Crystal structure of *cis*-bis[1,1-dibutyl-3-(4-chloro-benzoyl)-thioureato]-palladium(II), $Pd(C_{16}H_{22}ClN_2OS)_2$

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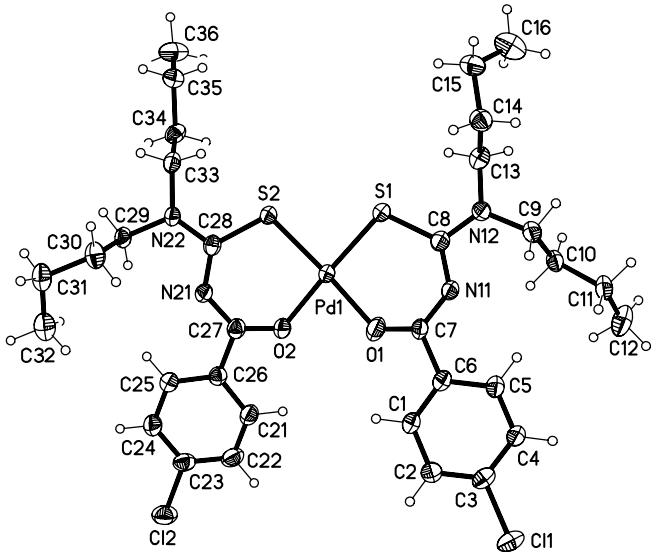

Abstract

$C_{32}H_{44}Cl_2N_4O_2PdS_2$, monoclinic, $P12_1/c1$ (no. 14), a = 16.857(2) Å, b = 8.3800(9) Å, c = 24.805(3) Å, β = 90.300(2)°, V = 3503.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.063, $wR_{ref}(F^2)$ = 0.193, T = 150 K.

Source of material

The ligand was prepared by a procedure reported in [1], which involved first converting 4-chlorobenzoyl chloride into 4-chlorobenzoyl iso-thiocyanate and then the condensation with the appropriate dibutylamine. The ligand was recrystallized from ethanol/dichloromethane (*v*/*v* 1:1). The solution of palladium(II)-chloride was added dropwise to the ligand solution in a 1:2 ratio with a small excess of ligand. The solid complex was filtered and recrystallized from ethanol/dichloromethane (*v*/*v* 1:2).

Discussion

Thiourea derivatives have a long history as a ligand in coordination chemistry being able to coordinate to a metal via sulphur and oxygen atoms. The structure of title compound, *cis*-bis[1,1-dibutyl-3-(4-chloro-benzoyl)-thioureato]palladium(II), consists of discrete complex molecules, being the asymmetric part. The complex presents a planar square environment about the Pd center with the ligands coordinating in a relatively undistorted manner (∠O2–Pd–S1 = 176.30(19)°, ∠O1–Pd–S2 = 175.89(19)°). The bond lengths of the thiocarbonyl C8—S1, 1.748(7) Å, and carbonyl C7—O1, 1.260(9) Å, bonds are longer than the average for C=S and C=O, respectively, while all C—N bonds of the complex ring are shorter than the average for C—N single bonds. They agree well with the related distances for *cis*-bis[*N*,*N*′-di(*n*-butyl)-*N*′-benzoyl-thioureato]platinum(II) [2] and *cis*-bis(1,1-diethyl-3-benzoylthio-ureato)palladium(II) [3].These results indicate extensive delocalization of electrons within the complex ring of the compounds. The two Pd—O bonds being significantly shorter than the two Pd—S bonds are consistent with those obtained in [3]. The divergent arrangement of two arms is in order to allow the sulfur atom to approach the metal atom within reasonable bonding distance. All other bond lengths fall within the expected range. According to all of the results, our studies have shown that 1,1-dibutyl-3-(4-chloro-benzoyl)thiourea ligands and palladium(II) metal form a neutral *cis*-[PdL_2] type complex.

