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Crystal structure of di-μ(N,S)-thiocyanato-bis[(N-benzylideneaniline-C^2,N)palladium(II)], $[Pd(C_6H_4CH{=}NC_6H_5)(\mu\text{-}SCN)]_2$

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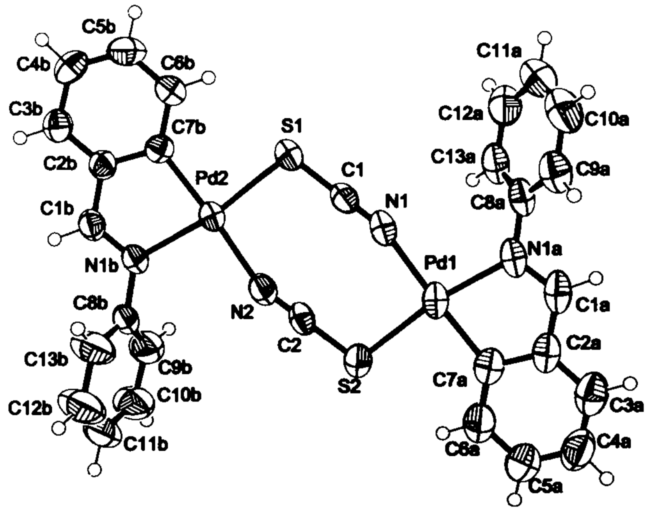

Abstract

$C_{28}H_{20}N_4Pd_2S_2$, monoclinic, $P12_1/c1$ (No. 14), $a = 11.325(1)$ Å, $b = 13.530(1)$ Å, $c = 17.925(1)$ Å, $\beta = 106.23(1)°$, $V = 2637.1$ Å^3, $Z = 4$, $R_{gt}(F) = 0.052$, $wR_{ref}(F^2) = 0.129$, $T = 293$ K.

Source of material

The new cyclopalladated complex $[Pd(C_6H_4CH{=}NC_6H_5)(\mu\text{-}SCN)]_2$ [1] was prepared by the reaction of the dimeric compound $[Pd(C_6H_4CH{=}NC_6H_5)(\mu\text{-}OOCMe)]_2$ [2] with KSCN, in methanol / acetone. Recrystallization from chloroform gave yellow-orange crystals, suitable for X-ray analysis.

Discussion

The NCS^- group is a versatile ligand which can coordinate to metals in both the terminal and bridging modes [3]. Despite many thiocyanato complexes of palladium(II) have been fully characterized by crystallographic methods, there are no reports about crystal structures of cyclopalladated compounds containing bridging NCS in the end-to-end mode. In addition, cyclopalladated compounds are successfully employed as antitumoral agents [4], liquid crystals [5] and nonlinear optical materials [6].

In the title structure, the metallic centers, bridged by thiocyanato groups in a end-to-end fashion, possess a distorted square planar environment and the bzan ligands (bzan = N-benzylideneaniline) are in a *trans* configuration. The thiocyanato groups in the structure are essentially linear with an average N–C–S angle of 179.2(7)°. However, the NCS ligands are not quite co-linear with the palladium atoms, since the angles Pd1–N1–C1 and Pd2–N2–C2 are equal to 163.8(5)° and 162.4(5)°, respectively. The N—C and C–S bond lengths have values of 1.128(9) Å, 1.148(9) Å, and 1.648(7) Å, 1.658 Å, respectively, showing the dominance of the mesomeric form S–C≡N. Curiously, the bond distances above mentioned for SCN group are comparable to those reported for terminally coordinated pseudohalide [7]. Within the five-membered ring, the angle N1a–Pd1–C7a is 80.9(3)°, with a Pd1—N1a bond length of 2.064(6) Å and the Pd1–C7a organometallic bond of 1.981(7) Å comparing well with those values found in related complex such as di(μ-N,S-1,2,3,4-thiatriazole-5-thiolate) bis[(benzylideneaniline-C^2,N)palladium(II)] [8]. The Pd(1)—Pd(2) distance of 5.586 Å exclude any Pd–Pd interaction.

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Table 1. Data collection and handling.

