

Note

Crystal Structure and Characterization of Pd(II) Bis(diisopropylthiocarbamate) Complex

XU, Liang-Zhong^a(许良忠) ZHAO, Pu-Su^b(赵朴素) ZHANG, Shu-Sheng^{*a}(张书圣)^aDepartment of Applied Chemistry, Qingdao Institute of Chemical Technology, Qingdao, Shandong 266042, China^bDepartment of Chemistry, Huaiyin Teacher's College, Huaiyin, Anhui 223001, China

The crystal and molecular structure of $[\text{Pd}(\text{iPr}_2\text{dtc})_2]$ (dtc = dithiocarbamate) have been determined by X-ray crystallography. The unit cell of the crystal structure consists of two discrete monomeric molecules of $[\text{Pd}(\text{iPr}_2\text{dtc})_2]$. The Pd(II) ion has an square-planar geometry. The electronic and IR spectral data are in agreement with the X-ray structure. The TG data indicate slight degradation of a few percent.

Keywords X-ray, dtc, palladium complexes

Introduction

Dialkyl-substituted dithiocarbamate anions have proved to be highly versatile chelating agents for the separation of metals as metal chelates by gas chromatography.¹ Their good performance in liquid-liquid extraction and other analytical procedures makes them attractive for the determination of metals by gas chromatography.² Some of dialkyl-substituted dithiocarbamate salts have also shown interesting biological effects which include anti-alkylation or anti-HIV properties.³ They are also used for the effective antidotes for cadmium intoxication.⁴ The ability of dtc binding to metals has been known for many years. It forms chelates with virtually all transition elements.⁵ In recent years, much attention has been focused on square-planar complexes of Pd(II) owing to the large variety of reactions in which they are involved as catalysts.

Further interest has been directed to these complexes since the discovery of the anticancer activity of some

of Pd-complexes.⁶ Palladium chelates have been used as internal standards in gas chromatographic determination of metals. In this paper, we report the crystal structure and the characterization of $[\text{Pd}(\text{iPr}_2\text{dtc})_2]$.

Experimental

Materials

All chemicals were obtained from commercial sources and used without further purification.

Preparation of the *N,N'*-diisopropylthiocarbamate sodium $[\text{Na}(\text{iPr}_2\text{dtc})]$

To a solution of diisopropyl-secondary amine (7.0 mL, 0.05 mol) in ethanol (5 mL) were added with stirring at below 4°C, carbon disulfide (3.1 mL, 0.052 mol) and sodium hydroxide (50% aqueous solution, 4 mL). After stirring for 5 h, evaporation of the volatiles was performed without heating. The pure $[\text{Na}(\text{iPr}_2\text{dtc})]$ was obtained by recrystallization from the solution of ethanol. Yield 89.7%.

Preparation of the complex

To a heated aqueous solution of $\text{Na}(\text{iPr}_2\text{dtc})$ (0.2 g, 1 mmol) was added an EtOH solution of palladium chloride (PdCl_2 , 0.08 g, 0.45 mmol) with stirring. The brown-yellow precipitate was deposited. Upon col-

* E-mail: zhangshs@public.qd.sd.cn

Received August 17, 2000; revised December 14, 2000; accepted December 27, 2000.

Project supported by the Natural Science Foundation of Shandong Province (Q99B16) and the National Natural Science Foundation of China (No. 29775012).

lection by filtration, the deposit was washed with water and dried overnight in air. The brown plate-like crystals were obtained by recrystallization from the solution of ethyl-acetate. They were collected, dried and submitted for elemental analysis (Anal. Calcd for $C_{14}H_{28}N_2PdS_4$: C 36.60, H 6.10, N 6.10, Pd 23.30, S 27.90; Found: C 36.14, H 6.42, N 6.75).

Physical measurements

Elemental analysis for carbon, hydrogen and nitrogen was performed on a Perkin-Elmer 240C analysis instrument. The UV spectroscopy in solutions was performed on a Shimadzu UV-200 recording spectrophotometer in the range of 190–900 nm. Infrared spectra were recorded in the range of 4000–300 cm^{-1} on a Perkin-Elmer 467 spectrometer by using pressed KBr plates. Thermal gravity (TG) and differential analysis (DTA) were recorded on a SDT 2980 simultaneously for

the samples of *ca.* 10 mg under a nitrogen atmosphere (150 mL/min) at a heating rate of 20°C/min.

