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氯化四硫脲合钯配合物 $Pd[(NH_2)_2CS]_4Cl_2$ 的晶体结构

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The Crystal Structure of Palladium (II) tetra (thiourea) Chloride Complex: Pd[(NH₂)₂CS]₄Cl₂

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The title compound, $Pd[(NH_2)_2CS]_4Cl_2$, has been synthesized and structurally characterized. It crystallizes in orthorhombic, Pna2(1) space group, with $M_r = 481.79(C_4H_{16}Cl_2N_8PdS_4)$, a = 12.943(3), b = 8.283(2), c = 15.148(3)Å, V = 1623.9(6)Å³, Z = 4. The Pd (II) ion has an square-planar geometry, and is coordinated by four S atom donors from four thiourea molecules. The two Cl⁻ anions found in the apical position balance the charge. In the solid state, the title compound forms three dimensional network structures through hydrogen bonds. The intermolecular hydrogen bonds connect the $\{Pd[(NH_2)_2CS]_4\}^{2+}$ and chloride ion to contribute to the stability of the structure. CCDC: 193379.

Keywords: crystal structure palladium complex thiourea ligand

0 Introduction

In recent years, much attention has been focused on Pd (II) square-planar complexes owing to the large variety of reactions in which they are involved as catalysts^[11]. Further interest has been directed to these complexes because of the discovery of the anticancer activity of some of them^[2,3]. Palladium chelate complex also have been used as internal standards in gas chromatographic determinations of metals^[4]. Thiourea is an important organic chemical product. It has been widely used in drug, bactericide, catalysis, flotation agent and accelerant^[5,6]. Some of substituted thiourea derivations have shown interesting biological effects, which include anti-HIV properties⁽⁷⁻⁹⁾. Thiourea are also good extracting agents for precious metals⁽¹⁰⁾. As a thiolate ligand with potential S and N donors, thiourea is interesting because of the structural chemistry of its multifunctional coordination modes (unidentate-N, unidentate-S or bidentate-N: S)⁽¹¹¹⁾. Herein we report the crystal structure of palladium thiourea complex.

1 Experimental

1.1 Synthesis

All chemicals were obtained from a commercial

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source and used without further purification.

To a warm solution of excess thiourea (0.31g, 4mmol) in EtOH (80mL) was added with stirring PdCl₂ (0.22g, 1mmol). The red crystalline solid formed after refluxing for 20min. Single crystals suitable for X-ray analysis were obtained by slow evaporation of EtOH solution in air at room temperature. The C, H and N contents were determined by elemental analysis (Found: C, 9.91; H, 3.55; N, 23.86%. Calcd. C, 9.97; H, 3.35; N, 23.26%).

1.2 Crystallographic Data Collection and Structure Determination

A summary of the key crystallographic information is given in Table 1. The final position parameters of non-hydrogen atoms are given in Table 2. Selected bond distances and angles are listed in Table 3. The selected crystal of the title compound was mounted on a Rigaku Raxis-IV diffractometer. Reflection data were measured at 20°C using graphite monochromated Mo Ka $(\lambda = 0.71073 \text{ Å})$ radiation. The technique used was ω -scan with θ limit of 2. 69° < θ < 27. 50°. Empirical absorption corrections were carried out by using the SADABS^[12] program. The structure of the title compound was solved by direct methods and refined by least squares on F^2 by using the SHELXTL^[13] software package. All non-H atoms were anisotropically refined. The hydrogen atoms were placed in the calculated positions assigned the fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached and allowed to ride on their respective parent atoms. The final conventional R(F)