Crystal:	yellow-orange prism, size 0.15 × 0.2 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	14.39 cm^{-1}
Diffractometer, scan mode:	Enraf Nonius TurboCAD4, ω
$2\theta_{max}$:	59.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7877, 7654
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3278
$N(param)_{refined}$:	325
Programs:	SHELXS-97 [9], SHELXL-97 [10], PSISCAN [11], WinGX [12], PLATON [13]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1a)	4e	–0.0823	–0.1124	0.4282	0.091
H(3a)	4e	0.1086	–0.1445	0.5408	0.106
H(4a)	4e	0.3164	–0.1172	0.5966	0.119
H(5a)	4e	0.4226	–0.0215	0.5347	0.138
H(6a)	4e	0.3323	0.0452	0.4154	0.129
H(9a)	4e	–0.2232	–0.1898	0.3139	0.100
H(10a)	4e	–0.4322	–0.1937	0.2511	0.136
H(11a)	4e	–0.5347	–0.0525	0.1997	0.137
H(12a)	4e	–0.4264	0.0943	0.2081	0.124
H(13a)	4e	–0.2172	0.0973	0.2649	0.099
H(1b)	4e	0.1826	0.2224	–0.1589	0.067
H(3b)	4e	–0.0023	0.2365	–0.2737	0.073
H(4b)	4e	–0.2155	0.2230	–0.3248	0.079
H(5b)	4e	–0.3311	0.1774	–0.2462	0.091
H(6b)	4e	–0.2463	0.1470	–0.1171	0.083
H(9b)	4e	0.2973	0.2918	0.0584	0.106

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(10b)	4*e*	0.5087	0.3053	0.1072	0.129
H(11b)	4*e*	0.6348	0.2078	0.0630	0.124
H(12b)	4*e*	0.5557	0.0953	–0.0317	0.144
H(13b)	4*e*	0.3447	0.0840	–0.0865	0.122