Crystallographic study

The crystal data and refinement statistics were given in Table 1. The selected crystal of $[Pd(iPr_2dtc)_2]$ was mounted on a SMART CCD diffractometer. Reflection data were measured at 20°C using graphite monochromated Mo K_α radiation ($\lambda = 0.071073$ nm) with a detector distance of 4 cm and swing angle of -35° . A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different starting ϕ angle (0, 88, 180°) and each exposure of 30 s covered 0.3° in ω . The collected data were reduced by using the program SAINT⁷ and empirical absorption correction was done by using the SADABS⁸ program. Reflections with $2\theta \leq 55^\circ$ were used for structure solution and refinement.

Table 1 Crystal data and structure refinement for the title compound

Formula	$C_{14}H_{28}N_2PdS_4$
Formula weight	918.05
Crystal system	Monoclinic
Space group	$P2(1)/c$
<i>a</i> (nm)	0.81664(1)
<i>b</i> (nm)	1.81265(2)
<i>c</i> (nm)	1.48699(2)
α (°)	90
β (°)	101.667(1)
γ (°)	90
<i>V</i> (cm ³)	2155.69(5)
<i>Z</i>	2
D_{ca} (g·cm ⁻³)	1.414
μ (mm ⁻¹)	1.244
<i>F</i> (000)	944
Colour	brown
Crystal size (mm)	0.44 × 0.36 × 0.08
Radiation: λ (Mo K_α) (nm)	0.071073
Temperature (K)	293(2)
Data collection, θ range (°)	2.78 to 25.00
Index ranges (<i>h, k, l</i>)	$-12 < h < 11, -27 < k < 22, -21 < l < 22$
Reflections collected	11271
Independent reflections [$R(\text{int}) = 0.0201$]	3762
T_{\max} and T_{\min}	0.876 and 0.696
Refinement method	Full-matrix least-squares on F^2
GOF	1.160
<i>R</i> [$I > 2\sigma(I)$]	$R_1 = 0.0283, wR_2 = 0.0651$
<i>R</i> (all data)	$R_1 = 0.0368, wR_2 = 0.0693$
Largest peak and hole ($\times 10^{-3}e \cdot nm^{-3}$)	0.288, -0.360

The structure of $[\text{Pd}(i\text{Pr}_2\text{dtc})_2]$ was solved by direct method and refined by least squares refinement method on F_{obs}^2 by using the SHELXTL⁹ software package. All non-hydrogen atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. The final conventional $R(F) = 0.0283$ and $wR(F^2) = 0.0651$ for 3160 reflections with $I > 2\sigma(I)$; the weighting scheme, $w = 1/[\sigma^2(F_0^2) + (0.0244P)^2 + 0.8552P]$, where $P = (F_0^2 + 2F_c^2)/3$. Atomic scattering factors and anomalous dispersion correctors were taken from International Table

for X-ray Crystallography.¹⁰

Results and discussion

Crystal and molecular structure of the title compound

The structure of the title compound $[\text{Pd}(i\text{Pr}_2\text{dtc})_2]$ is a centro-symmetric monomeric molecule. Fig. 1 shows a perspective view of the molecule in the unit cell with the atomic numbering scheme. Selected bond distances and angles are listed in Table 2.

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for the title compound

Pd(1A)—S(2A)	0.23152(7)	Pd(1A)—S(1A)	0.23201(7)
S(2A)—C(1A)	0.1724(2)	N(1A)—C(1A)	0.1316(3)
C(2A)—C(3A)	0.1519(6)	N(1A)—C(2A)	0.1488(4)
S(2A)-Pd(1A)-S(1A)	75.09(2)	S(2AA)-Pd(1A)-S(1A)	104.91(2)
C(1A)-S(1A)-Pd(1A)	87.45(8)	C(1A)-N(1A)-C(2A)	120.3(2)

Symmetry transformations used to generate equivalent atoms: $a: -x, -y, -z$.

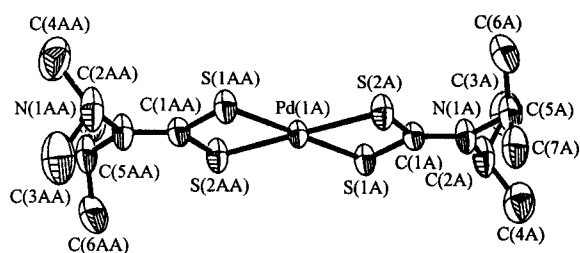


Fig. 1 Molecular structure for $\text{Pd}(i\text{Pr}_2\text{dtc})_2$ with the atomic numbering scheme.

