complete absence of any strong interaction between molecules in the solid. As shown in Figure 2, "zig-zag" layers are formed, in a direction parallel to the *b* axis. Molecules are held together by weak Van der Waals forces. An interesting feature is the existence of many contacts between the two bromine atoms and the carbon atoms.

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Supplementary data

Full lists of bond lengths and angles, anisotropic thermal parameters and observed and calculated structure factors are available from the authors upon request.

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