Crystal structure of bis[μ_2-(3-benzimidazol-2-yl)-2-ethanethiolato-*N*,*S*,*S*)-chloro-palladium(II)], $[(C_6H_4N_2HCCH_2CH_2S)PdCl]_2 \cdot C_2H_5OH$

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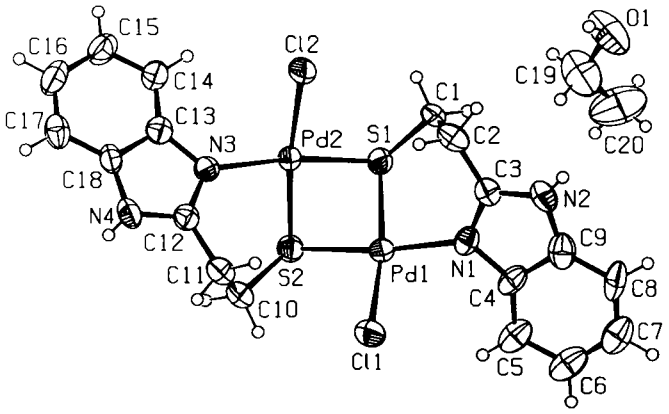

Abstract

$C_{20}H_{24}Cl_2N_4OPd_2S_2$, triclinic, $P\bar{1}$ (no. 2), $a = 8.796(1)$ Å, $b = 9.844(1)$ Å, $c = 14.718(2)$ Å, $\alpha = 94.330(6)°$, $\beta = 98.546(6)°$, $\gamma = 99.258(7)°$, $V = 1237.3$ Å^3, $Z = 2$, $R_{gt}(F) = 0.068$, $wR_{ref}(F^2) = 0.142$, $T = 295$ K.

Source of material

Deoxygenated solutions of ligand 1,6-bis(3-benzimidazyl)-3,4-dithiahexane [1] (100 mg, 28 mmol) and $PdCl_2$ (50 mg, 28 mmol) in ethanol (10 ml, abs.) were refluxed under nitrogen atmosphere with constant stirring overnight. The mixture was filtered while still hot. The filtrate was cooled to room temperature and allowed to sit until prismatic orange crystals formed (yield 50 %, decomp. 575 K). Molar conductivity is 6.1 $W^{-1}cm^2mol^{-1}$. ^1H NMR and ^{13}C NMR data are available in the CIF.

Experimental details

Positions of all hydrogen atoms were sequentially determined from Fourier difference maps. In the final steps of refinement all but those hydrogens bonded to nitrogen atoms were included using riding models and displacement parameters scaled to respective parent atoms. H2N and H4N were refined but constrained to a common distance and displacement parameter. Large displacement parameters of the solvent atoms are indicative of a loosely bounded situation and associated partial loss in course of crystal preparation. Refinement of partial occupancy was not attempted.

Discussion

In the binuclear complex, two palladium and two sulfur atoms form a butterfly-like four-membered ring with *d*(Pd—S) varying between 2.285(3) Å – 2.305(3) Å. Pd atoms are further coordinated by one Cl (*d*(Pd—Cl) = 2.337(3) Å, 2.342(3) Å) and one N (*d*(Pd—N) = 2.038(7) Å, 2.053(8) Å) atom each, in square-planar environment, the deviation from planarity is small (6.6°). The bond angles within the Pd_2S_2 moiety are 77.84(9)°, 78.0(1)°, 81.51(9)°, and 81.98(8)°. The six *exo*-cyclic angles ∠N–Pd–S, ∠Cl–Pd–N and ∠Cl–Pd–N vary between 91.8(2)° and 97.7(1)°. Both the Pd—ligand bond lengths and bond angles are in good agreement with previously reported values [2-4].

Table 1. Data collection and handling.