Table 1 Crystal Data and	d Structure Refinement for				
the Title Comp	ound				
empirical formula	C4H16Cl2N8PdS4				
formula weight	481. 77				
<i>T∕</i> K	293(2)				
wavelength / Å	0. 71073				
crystal system	orthorhombic				
space group	Pna2(1)				
a∕Å	12.943(3)				
b∕Å	8.283(2)				
c/Å	15.148(3)				
volume / ų	1623.9(6)				
Z	4				
calculated density/(g · cm ⁻³)	1970				
absorption coefficient/mm ⁻¹	1. 984				
F(000)	960				
crystal size/mm ³	$0.2 \times 0.2 \times 0.3$				
θ∕(°)	2. 69 to 27. 50				
limiting indices	$0 \leq h \leq 16, -10 \leq k \leq 10,$				
	$-18 \leq l \leq 19$				
reflections collected/unique	6125/3387[R(int) = 0.0224]				
completeness to $\theta = 27.50$	96. 4%				
refinement method	full-matrix least-squares on F^2				
data/restraints/parameters	3387/1/148				
goodness-of-fit on F^2	1.072				
final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0359, w R_2 = 0.0923$				
R indices (all data)	$R_1 = 0.0388$, w $R_2 = 0.0934$				
absolute structure parameter	0.38(4)				
extinction efficient	0.0107(7)				
largest diff. peak and hole ∕(e・Å ⁻³)	2. 102, -0. 691				

= 0. 0359 and w $R(F^2)$ = 0. 0923 for 3387 reflections $I > 2\sigma(I)$ with weighting scheme, $w = 1/[\sigma^2(F^2) + (0.0670P)^2 + 0.0000P]$, where $P = (F^2 + 2F_c^2)/3$. The molecular graphics were plotted using SHELXTL^[14]. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography^[15].

	x	y	Z	U(eq)		x	y	Z	U(eq)
Pd(1)	8763(1)	9895(1)	3339(1)	23(1)	S(1)	10473(1)	9950(2)	2825(1)	39(1)
S(3)	9250(1)	11894(1)	4332(1)	29(1)	S(2)	8325(1)	7725(2)	2438(1)	29(1)
Cl(2)	8532(1)	13145(2)	1767(1)	44(1)	Cl(1)	8986(1)	6422(2)	4958(1)	45(1)
S(4)	7051(1)	10043(1)	3831(1)	32(1)	C(3)	8840(4)	7979(6)	1396(3)	30(1)
C(2)	8661(4)	11534(6)	5347(3)	27(1)	C(1)	11298(4)	9524(7)	3698(4)	35(1)
N(4)	8948(4)	6677(6)	891(3)	37(1)	N(3)	9052(4)	9422(6)	1072(3)	36(1)
N(2)	8391(4)	10088(5)	5611(3)	34(1)	N(1)	8554(4)	12809(6)	5866(3)	39(1)
N(8)	5221(4)	10109(5)	3099(3)	40(1)	N(6)	12230(5)	10143(6)	3656(4)	48(1)
N(7)	6506(4)	10984(5)	2191(3)	37(1)	N(5)	11028(4)	8618(6)	4373(3)	43(1)
C(4)	6206(4)	10399(6)	2956(3)	28(1)					

Table 2Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å² $\times 10^2$) for the Title Compound

 U_{eq} is defined as one third of the trace of the orthogonalized U_{u} tensor.

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	Table 3 Bond Lengths(Å) and Angles(°) for the Title Compound						
Pd(1)-S(3)	2. 3249(13)	Pd(1)-S(2)	2.3269(13)	Pd(1)-S(4)	2.3406(14)		
Pd(1)-S(1)	2.3456(15)	S(1)-C(1)	1.736(6)	S(3)-C(2)	1.741(5)		
S(2)-C(3)	1.726(5)	S(4)-C(4)	1.743(5)	C(3)-N(3)	1.320(7)		
C(3)-N(4)	1.329(7)						
S(3)-Pd(1)-S(2)	174. 86(5)	S(3)-Pd(1)-S(4)	90. 76(4)	S(2)-Pd(1)-S(4)	89.80(4)		
S(3)-Pd(1)-S(1)	86.86(5)	S(2)-Pd(1)-S(1)	92.88(5)	S(4)-Pd(1)-S(1)	175.82(5)		
C(1)-S(1)-Pd(1)	108.9(2)	C(2)-S(3)-Pd(1)	109.30(17)	C(3)-S(2)-Pd(1)	110.38(18)		
C(4)-S(4)-Pd(1)	111.16(18)	N(3)-C(3)-N(4)	119.9(5)	N(3)-C(3)-S(2)	122.0(4)		

CCDC: 193379.

