Crystal structure of di- $\mu(N,S)$ -thiocyanato-bis[(*N*-benzylideneaniline- C^2,N)palladium(II)], $[\text{Pd}(\text{C}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5)(\mu\text{-SCN})]_2$

A. M. Santana^I, A. V. De Godoy Netto^{II}, E. T. De Almeida^{II}, A. E. Mauro^I, J. Souza Jr.^{III} and R. H. A. Santos^{*,III}

^I UNESP, Departamento de Química Inorgânica, Instituto de Química de Araraquara, Caixa Postal 355, 14.801-970, Araraquara- SP, Brazil

^{II} Universidade Católica de Brasília, Curso de Química, Caixa Postal 5490, 72030-170 Águas Claras, Taguatinga, Brasília, DF, Brazil

^{III} Universidade de São Paulo, Depto. de Química e Física Molecular, Instituto de Química de São Carlos, Caixa Postal 780, 13560-970 - São Carlos - SP, Brazil

Received November 22, 2001, accepted February 13, 2002; CCDC-No. 1267/772

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.

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
Diffractionmeter, scan mode:	Enraf Nonius TurboCAD4, ω
$2\theta_{\text{max}}$:	59.94°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	7877, 7654
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 3278
$N(\text{param})_{\text{refined}}$:	325
Programs:	SHELXS-97 [9], SHELXL-97 [10], PSISCAN [11], WinGX [12], PLATON [13]

Abstract

$\text{C}_{28}\text{H}_{20}\text{N}_4\text{Pd}_2\text{S}_2$, monoclinic, $P12_1/c1$ (No. 14), $a = 11.325(1)$ Å, $b = 13.530(1)$ Å, $c = 17.925(1)$ Å, $\beta = 106.23(1)^\circ$, $V = 2637.1$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.052$, $wR_{\text{ref}}(F^2) = 0.129$, $T = 293$ K.

Source of material

The new cyclopalladated complex $[\text{Pd}(\text{C}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5)(\mu\text{-SCN})]_2$ [1] was prepared by the reaction of the dimeric compound $[\text{Pd}(\text{C}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5)(\mu\text{-OOCMe})]_2$ [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 anti-tumoral 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 bzán ligands (bzán = *N*-benzylideneaniline) are in a *trans* configuration. The thiocyanato groups in the structure are essentially linear with an average N–C–S angle of

Table 2. Atomic coordinates and displacement parameters (in Å²).

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

* Correspondence author (e-mail: reginas@iqsc.sc.usp.br)

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(10b)	4e	0.5087	0.3053	0.1072	0.129
H(11b)	4e	0.6348	0.2078	0.0630	0.124

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(12b)	4e	0.5557	0.0953	-0.0317	0.144
H(13b)	4e	0.3447	0.0840	-0.0865	0.122

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Pd(1)	4e	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)	4e	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)	4e	-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)	4e	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)	4e	-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)	4e	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)	4e	-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)	4e	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)	4e	-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)	4e	-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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	-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)	4e	-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)	4e	-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)	4e	-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)	4e	-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)	4e	-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)	4e	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)	4e	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)	4e	-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)	4e	-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)	4e	-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)	4e	-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)	4e	-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)	4e	-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)	4e	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)	1e	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)	4e	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)	4e	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)	4e	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)	4e	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)

Acknowledgments. This work received partial support from FAPESP, CAPES and CNPq.

References

- Santana, A. M.; Mauro, A. E.; Zorel Jr., H. E.; Mattioli, M. P. D.; De Lucca Neto, V. A.: Thermal and spectroscopy investigation of cyclopalladated compounds of the type [Pd(C₁₃H₁₀N)(μ-X)]₂, (X= H₃COO, NCO, SCN, CN). *J. Thermal Anal.*, accepted.
- Onoue, H.; Moritani, I.: Ortho-metalation reactions of *N*-phenylbenzaldimine and its related compounds by palladium(II) acetate. *J. Organomet. Chem.* **43** (1972) 431-436.
- Burmeister, J. L.: Ambidentate ligands, the schizophrenics of Coord. Chem. *Coord. Chem. Rev.* **105** (1990) 77-133.
- Caires, A. C. F.; De Almeida, E. T.; Mauro, A. E.; Hemerly, J. P.; Valentini, S. R.: Síntese e atividade citotóxica de alguns azido-ciclopalladados estabilizados com ligantes bifosfínicos. *Química Nova* **22** (1999) 329-334.
- Saccomando, D. J.; Black, C.; Cave, G. W. V.; Lydon, D. P.; Rourke, J. P.: Chiral cyclopalladated liquid crystals from amino acids. *J. Organomet. Chem.* **601** (2000) 305-310.
- Caruso, U.; Di Matola, A.; Panunzi, B.; Roviello, A.; Sirigu, A.: Side chain organometallic polymers containing cyclopalladated potentially second order nonlinear optical active fragments as pendants. *Polymer* **42** (2001) 3973-3980.
- De Godoy Netto, A. V.; Frem, R. C. G.; Mauro, A. E.; Almeida Santos, R. H.; Zóia, J. R.: Crystallographic and Spectroscopically Studies on Palladium(II) Complexes Containing Pyrazole Type Ligand and Thiocyanate. *Trans. Met. Chem.*, in press.
- Santana, A. M.; Mauro, A. E.; De Almeida, E. T.; De Godoy Netto, A. V.; Klein, S. I.; Santos, R. H. A.; Zóia, J. R.: 1,3-dipolar cycloaddition of CS₂ to the coordinated azide in the cyclopalladated [Pd(bzan)(μ-N₃)]₂ Crystal and molecular structure of di(μ-N,S-1,2,3,4-thiazotriazole-5-thiolate) bis[(benzylideneaniline-C²,N)palladium(II)]. *J. Coord. Chem.* **53** (2001) 163-172.
- Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
- Sheldrick, G. M.: SHELXL-97. Programs for the Refinement of Crystal Structures Analysis (Release 97-2). Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany 1998.
- North, A. C. T.; Phillips, D. C.; Mathews, F. S.: A semi-empirical method of absorption correction *Acta Crystallogr. A* **24** (1968) 351-359.
- Farrugia, L. J.: WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* **32** (1999) 837-838.
- Spek, A. L.: PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands 1998.