

Molecular and Crystal Structure of Di(μ -*N,S*-thiocyanato)-bis[*(N,N*-dimethylbenzylamine-*C*²,*N*)palladium(II)]

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The cyclopalladated complex $[\text{Pd}(\text{C}^2, \text{N-dmba})(\mu\text{-SCN})]_2$, where dmba = *N,N*-dimethylbenzylamine, was structurally characterized by single-crystal X-ray diffraction. This compound crystallizes in the monoclinic system, space group $P2_1/n$ with $a = 9.578(1)\text{\AA}$, $b = 12.323(2)\text{\AA}$, $c = 10.279(2)\text{\AA}$, $\beta = 117.03(1)^\circ$, $V = 1080.7(3)\text{\AA}^3$, $Z = 2$. Each Pd(II) center displays a distorted square-planar coordination environment, formed by the C and N atoms from the dmba ligand, and one set of N and S atoms from the bridging SCN groups.

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Since the pioneering work of Cope and Siekman describing the cyclopalladation of azobenzene, such reactions have attracted enormous interest in a wide variety of contexts. Palladium(II) cyclometallated complexes have been used as pathways to new products in organic synthesis, as catalysts, as anti-tumor drugs, in photochemistry and for the design of metallomesogens.^{1,2} Many different types of cyclopalladated compounds have been prepared² by varying the donor atom (N, P, As, O, S or Se), the ring size (5, 6 or more members) and the nature of metallated carbon ($\text{C}(\text{sp}^3)$, $\text{C}(\text{sp}^2)$ or $\text{C}(\text{sp})$). The benzylamines are ligands able to generate cyclopalladated species in which the aromatic sp^2 carbon at an *ortho* position is bound to the metal.³ In particular, pseudohalide-bridged dimers bearing the dmba moiety are good candidates for the synthesis of novel cyclometallated species, as well as for reactions with several nucleophiles, like tertiary phosphines, heterocyclic thiols, pyrazoles or pyridines, affording new mono or dinuclear compounds.^{1,3} In addition, the SCN group is a highly versatile ambidentate ligand with two donor atoms. It can coordinate through either the nitrogen or the sulfur atom, or both, giving

rise to linkage isomers or polymers.⁴ Focusing our interest on the cyclometallated and supramolecular chemistry of palladium-based compounds,^{1,3,5} we herein describe the single-crystal X-ray structure of $[\text{Pd}(\text{C}^2, \text{N-dmba})(\mu\text{-SCN})]_2$ (dmba = *N,N*-dimethylbenzylamine). A schematic diagram of the complex is

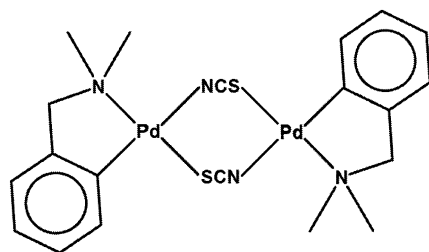


Fig. 1 Chemical structure of $[\text{Pd}(\text{C}^2, \text{N-dmba})(\mu\text{-SCN})]_2$.

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Table 1 Crystal and experimental data

Chemical Formula: $\text{C}_{20}\text{H}_{24}\text{N}_4\text{S}_2\text{Pd}_2$
Formula weight: 597.41
$T = 293\text{ K}$
Crystal system: monoclinic
Space group: $P2_1/n$
$a = 9.578(1)\text{\AA}$
$b = 12.323(2)\text{\AA}$
$c = 10.279(2)\text{\AA}$
$\beta = 117.03(4)^\circ$
$V = 1080.7(3)\text{\AA}^3$
$Z = 2$
$D_x = 1.836\text{ g cm}^{-3}$
Radiation: Mo K_α ($\lambda = 0.71073\text{ \AA}$)
$\mu(\text{Mo } K_\alpha) = 1.871\text{ mm}^{-1}$
$F(0\ 0\ 0) = 592$
Crystal size = $0.15 \times 0.15 \times 0.20\text{ mm}$
No. of reflections collected = 3313; $R_{\text{int}} = 0.058$
Reflections observed ($I > 2\sigma(I)$) = 1782
θ range for data collection: 2.3 to 23.4°
Data/restraints/parameters = 3150/0/129
Goodness-of-fit = 0.944
R indices [$I > 2\sigma(I)$]: $R1 = 0.0477$, $wR2 = 0.0941$
R indices (all data): $R1 = 0.1292$, $wR2 = 0.1167$
$(\Delta\rho)_{\text{max}} = 0.71\text{ e.\AA}^{-3}$
$(\Delta\rho)_{\text{min}} = -0.78\text{ e.\AA}^{-3}$
Measurements: Enraf-Nonius CAD4
Program system: WinGX
Structure determination: direct method (SIR2004)
Refinement: full-matrix least-squares on F^2 (SHELXL-97)
CCDC deposition number: 704942