In the crystal of the title compound, the asymmetric unit contains a pair of independent half-molecules of the complex $[\text{Pd}(i\text{Pr}_2\text{dtc})_2]$. The Pd atoms of these crystallographically independent molecules lie on the inversion center and one half of each molecule is inversion related to the other half. Two dithiocarbamate ligands coordinate to one Pd atom through the S atoms. The Pd atoms adopt a square-planar geometry and the mean PdS_4 planes of the two molecules are almost perpendicular to each other, the dihedral angle being $88.61(2)^\circ$. The dimensions within each ligand are normal. The dihedral angles between the PdS_4 and S_2CNC_2 planes are $2.34(4)$ and $0.07(3)^\circ$ for molecules A and B, respectively.

The bond lengths of $\text{S}(1\text{A})-\text{Pd}(1\text{A})$ and $\text{S}(2\text{A})-\text{Pd}(1\text{A})$ are $0.23201(6)$ and $0.23152(7)$ nm, respectively; and the bond angles of $\text{S}(1\text{A})-$

$\text{Pd}(1\text{A})-\text{S}(2\text{A})$ and $\text{S}(1\text{A})-\text{Pd}(1\text{A})-\text{S}(2\text{AA})$ are $75.09(2)^\circ$ and $104.91(2)^\circ$, respectively. All these parameters are in agreement with those reported before.¹¹ The carbon-sulfur bonds have an average distance of $0.1726(3)$ nm. The ligand "bite" angles S-C-S have a mean value of $109.66(13)^\circ$. The $\text{N}(1\text{A})-\text{C}(1\text{A})$ bond distance ($0.1316(3)$ nm) is shorter than the other N—C bond distances, which are indicative of considerable double-bond character.

When comparing the structural data with other dialkylthiocarbamate chelates of $\text{Pd}(\text{II})$ ¹² $[\text{Pd}(\text{R}_2\text{dtc})_2]$, $\text{R} = \text{Et}$, $n\text{-Pr}$ and $n\text{-Bu}$] it is noted that intramolecular interactions between hydrogen in the α -carbon of the ligand and substituents and sulfur atom are the shortest in $\text{Pd}(\text{II})$ diisopropylthiocarbamate chelates ($0.2527(3) - 0.2568(5)$ nm). Also, The Pd—S distances show small decreases along the series: $n\text{Pr} > \text{Et} > n\text{-Bu} \geq i\text{Pr}$ [$0.2323(2)$, $0.2317(3)$, $0.2316(3)$ and $0.23152(7)$ nm for $n\text{-Pr}$, Et , $n\text{-Bu}$ and $i\text{-Pr}$, respectively],^{2,12} the biggest change being the diisopropyl complex which has the shortest Pd—S distance in the solid. The results for the $\text{Pd}(\text{II})$ complexes are consistent with the increased ligand-field strength of the ligands resulting in shorter Pd—S distances.

IR spectra

The IR spectra of the title compound exhibit the

characteristic absorption. The strong band between 1340 and 1500 cm^{-1} is attributed to the $\nu(\text{C—N})$ stretching vibration, and the band in the 945 cm^{-1} to the $\nu(\text{C—S})$ stretching vibration. The band between 920 and 1010 cm^{-1} in the metal complexes is assigned to asymmetric stretching modes of the CSS group. This band must be highly coupled with other modes and is very sensitive to environmental change. Accordingly, this band has been used to distinguish between disulfur and unisulfur chelation. With disulfur chelation a single band is usually found, whereas when unisulfur chelation occurs, this band is split. The asymmetric band in our case is unsplit, indicating the bidentate modes of the dithio-ligands. In addition, the coordination of the gem-disulfide ligands is further confirmed by the M—S stretching frequencies observed in the 300—400 cm^{-1} region. The IR data and the diamagnetic nature of the title compound under investigation allowed us to suggest a square-planar configuration.

Electronic spectra

The solution electronic spectra were recorded in benzene and acetonitrile, which all exhibit three bands at 450, 360 and 310 nm. The increase of the polarity of the solvent leads to an increase in the band intensity and a blue shift. The band at 450 nm is assigned to a CT transition, the band at 360 nm is attributed to a second transition of the type $\pi^* \leftarrow \pi$ in the $\text{S} \cdots \text{C} \cdots \text{S}$ group, and the band at 310 nm is ascribed to the intra-ligand transition of the thione ligand.

