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Crystal Structure of *cis*-bis(*N*,*N*-dimethyl-*N*′-benzoylthioureato)palladium(II)

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In this study *cis*-bis(*N*,*N*-dimethyl-*N*'-benzoylthioureato)palladium(II) is synthesised and the crystal structure is determined by X-ray diffraction methods. It crystallises in the space group $P2_1/c$, with $a = 11.943(1)$ Å, $b = 11.713(1)$ Å, $c = 15.345(1)$ Å, $\beta = 93.90(1)^\circ$, and $D_{calc} = 1.616$ g cm^{-1} for $Z = 4$. The Pd(II) atom is in a four-coordinate geometry consisting of two thiocarbonyl S and two carbonyl O atoms from two ligand groups. The Pd-S and Pd-O bond lengths are 2.2313(6) and 2.0211(16) Å, respectively.

Key Words: Complex, X-ray structure, single crystal, *N*,*N*-dimethyl-*N*′-benzoylthiourea.

Introduction

Some thiourea derivatives are selective analytical reagents, especially for the determination of transition metals in complex interfering matrices[1,2]. The complexation capacity of some thiourea derivatives has been reported in several papers[3,4]. The biological activities of complexes with thiourea derivatives have been successfully screened for various biological actions. The Pt complexes have been used as anti-tumour agents in chemotherapy for some types of cancer[5]. *N*,*N*-dialkyl-*N*′-benzoylthioureas have been found to be useful ligands for determination of traces of the transition metals by means of normal phase chromatography[2,4].

In previous studies, *N*,*N*-dialkyl-*N*′-benzoylthiourea derivatives with such properties and their metal complexes were synthesised and their thermal behaviours examined[6–9]. We found no report in our literature search for the crystal structural analysis of Pd(II) complex of *N*,*N*-dimethyl-*N*′-benzoylthiourea (DMBT).

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In this study, the crystal structure of *cis*-bis(*N*,*N*-dimethyl-*N*'-benzoylthioureato)palladium(II) complex is investigated.

Experimental

Apparatus

Single crystal X-ray data were collected on a Bruker AXS P4 diffractometer using monochromated MoK_α radiation (λ = 0.71073 Å). Standard reflections were monitored after every 300 reflections, which showed random deviations. LP corrections and empirical absorption corrections via psi-scans were applied. The structure was solved by direct and conventional Fourier methods. A full-matrix least-squares refinement based on F^2 was corrected. The program used for calculations was SHELXTL[10]. The details concerning data collection and refinement are given in Table 1.

Synthesis

The synthesis of ligand and palladium complex was reported before[11]. The solution of Pd(II) was prepared from analytical purity reagent $PdCl_2$ (60% Merck) salt. A 0.1 mol/L ligand solution prepared in EtOH was added into the 0.01 mol/L aqueous metal solution in stoichiometric ratio while stirring vigorously. The neutral complex insoluble in aqueous solution was filtered and purified by recrystallisation from Me_2CO-EtOH (1:1).

Results and Discussion

The molecular structure of the palladium complex is shown in Figure, and selected bond lengths and angles are listed in Table 2. Atomic coordinates and equivalent isotopic displacement parameters for non-hydrogen atoms are given in Table 3.

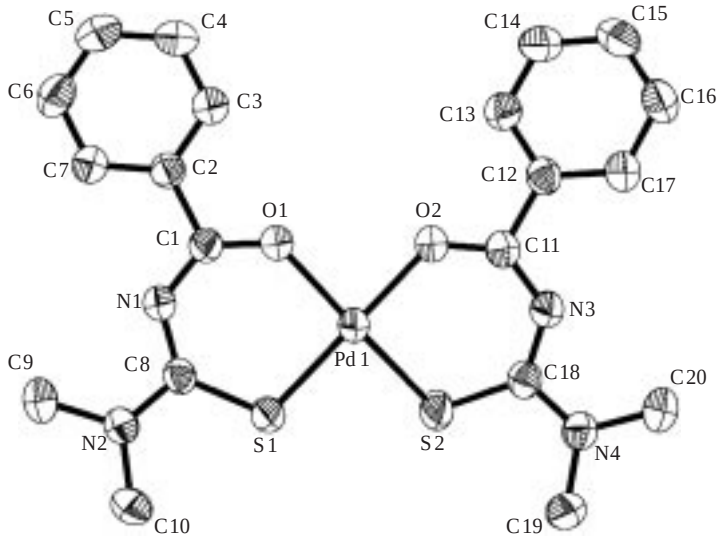

Figure ORTEP drawing of *cis*-bis(*N*,*N*-dimethyl-*N*'-benzoylthioureato)palladium(II) with hydrogen atoms omitted for clarity.

Table 1. Crystallographic data and parameters of the Pd(II) complex.

Empirical formula	$C_{20}H_{22}N_4O_2PdS_2$
Formula weight	520.94
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.943(1) Å
	b = 11.713(1) Å
	c = 15.345(1) Å
	$\alpha = 90°$
	$\beta = 93.90\ (1)°$
	$\gamma = 90°$
Volume	2141.6(3) $Å^3$
Z	4
Density (calculated)	1.616 Mg/m^3
Absorption coefficient	1.085 mm^{-1}
F(000)	1056
Crystal size	0.32 x 0.58 x 0.40 mm^3
Theta range for data collection	2.66 to 27.50°
Index ranges	-15<=h<=1, -1<=k<=15, -19<=1<=19
Reflections collected	6137
Independent reflections	4907 [R(int) = 0.0120]
Absorption correction	Psi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4907 / 0 / 266
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0259, wR2 = 0.0639
R indices (all data)	R1 = 0.0348, wR2 = 0.0677
Largest diff. peak and hole	0.337 and -0.290 e. $Å^{-3}$

Table 2. Selected bond lengths (Å) and angles (°) of Pd(II) complex of DMBT.