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Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.25 × 0.25 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.36 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	52.76°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	19334, 7094
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5677
$N(param)_{refined}$:	393
Program:	SHELXTL [4]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.8774	0.5281	0.3952	0.048
H(2A)	4*e*	0.9693	0.5713	0.4647	0.051
H(4A)	4*e*	1.1398	0.6589	0.3544	0.047
H(5A)	4*e*	1.0473	0.6244	0.2848	0.049
H(9A)	4*e*	1.0085	0.7114	0.1827	0.049
H(9B)	4*e*	1.0219	0.6707	0.1204	0.049
H(10A)	4*e*	1.0629	0.4126	0.1414	0.050
H(10B)	4*e*	1.0397	0.4366	0.2034	0.050
H(11A)	4*e*	1.1667	0.5984	0.1492	0.063
H(11B)	4*e*	1.1398	0.6449	0.2090	0.063
H(12A)	4*e*	1.1678	0.3627	0.2313	0.110
H(12B)	4*e*	1.2426	0.4782	0.2239	0.110
H(12C)	4*e*	1.2166	0.3605	0.1762	0.110
H(13A)	4*e*	0.8436	0.4766	0.0987	0.050
H(13B)	4*e*	0.9319	0.4867	0.0756	0.050
H(14A)	4*e*	0.8340	0.7638	0.0892	0.054
H(14B)	4*e*	0.9187	0.7619	0.0603	0.054
H(15A)	4*e*	0.8172	0.7724	–0.0039	0.065
H(15B)	4*e*	0.7790	0.6129	0.0198	0.065
H(16A)	4*e*	0.9311	0.6123	–0.0285	0.113
H(16B)	4*e*	0.8518	0.5776	–0.0623	0.113
H(16C)	4*e*	0.8781	0.4593	–0.0148	0.113
H(21A)	4*e*	0.7355	0.2715	0.4236	0.050
H(22A)	4*e*	0.7312	0.1726	0.5110	0.057

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(24A)	4*e*	0.4914	0.1759	0.5045	0.056
H(25A)	4*e*	0.4959	0.2767	0.4171	0.050
H(29A)	4*e*	0.4157	0.2883	0.3290	0.044
H(29B)	4*e*	0.3506	0.3283	0.2836	0.044
H(30A)	4*e*	0.3600	0.6038	0.3060	0.057
H(30B)	4*e*	0.4236	0.5619	0.3519	0.057
H(31A)	4*e*	0.2877	0.6039	0.3848	0.064
H(31B)	4*e*	0.2637	0.4404	0.3558	0.064
H(32A)	4*e*	0.3440	0.2963	0.4132	0.093
H(32B)	4*e*	0.2894	0.4093	0.4494	0.093

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(32C)	4*e*	0.3800	0.4562	0.4387	0.093
H(33A)	4*e*	0.4760	0.5149	0.1919	0.044
H(33B)	4*e*	0.3866	0.5171	0.2130	0.044
H(34A)	4*e*	0.3747	0.2429	0.1915	0.048
H(34B)	4*e*	0.4634	0.2446	0.1687	0.048
H(35A)	4*e*	0.3376	0.4340	0.1236	0.053
H(35B)	4*e*	0.4256	0.4241	0.0997	0.053
H(36A)	4*e*	0.4060	0.1543	0.0766	0.095
H(36B)	4*e*	0.3368	0.2588	0.0499	0.095
H(36C)	4*e*	0.3197	0.1572	0.1032	0.095