Thermal analysis

Thermal analysis curves of the title compound are shown in Fig. 2. The complex first undergoes fusion at temperatures ranging from 235°C to 325°C. At 325°C, the complex volatilizes quickly until the lost weight is 96.25% at 392.7°C, which indicates slight degradation of a few percent. From DTA-curve we can see that there is a strong endothermic peak at 387.65°C. No apparent structural phase transition was found in the title compound.

Conclusions

In this paper, we report the crystal structure and

the characterization of $[\text{Pd}(\text{iPr}_2\text{dtc})_2]$. The crystal and molecular structure of $[\text{Pd}(\text{iPr}_2\text{dtc})_2]$ (dtc = dithiocarbamate) have been determined by X-ray crystallography. The unit cell of the crystal structure consists of two discrete monomeric molecules of $[\text{Pd}(\text{iPr}_2\text{dtc})_2]$. The Pd(II) ion has an square-planar geometry. Comparing with other dialkyldithiocarbamate chelates of Pd(II), the title compound has the shortest Pd—S distance and the strongest C—H \cdots S intramolecular interactions. The electronic and IR spectral data are in agreement with the X-ray structure. The TG data indicate slight degradation of a few percent.

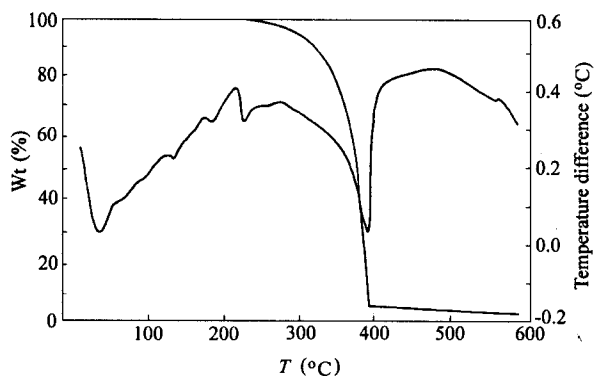


Fig. 2 TG-DTA diagram of the complex.

References

- Riekkola, M. L.; Makitie O.; Sundberg, M. *Kem. Kemi.* **1979**, *6*, 525.
- Riekkola, M. L.; Pakkanen, T.; Niinisto, L. *Acta Chem. Scand.* **1983**, *A 37*, 807.
- Hersh, E. M.; Brewton, G.; Abrams, D.; Bartlett, J.; Gill, P.; Gorter, R.; Gotlieb, M.; Jonikas, J. J.; Landesman, S.; Levine, A.; Marcel, A.; Petersen, E. A.; Whiteside, M.; Zahradnik, J.; Negron, C.; Boutitie, F.; Caraux, J.; Dupuy J. M.; Saimi, R. *J. Am. Med. Assoc.* **1991**, *265*, 1538.
- Shinobu, L. A.; Jones S. G.; Jones, M. M. *Acta Pharmacol. Toxicol.* **1984**, *54*, 189.
- Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31.
- Stettenko, A. I.; Presnov, M. A.; Konovalova, A. L. *Russ. Chem. Rev. (Engl. Transl.)* **1981**, *50*, 353.
- Sheldrick, G. M. *SAINTE v4 Software Reference Manual*, Siemens Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, **1996**.
- Sheldrick, G. M. *SADABS. Program for Empirical Absorption Correction of Area Detector Data*, University of Gottingen, Germany, **1996**.

- 9 Sheldrick, G. M. *SHELXTL, v5 Reference Manual*, Siemens Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1996.
- 10 Wilson, A. J. *International Table for X-ray Crystallography*, Vol. C, Kluwer Academic Publishers, 1992, Dordrecht: Tables 6.1.1.4 (pp. 500—502) and 4.2.6.8 (pp. 219—222) respectively.
- 11 Nikolov, G. S. *J. Inorg. Nucl. Chem.* **1981**, *43*, 3131.
- 12 Beurskens, P. T., Cras, J. A., Hummelink, Th. W.; Noordik, J. H. *J. Cryst. Mol. Struct.* **1971**, *1*, 253.

(E20000816 SONG, J.P.)