Bond lengths		Bond angles	
Pd(1)-O(1)	2.0211(16)	O(1)-Pd(1)-O(2)	85.56(7)
Pd(1)-O(2)	2.0245(16)	O(1)-Pd(1)-S(1)	94.15(5)
Pd(1)-S(1)	2.2313(6)	O(2)-Pd(1)-S(1)	177.27(6)
Pd(1)-S(2)	2.2373(6)	O(1)-Pd(1)-S(2)	176.36(6)
S(1)-C(8)	1.731(2)	O(2)-Pd(1)-S(2)	93.28(5)
S(2)-C(18)	1.737.(2)	S(1)-Pd(1)-S(2)	87.17(2)
O(1)-C(1)	1.262(3)	C(8)-S(1)-Pd(1)	108.21(8)
O(2)-C(11)	1.268(3)	C(18)-S(2)-Pd(1)	106.84(8)
N(1)-C(1)	1.319(3)	C(1)-O(1)-Pd(1)	129.29(15)
N(1)-C(8)	1.342(3)	C(11)-O(2)-Pd(1)	129.35(15)
N(2)-C(8)	1.333(3)	C(1)-N(1)-C(8)	126.64(19)
N(2)-C(9)	1.456(3)	O(1)-C(1)-N(1)	130.3(2)
N(2)-C(10)	1.462(3)	O(1)-C(1)-C(2)	114.72(18)
C(1)-C(2)	1.498(3)	N(1)-C(1)-C(2)	115.00(19)
C(2)-C(7)	1.385(3)	C(7)-C(2)-C(3)	118.8(2)
C(5)-C(6)	1.366(4)	N(2)-C(8)-N(1)	115.14(19)
C(6)-C(7)	1.382(3)	N(1)-C(8)-S(1)	129.41(16)

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for *cis*-bis(*N*,*N*-dimethyl-*N*'-benzoylthioureato)palladium(II).

	x/*a*	*y*/*b*	*z*/*c*	*U*eq*
Pd(1)	2289(1)	-8523(1)	600(1)	41(1)
S(1)	1478(1)	-8131(1)	1833(1)	52(1)
S(2)	2204(1)	-10365(1)	975(1)	58(1)
O(1)	2292(2)	-6880(1)	198(1)	57(1)
O(2)	3097(2)	-8859(2)	-489(1)	59(1)
N(1)	1423(2)	-5867(2)	1282(1)	42(1)
N(2)	951(2)	-6280(2)	2646(1)	48(1)
N(3)	3713(2)	-10748(2)	-294(1)	45(1)
N(4)	3537(2)	-12087(2)	742(1)	47(1)
C(1)	1819(2)	-6022(2)	509(1)	40(1)
C(2)	1722(2)	-5009(2)	-87(1)	40(1)
C(3)	2124(2)	-5072(2)	-913(2)	53(1)
C(4)	2020(2)	-4154(2)	-1476(2)	62(1)
C(5)	1522(2)	-3158(2)	-1213(2)	61(1)
C(6)	1116(2)	-3090(2)	-404(2)	57(1)
C(7)	1203(2)	-4013(2)	158(2)	47(1)
C(8)	1290(2)	-6668(2)	1891(1)	40(1)
C(9)	826(3)	-5060(2)	2794(2)	72(1)
C(10)	665(2)	-7032(2)	3358(2)	59(1)
C(11)	3585(2)	-9766(2)	-707(1)	43(1)
C(12)	4117(2)	-9701(2)	-1561(1)	42(1)
C(13)	3847(2)	-8803(2)	-2130(2)	49(1)
C(14)	4303(2)	-8763(2)	-2938(2)	55(1)
C(15)	5057(2)	-9585(2)	-3168(2)	58(1)
C(16)	5355(2)	-10445(2)	-2590(2)	62(1)
C(17)	4877(2)	-10516(2)	-1796(2)	52(1)
C(18)	3228(2)	-11071(2)	430(1)	42(1)
C(19)	3149(2)	-12555(2)	1554(2)	59(1)
C(20)	4315(2)	-12803(2)	286(2)	63(1)

*Ueq is defined as one third of the trace of the orthogonalised U^{ij} tensor.

This study showed that *N*,*N*-dimethyl-*N*′-benzoylthiourea preferentially forms a neutral *cis*-[PdL_2] type complex. As presented in the Figure 1, the palladium atom is bounded by two S and two O atoms with (O(1)-Pd-S(2)i=176.36°, O(2)-Pd-S(1)i=177.27°) in square planar coordination geometry. The Pd-S(1) bond length of 2.2313(6) Å corresponds to the Pd-S single bond, and the Pd-O(1) bond distance of 2.0211(16) Å lies within the range of those found for Pd-O (carbonyl)[12].

The lengths of C-O, C-S and C-N bonds in the chelate ring given in Table 2 are between characteristic single and double bond lengths, which are shorter than single and longer than double bonds. These results can be explained by the existence of delocalisation in the chelate ring, which is also supported by IR data[11−13]

The dihedral angle between the planes of O(2)-Pd-S(2) and O(1)-Pd-S(1) was calculated to be 3.7(2)°. This result indicates that the complex coordination geometry is a distorted squareplane.

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