Results and Discussion 2

The X-ray structure of the complex Pd[(NH₂)₂ CS]₄Cl₂ is built up of monomeric molecules. Fig. 1 shows a perspective view of the monomeric unit with the atomic numbering scheme of the title compound. Fig. 2 shows a perspective view of the crystal packing in the unit cell. The crystal structure of the title complex consists of monomeric [Pd[(NH₂)₂CS]₄]²⁺ cations and two chloride anions in which the Pd (II) ion coordinated by four S-atom donors. Four thiourea molecules through sulfur atoms are coordinated to each Pd (II) ion forming a square-planar. The two chloride anions occupy the axial position balancing the charge. The bond distances of Pd-S(1), Pd-S(2), Pd-S(3) and Pd-S(4) are 2. 3456(15), 2. 3269(13), 2. 3249(13) and 2. 3406 (14) Å, respectively. All these parameters are slightly longer than those found in usual square planar coordination environment of Pd (II) complexes; such as



Molecular structure for the title compound with the atomic Fig. 1 numbering scheme



Fig. 2 A view of the crystal packing down the *a* axis for the title compound

 $[Pd(C_{12}H_9N_5S)_2]$ [2.241(1)Å and 2.239(1)Å]^[16], $[Pd(MeO)_{2}P(S) NMeNH_{2}Cl_{2}] = [2.285(2) Å]^{[17]}$, $[Pd(iPr_2NCS_2)_2]$ [2. 3127(8)Å]^[18], $[Pd(C_6H_{11}S_2)]$ $[2.266(3) \text{ Å} \text{ and } 2.255(2) \text{ Å}]^{[19]}$ and OH) Cl₂] $[Pd_4Cl_4(C_3H_6NO_2S)_4] \cdot 3C_2H_6OS \cdot C_4H_{10}O$ [2.2686 (9)Å and 2. 2847(9)Å]^[20]. The angles of S(1)-Pd-S (2), S(1)-Pd-S(3), S(3)-Pd-S(4) and S(4)-Pd-S(2)are 92. 88°, 86. 86°, 90. 76° and 89. 80°, respectively, they are a little deviation from the ideal 90°. This can be interpreted on the basis of the interaction effect between the two chloride anions and Pd (II). The Pd…Cl distances of [3.791(1) Å and 3.605(4) Å] are much longer than those usually Pd-Cl bonded distances (ca. 2.33Å), which assigned that there are not forming chemical bond between them. The C-S bond distances of 1.726(5) ~ 1.743(5) Å agree very well with those in related compounds, being intermediate between 1.82Å for a C-S single bond and 1.56Å for a C = Sdouble bond^[21]. The corresponding C-N bond distances

of 1. $310(6) \sim 1.329(7)$ Å are indicative of some double-bond character.

The atoms of each thiourea ligand are nearly coplanar, with the maximum deviation of atoms 0.002°, 0.027°, 0.023°, 0.012°, respectively. The plane formed by S(2), C(3), N(3), N(4) are almost parallel to the plane of S(3), C(2), N(1), N(2), with the dihedral angle of 4. 30°. The dihedral angles between the mean PdS₄ plane and thiourea planes are 73. 86°, 53. 42°, 57. 72°, 65. 14° for C1, C2, C3 and C4, respectively. There are some intermolecular hydrogen bonds in the crystal of the complex. The neighboring [Pd[(NH₂)₂CS]₄]²⁺ cations are linked with each other by $N(3) - H \cdots N(5)$ intermolecular hydrogen bond, with the donor and acceptor distance of 3. 044(0)Å. The two Cl- anions with the NH₂ group of the thiourea moieties form hydrogen bond network. The N···· Cl distances are between 3. 2588Å to 3. 4594Å, which are comparable with the corresponding values of N - H…Cl [3. 265 ~ 3. 288Å]^[22]. These intermolecular hydrogen bonds link the thiourea ligand and chloride atoms to form three-dimensional network which stabilize the structure.

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