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*	0.72695(3)	0.44796(7)	0.26609(2)	0.0231(3)	0.0390(3)	0.0314(3)	–0.0019(2)	–0.0002(2)	–0.0006(2)
Cl(1)	4*e*	1.1319(1)	0.6386(3)	0.46698(9)	0.050(1)	0.059(1)	0.052(1)	–0.006(1)	–0.022(1)	–0.001(1)
Cl(2)	4*e*	0.6080(1)	0.0940(3)	0.58131(9)	0.064(1)	0.074(2)	0.040(1)	–0.013(1)	–0.009(1)	0.012(1)
S(1)	4*e*	0.7756(1)	0.5246(3)	0.18607(8)	0.0268(9)	0.067(1)	0.0331(9)	–0.0033(9)	–0.0021(7)	0.0019(9)
S(2)	4*e*	0.6073(1)	0.4271(2)	0.22734(7)	0.0253(8)	0.050(1)	0.0315(9)	–0.0020(8)	–0.0004(7)	–0.0050(8)
O(1)	4*e*	0.8301(3)	0.4753(8)	0.3050(2)	0.028(3)	0.070(4)	0.059(4)	–0.004(3)	–0.003(3)	0.014(3)
O(2)	4*e*	0.6893(3)	0.3692(8)	0.3375(2)	0.027(3)	0.079(4)	0.040(3)	–0.012(3)	0.001(2)	0.010(3)
N(11)	4*e*	0.9171(3)	0.5800(8)	0.2410(2)	0.025(3)	0.046(4)	0.035(3)	–0.003(3)	0.000(2)	–0.006(3)
N(12)	4*e*	0.9213(4)	0.5749(8)	0.1505(2)	0.033(3)	0.042(4)	0.035(3)	–0.002(3)	0.000(3)	0.008(3)
N(21)	4*e*	0.5506(3)	0.3552(7)	0.3301(2)	0.028(3)	0.037(3)	0.036(3)	0.003(3)	–0.001(2)	0.002(3)
N(22)	4*e*	0.4622(3)	0.4026(7)	0.2634(2)	0.024(3)	0.041(4)	0.035(3)	–0.002(2)	0.002(2)	0.003(3)
C(1)	4*e*	0.9308(4)	0.554(1)	0.3867(3)	0.027(3)	0.051(5)	0.042(4)	0.003(3)	–0.001(3)	0.001(4)
C(2)	4*e*	0.9852(5)	0.579(1)	0.4281(3)	0.038(4)	0.051(5)	0.038(4)	0.003(4)	–0.001(3)	0.005(4)
C(3)	4*e*	1.0623(5)	0.615(1)	0.4152(3)	0.037(4)	0.041(4)	0.048(4)	0.002(3)	–0.012(3)	0.002(4)
C(4)	4*e*	1.0864(4)	0.632(1)	0.3624(3)	0.028(4)	0.049(5)	0.040(4)	–0.001(3)	–0.001(3)	–0.004(3)
C(5)	4*e*	1.0319(4)	0.610(1)	0.3213(3)	0.029(4)	0.052(5)	0.042(4)	–0.001(3)	0.003(3)	–0.004(4)
C(6)	4*e*	0.9532(4)	0.5672(9)	0.3337(3)	0.027(3)	0.037(4)	0.042(4)	0.002(3)	–0.002(3)	–0.001(3)
C(7)	4*e*	0.8939(4)	0.5394(9)	0.2899(3)	0.024(3)	0.037(4)	0.038(4)	0.000(3)	0.003(3)	–0.001(3)
C(8)	4*e*	0.8769(4)	0.5610(9)	0.1949(3)	0.031(4)	0.041(4)	0.038(4)	0.000(3)	–0.001(3)	–0.002(3)
C(9)	4*e*	1.0046(4)	0.626(1)	0.1553(3)	0.037(4)	0.049(5)	0.036(4)	–0.008(4)	0.006(3)	0.000(3)
C(10)	4*e*	1.0603(4)	0.492(1)	0.1711(3)	0.033(4)	0.056(5)	0.037(4)	–0.004(3)	0.009(3)	–0.005(4)