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	4*e*	0.06168(5)	0.02355(4)	0.29516(3)	0.0725(4)	0.0532(3)	0.0518(3)	–0.0047(3)	0.0325(3)	0.0033(2)
Pd(2)	4*e*	0.03399(4)	0.14641(4)	–0.00675(3)	0.0453(3)	0.0560(3)	0.0469(3)	–0.0001(2)	0.0212(2)	0.0014(2)
S(1)	4*e*	–0.1412(2)	0.1024(2)	0.0271(1)	0.0474(9)	0.110(2)	0.064(1)	0.001(1)	0.0254(9)	0.021(1)
S(2)	4*e*	0.2361(2)	0.0824(1)	0.26535(9)	0.066(1)	0.077(1)	0.0508(9)	–0.0071(9)	0.0220(8)	0.0088(9)
N(1)	4*e*	–0.0523(5)	0.0500(4)	0.1825(3)	0.061(3)	0.061(3)	0.061(3)	–0.009(3)	0.035(3)	0.002(3)
N(2)	4*e*	0.1499(4)	0.1253(4)	0.1062(3)	0.051(3)	0.074(4)	0.057(3)	–0.013(3)	0.024(3)	0.000(3)
C(1)	4*e*	–0.0884(5)	0.0719(5)	0.1195(4)	0.045(4)	0.059(4)	0.057(4)	–0.007(3)	0.023(3)	–0.003(3)
C(2)	4*e*	0.1851(5)	0.1070(4)	0.1712(4)	0.053(4)	0.050(4)	0.056(4)	–0.014(3)	0.027(3)	–0.003(3)
N(1a)	4*e*	–0.0734(5)	–0.0388(4)	0.3371(3)	0.076(4)	0.054(3)	0.064(4)	–0.006(3)	0.043(3)	0.004(3)
C(1a)	4*e*	–0.0312(7)	–0.0784(5)	0.4044(4)	0.100(6)	0.058(4)	0.068(5)	0.000(4)	0.048(5)	0.012(4)
C(2a)	4*e*	0.0990(7)	–0.0677(5)	0.4418(4)	0.088(5)	0.058(4)	0.056(4)	0.002(4)	0.036(4)	0.007(3)
C(3a)	4*e*	0.1541(8)	–0.1073(6)	0.5151(4)	0.109(7)	0.068(5)	0.076(5)	0.011(5)	0.040(5)	0.016(4)
C(4a)	4*e*	0.2770(9)	–0.0901(7)	0.5484(4)	0.108(7)	0.113(7)	0.059(5)	0.022(6)	0.033(5)	0.020(5)
C(5a)	4*e*	0.3398(8)	–0.0339(8)	0.5111(5)	0.086(6)	0.171(9)	0.062(5)	–0.001(6)	0.021(5)	0.016(6)
C(6a)	4*e*	0.2857(8)	0.0059(7)	0.4391(5)	0.090(6)	0.143(8)	0.066(5)	–0.023(6)	0.024(5)	0.021(5)
C(7a)	4*e*	0.1629(7)	–0.0116(5)	0.4010(4)	0.077(5)	0.061(4)	0.054(4)	0.001(4)	0.025(4)	0.005(3)
C(8a)	4*e*	–0.2009(6)	–0.0450(5)	0.2975(4)	0.069(5)	0.059(5)	0.064(4)	0.000(4)	0.042(4)	0.006(3)
C(9a)	4*e*	–0.2639(7)	–0.1324(6)	0.2925(4)	0.086(6)	0.068(5)	0.087(5)	–0.006(4)	0.041(5)	0.010(4)
C(10a)	4*e*	–0.3895(9)	–0.1343(8)	0.2549(5)	0.093(7)	0.111(8)	0.119(8)	–0.021(6)	0.047(6)	0.017(6)
C(11a)	4*e*	–0.4506(8)	–0.0508(9)	0.2238(5)	0.069(6)	0.140(9)	0.112(7)	–0.009(6)	0.033(5)	0.033(7)
C(12a)	4*e*	–0.3856(8)	0.0366(7)	0.2287(5)	0.089(6)	0.117(8)	0.087(6)	0.008(6)	0.038(5)	0.030(5)
C(13a)	4*e*	–0.2609(7)	0.0389(6)	0.2639(4)	0.087(6)	0.080(6)	0.076(5)	–0.004(5)	0.048(5)	0.015(4)
N(1b)	4*e*	0.1706(4)	0.1870(4)	–0.0561(3)	0.044(3)	0.055(3)	0.051(3)	–0.005(2)	0.020(2)	0.002(2)
C(1b)	4*e*	0.1296(5)	0.2053(4)	–0.1296(3)	0.052(4)	0.055(4)	0.052(4)	–0.002(3)	0.025(3)	0.007(3)
C(2b)	4*e*	–0.0002(5)	0.1984(4)	–0.1644(3)	0.048(3)	0.052(4)	0.048(3)	0.006(3)	0.016(3)	0.007(3)
C(3b)	4*e*	–0.0514(6)	0.2182(4)	–0.2422(4)	0.061(4)	0.054(4)	0.056(4)	–0.001(3)	0.020(3)	0.005(3)
C(4b)	4*e*	–0.1783(6)	0.2101(5)	–0.2725(4)	0.073(5)	0.056(4)	0.048(4)	0.009(4)	0.006(4)	0.010(3)
C(5b)	4*e*	–0.2464(6)	0.1833(5)	–0.2255(4)	0.049(4)	0.072(5)	0.079(5)	–0.001(4)	0.000(4)	0.009(4)
C(6b)	4*e*	–0.1958(6)	0.1643(5)	–0.1480(4)	0.046(4)	0.086(5)	0.061(4)	–0.007(4)	0.017(3)	0.003(4)
C(7b)	4*e*	–0.0705(5)	0.1709(4)	–0.1157(3)	0.046(3)	0.041(3)	0.047(3)	0.003(3)	0.012(3)	0.002(3)
C(8b)	4*e*	0.3007(5)	0.1891(5)	–0.0203(3)	0.044(3)	0.075(4)	0.049(4)	–0.009(3)	0.020(3)	–0.002(3)
C(9b)	1*e*	0.3487(6)	0.2528(6)	0.0383(4)	0.062(5)	0.115(7)	0.067(5)	0.003(5)	0.019(4)	–0.013(5)
C(10b)	4*e*	0.4755(7)	0.2596(7)	0.0682(4)	0.063(5)	0.151(9)	0.077(6)	–0.010(6)	0.008(4)	–0.039(6)
C(11b)	4*e*	0.5501(7)	0.2024(8)	0.0422(5)	0.047(4)	0.157(9)	0.081(6)	–0.003(5)	0.017(4)	–0.018(6)
C(12b)	4*e*	0.5032(7)	0.1364(8)	–0.0143(5)	0.054(5)	0.156(9)	0.122(8)	0.008(5)	0.026(5)	–0.034(7)
C(13b)	4*e*	0.3769(6)	0.1292(7)	–0.0469(5)	0.051(4)	0.128(7)	0.100(6)	0.003(5)	0.019(4)	–0.036(5)

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