Crystal:	orange prism, size 0.08 × 0.13 × 0.17 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	18.58 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7 & Mercury CCD, ω/φ
$2\theta_{max}$:	47.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9170, 3726
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3038
$N(param)_{refined}$:	290
Programs:	SHELXS-97 [5], SHELXL-97 [6], ATOMS [7]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(11)	2*i*	0.7418	0.5797	0.5312	0.068
H(12)	2*i*	0.8347	0.4958	0.4712	0.068
H(21)	2*i*	1.0044	0.6877	0.5395	0.073
H(22)	2*i*	0.9695	0.7070	0.4342	0.073
H(2N)	2*i*	0.984(9)	0.91(1)	0.631(5)	0.03(3)
H(51)	2*i*	0.5948	1.0941	0.4230	0.078
H(61)	2*i*	0.5985	1.2813	0.5289	0.093
H(71)	2*i*	0.7374	1.2990	0.6746	0.098
H(81)	2*i*	0.9055	1.1534	0.7136	0.089
H(101)	2*i*	0.5211	0.6977	0.0397	0.067
H(102)	2*i*	0.5810	0.8399	0.0994	0.067
H(111)	2*i*	0.7802	0.7934	0.0210	0.067
H(112)	2*i*	0.8375	0.7826	0.1261	0.067
H(4N)	2*i*	0.81(1)	0.578(9)	−0.077(5)	0.03(3)
H(141)	2*i*	0.7794	0.2248	0.1404	0.070
H(151)	2*i*	0.8067	0.0568	0.0314	0.085
H(161)	2*i*	0.8349	0.1066	−0.1161	0.094
H(171)	2*i*	0.8485	0.3269	−0.1569	0.073
H(1O)	2*i*	0.9018	0.6980	−0.2108	0.178
H(191)	2*i*	0.6488	0.6271	−0.2739	0.151
H(192)	2*i*	0.7353	0.7729	−0.2898	0.151
H(201)	2*i*	0.5509	0.7232	−0.1580	0.231
H(202)	2*i*	0.5043	0.7871	−0.2503	0.231