C(11)	4*e*	1.1435(5)	0.556(1)	0.1829(4)	0.035(4)	0.070(6)	0.052(5)	–0.012(4)	0.012(4)	–0.001(5)
C(12)	4*e*	1.1973(5)	0.428(1)	0.2056(5)	0.035(5)	0.084(8)	0.101(8)	0.000(5)	0.000(5)	0.003(7)
C(13)	4*e*	0.8912(5)	0.545(1)	0.0964(3)	0.036(4)	0.040(4)	0.050(5)	0.000(3)	–0.002(3)	–0.003(4)
C(14)	4*e*	0.8697(5)	0.699(1)	0.0664(3)	0.046(5)	0.044(5)	0.043(4)	0.005(4)	0.003(4)	0.004(4)
C(15)	4*e*	0.8298(6)	0.668(1)	0.0130(3)	0.060(6)	0.064(6)	0.037(4)	–0.002(5)	–0.003(4)	0.003(4)
C(16)	4*e*	0.8768(8)	0.571(1)	–0.0266(4)	0.104(9)	0.068(7)	0.056(6)	–0.001(6)	0.009(6)	0.000(5)
C(21)	4*e*	0.6856(4)	0.252(1)	0.4400(3)	0.030(4)	0.048(5)	0.045(4)	–0.004(3)	–0.002(3)	0.003(4)
C(22)	4*e*	0.6834(5)	0.194(1)	0.4918(3)	0.042(4)	0.057(5)	0.045(4)	–0.008(4)	–0.013(4)	0.002(4)
C(23)	4*e*	0.6104(5)	0.169(1)	0.5157(3)	0.047(5)	0.045(5)	0.036(4)	–0.010(4)	–0.008(3)	–0.002(3)
C(24)	4*e*	0.5410(5)	0.197(1)	0.4880(3)	0.035(4)	0.060(5)	0.045(4)	–0.002(4)	0.005(3)	0.008(4)
C(25)	4*e*	0.5439(4)	0.255(1)	0.4360(3)	0.032(4)	0.054(5)	0.039(4)	–0.001(4)	–0.001(3)	0.002(4)
C(26)	4*e*	0.6164(4)	0.2819(9)	0.4109(3)	0.031(4)	0.032(4)	0.036(4)	–0.003(3)	0.000(3)	–0.004(3)
C(27)	4*e*	0.6193(4)	0.3418(9)	0.3548(3)	0.031(4)	0.035(4)	0.040(4)	–0.004(3)	0.000(3)	–0.004(3)
C(28)	4*e*	0.5381(4)	0.3938(9)	0.2783(3)	0.029(4)	0.031(4)	0.041(4)	–0.004(3)	0.002(3)	0.000(3)
C(29)	4*e*	0.3978(4)	0.3702(9)	0.3028(3)	0.026(3)	0.043(4)	0.042(4)	–0.004(3)	0.004(3)	0.009(3)
C(30)	4*e*	0.3761(5)	0.522(1)	0.3326(4)	0.043(4)	0.040(5)	0.060(5)	–0.001(4)	0.012(4)	0.001(4)
C(31)	4*e*	0.3078(5)	0.498(1)	0.3738(4)	0.038(4)	0.054(5)	0.067(6)	–0.004(4)	0.013(4)	–0.007(4)
C(32)	4*e*	0.3324(6)	0.407(1)	0.4230(4)	0.049(5)	0.069(7)	0.069(6)	0.002(5)	0.013(5)	–0.003(5)
C(33)	4*e*	0.4345(4)	0.4497(9)	0.2093(3)	0.027(3)	0.038(4)	0.045(4)	0.001(3)	0.002(3)	0.007(3)
C(34)	4*e*	0.4151(5)	0.3102(9)	0.1737(3)	0.036(4)	0.038(4)	0.046(4)	0.000(3)	–0.007(3)	0.009(3)
C(35)	4*e*	0.3839(5)	0.363(1)	0.1186(3)	0.045(4)	0.051(5)	0.036(4)	0.003(4)	0.000(3)	0.005(4)

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