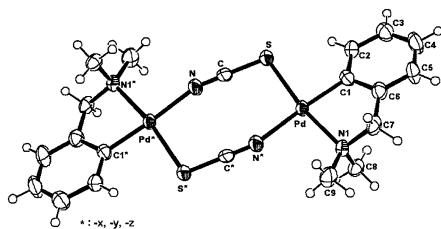


Fig. 2 ORTEP representation of $[\text{Pd}(\text{C}^2, \text{N-dmba})(\mu\text{-SCN})]_2$ showing the labeling of the atoms. Displacement ellipsoids are drawn at the 50% probability level.

Table 2 Selected bond lengths (Å) and bond angles (°)

Bond distances (Å)		Bond angles (°)	
Pd-S	2.322(2)	S-Pd-C1	88.9(2)
Pd-N*	2.103(5)	S-Pd-N*	93.9(1)
Pd-N1	2.098(5)	S-Pd-N1	170.1(1)
Pd-C1	1.983(5)	N1-Pd-C1	82.3(2)
S-C	1.656(6)	N*-Pd-N1	95.0(2)
N-C	1.157(7)	N*-Pd-C1	176.7(2)
N1-C7	1.495(7)	Pd-S-C	103.5(2)
N1-C8	1.485(7)	Pd-N-C	162.5(5)
N1-C9	1.481(8)	S-C-N	179.1(6)

given in Fig. 1.

This compound was prepared as previously reported,⁶ and single-crystals suitable for X-ray diffraction measurements were obtained from the mother liquor. Table 1 summarizes the crystal and experimental data.

In the molecular structure of the $[\text{Pd}(\text{C}^2, \text{N-dmba})(\mu\text{-SCN})]_2$ (Fig. 2), the coordination geometry at the Pd atoms is essentially square planar, and is defined by the C and N atoms from the dmba ligand and, one set of N and S atoms from the end-to-end thiocyanate groups. The SCN groups act as bridges between two $[\text{Pd}(\text{dmba})]$ moieties, giving rise to a dinuclear species. The two halves of the dimer are related by the crystallographic inversion center, in the centroid of the $\text{Pd}(\mu\text{-1,3-SCN})_2\text{Pd}$ rings.

The Pd-Pd distance of 5.59(1) Å excludes any Pd-Pd interaction, and is comparable to those reported for other cyclopalladated thiocyanate-bridged dimeric compounds.⁷ The bond angles around the palladium deviate slightly from 90° (S-Pd-N = 93.9(1)° and S-Pd-C1 = 88.9(2)°). The metal atom is 0.233(1) Å out of the plane of the coordinated atoms. Selected bond lengths and bond angles are given in Table 2.

The Pd-N1 bond distance of 2.098(5) Å is significantly shorter

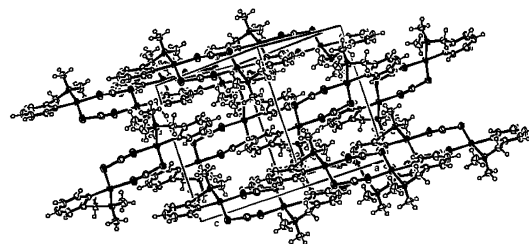


Fig. 3 Crystal packing of $[\text{Pd}(\text{C}^2, \text{N-dmba})(\mu\text{-SCN})]_2$.

than that found for $[\text{Pd}(\text{C}^2, \text{N-dmba})(\text{NCO})(2,3\text{-lut})]$ (2.158(7) Å) (2,3-lut = 2,3-lutidine).¹ The thiocyanate ion is essentially linear with the N-C-S angle equal to 179.1(6)°. In addition, the bond length values of 1.656(6) and 1.157(7) Å found for S-C and C-N, respectively, indicate the dominance of the mesomeric form S-C=N.

The Pd-S and Pd-N* bond lengths are equal to 2.322(2) and 2.102(5) Å, respectively, and agree well with the values found for the complex $[\text{Pd}(\text{C}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5)(\mu\text{-SCN})]_2$.⁷ The crystal packing of $[\text{Pd}(\text{C}^2, \text{N-dmba})(\mu\text{-SCN})]_2$ is illustrated by Fig. 3. Weak hydrogen-bonds are formed between the phenyl hydrogen atoms and the sulfur atoms from a thiocyanate ion (C2...S 3.186(7) Å and C2-H2...S 113.0°). Further details about the crystal-structure investigation are available free of charge at www.ccdc.ac.uk/conts/retrieving.html or deposit@ccdc.cam.ac.uk, No. CCDC 704942.

Acknowledgements

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