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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)	2*i*	0.67360(9)	0.79780(8)	0.32781(5)	0.0484(5)	0.0473(5)	0.0431(4)	0.0180(4)	0.0060(3)	0.0043(3)
Pd(2)	2*i*	0.73259(9)	0.53078(8)	0.23896(5)	0.0502(5)	0.0468(5)	0.0368(4)	0.0154(4)	0.0058(3)	0.0027(3)
Cl(1)	2*i*	0.7381(4)	1.0046(3)	0.2623(2)	0.103(2)	0.055(2)	0.060(2)	0.017(2)	0.001(2)	0.013(1)
Cl(2)	2*i*	0.9375(4)	0.4234(3)	0.3007(2)	0.092(2)	0.086(2)	0.048(2)	0.055(2)	0.003(1)	0.007(1)
S(1)	2*i*	0.6436(3)	0.5798(3)	0.3753(2)	0.060(2)	0.049(1)	0.044(1)	0.012(1)	0.016(1)	0.006(1)
S(2)	2*i*	0.5502(3)	0.6644(3)	0.1950(2)	0.045(1)	0.064(2)	0.047(1)	0.020(1)	0.001(1)	0.002(1)
C(1)	2*i*	0.792(1)	0.580(1)	0.4767(6)	0.090(8)	0.057(6)	0.034(5)	0.036(6)	0.015(5)	0.016(5)
C(2)	2*i*	0.924(1)	0.702(1)	0.4903(8)	0.050(6)	0.073(8)	0.057(6)	0.011(6)	−0.002(5)	0.020(5)
C(3)	2*i*	0.875(1)	0.837(1)	0.5135(7)	0.053(6)	0.056(6)	0.043(6)	0.008(5)	0.004(5)	0.005(5)
N(1)	2*i*	0.771(1)	0.8895(8)	0.4578(5)	0.052(5)	0.049(5)	0.049(5)	0.008(4)	0.019(4)	−0.003(4)
N(2)	2*i*	0.918(1)	0.914(1)	0.5940(6)	0.059(6)	0.079(7)	0.041(5)	0.011(5)	−0.006(5)	0.007(5)
C(4)	2*i*	0.750(1)	1.011(1)	0.5050(8)	0.055(7)	0.051(6)	0.071(7)	0.015(5)	0.032(6)	−0.003(5)
C(5)	2*i*	0.657(1)	1.104(1)	0.4808(9)	0.051(6)	0.055(7)	0.093(9)	0.005(6)	0.039(6)	−0.002(6)
C(6)	2*i*	0.658(2)	1.214(1)	0.545(1)	0.066(8)	0.055(7)	0.12(1)	0.008(6)	0.049(8)	0.002(7)
C(7)	2*i*	0.745(2)	1.227(2)	0.632(1)	0.08(1)	0.076(9)	0.09(1)	0.013(8)	0.037(8)	−0.014(7)
C(8)	2*i*	0.841(2)	1.139(1)	0.6564(8)	0.10(1)	0.073(8)	0.052(7)	−0.003(8)	0.035(6)	−0.023(6)
C(9)	2*i*	0.842(1)	1.024(1)	0.5931(8)	0.067(8)	0.076(8)	0.054(7)	−0.004(7)	0.024(6)	0.001(6)
C(10)	2*i*	0.595(1)	0.744(1)	0.0926(7)	0.059(7)	0.064(7)	0.044(6)	0.017(6)	−0.003(5)	0.010(5)
C(11)	2*i*	0.762(1)	0.740(1)	0.0725(7)	0.058(7)	0.061(7)	0.048(6)	0.010(6)	0.002(5)	0.011(5)
C(12)	2*i*	0.784(1)	0.596(1)	0.0502(6)	0.039(5)	0.052(6)	0.044(5)	0.009(5)	0.000(4)	0.001(5)
N(3)	2*i*	0.7754(9)	0.4994(8)	0.1073(5)	0.046(5)	0.045(5)	0.042(4)	0.008(4)	0.010(4)	0.006(4)
N(4)	2*i*	0.805(1)	0.546(1)	−0.0337(6)	0.059(6)	0.078(7)	0.033(5)	0.017(5)	0.007(4)	0.007(5)
C(13)	2*i*	0.795(1)	0.377(1)	0.0574(7)	0.041(6)	0.057(6)	0.050(6)	0.009(5)	0.003(4)	0.001(5)
C(14)	2*i*	0.792(1)	0.246(1)	0.0812(7)	0.065(7)	0.059(7)	0.053(6)	0.015(6)	0.010(5)	−0.003(5)
C(15)	2*i*	0.808(2)	0.147(1)	0.0164(9)	0.080(9)	0.052(7)	0.076(9)	0.011(6)	0.005(7)	−0.013(6)
C(16)	2*i*	0.826(2)	0.178(1)	−0.0728(9)	0.086(9)	0.070(9)	0.075(9)	0.021(7)	0.008(7)	−0.026(7)
C(17)	2*i*	0.832(1)	0.306(1)	−0.0982(7)	0.041(6)	0.091(9)	0.046(6)	0.011(6)	0.001(5)	−0.005(6)
C(18)	2*i*	0.811(1)	0.407(1)	−0.0316(6)	0.055(6)	0.069(7)	0.033(5)	0.016(6)	0.003(4)	−0.001(5)
O(1)	2*i*	0.828(1)	0.699(2)	−0.1831(7)	0.077(7)	0.22(1)	0.080(7)	0.046(8)	0.021(5)	0.055(8)
C(19)	2*i*	0.700(2)	0.717(2)	−0.243(1)	0.11(1)	0.19(2)	0.09(1)	0.04(1)	0.02(1)	0.03(1)
C(20)	2*i*	0.589(2)	0.779(2)	−0.203(2)	0.10(1)	0.13(2)	0.25(3)	0.06(1)	0.03(2)	0.02(2)

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