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Synthesis and crystal structure of bis(4-methylpiperidine-dithiocarbamato-S,S′)-palladium(II)

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The complex bis(4-methylpiperidine-dithiocarbamato-S,S′)-palladium(II) was synthesized by the reaction of 4-methyl-1-piperidine dithiocarbamic acid with palladium(II) chloride. Its structure was determined by X-ray crystal diffraction analysis. It crystallizes in the monoclinic $P2_1/c$ space group with the crystal cell parameters $a = 8.6491(8)$ Å, $b = 18.7305(16)$ Å, $c = 11.9933(10)$ Å, $\beta = 107.074(1)^\circ$, $V = 1857.3(3)$ Å^3 and $Z = 4$. The palladium (II) ion is bonded to four sulfur atoms, belonging to two dithiocarbamate ligands, in a distorted square planar geometry. The X-ray data suggest a pronounced electronic delocalization in the two NCS_2 moieties.

KEY WORDS: Dithiocarbamate; Palladium(II) complex; Crystal structure.

Introduction

Dithiocarbamate ligands are known for their antifungal, antibacterial and biocide activity.[1] They form complexes with transition metals, leading to the stabilization of a wide range of oxidation states.[2] These complexes have found applications in diverse areas such as materials science and medicine.[3,4] Some dithiocarbamate Pd(II) complexes have been recently reported to have very close cytotoxicity activity to that of cisplatin.[5] Understanding bonding in these complexes will allow the design of new effective drugs having reduced toxicity with respect to the currently used systems. In continuation of our previous work,[6–8] we report here the crystal structure of bis(4-methylpiperidine-dithiocarbamato-S,S′)-palladium(II).

Experimental

Synthesis of 4-methyl-1-piperidine dithiocarbamic acid

To a solution of CS_2 (6 mL, 1 mmol) in methanol (15 mL) was added dropwise an equimolar amount of 4-methylpiperidine (10 mL, 1 mmol) in methanol (15 mL). The reaction mixture was stirred for 4 h at room temperature. The light yellow precipitate was filtered, washed with 150 mL diethyl ether and air-dried.

Yield 70%, m.p. 178–180°C. Analysis: Calculated for $C_7H_{13}NS_2$: C, 48.00; H, 7.42; N, 8.00; S, 36.57. Found: C, 48.12; H, 7.45; N, 7.98; S, 36.52. ^{1}H NMR (DMSO-d$_6$, ppm), $^nJ(^1H, ^1H)$, 2.80 (m, 4H), 1.56 (m, 4H), 1.74 (m, 1H), 1.27

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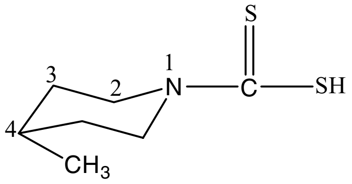
(s, 1H), 0.99 (d, 3H, CH_3, (7.8)). ^{13}C NMR (DMSO-d_6, ppm), 212.1 (CSS), 51.91 (C–2,6), 31.78 (C–3,5), 30.1 (C–4), 21.52 (CH_3). IR (KBr, cm^{-1}), 962 ν (C=S), 1003 ν (C–S), 2754 ν (S–H), 1410 ν (C–N).



Synthesis of bis(4-methylpiperidine-dithiocarbamato-S,S′)-palladium(II)

To a solution of 4-methyl-1-piperidine dithiocarbamic acid (0.350 g, 2.00 mmol) in acetone was added an aqueous solution of palladium(II) chloride (0.175 g, 1.00 mmol) dropwise with constant stirring at room temperature in 100 mL round bottom flask. After 0.5 h the yellow precipitates were filtered and dried in air. The crystals suitable for X-ray diffraction were grown by recrystallization from chloroform.

Yield 80%, m.p. 282–284°C. Analysis: Calculated for $C_{14}H_{26}N_2S_4Pd$: C, 36.79; H, 5.73; N, 6.13; S, 28.06. Found: C, 36.83; H, 5.78; N, 6.18; S, 28.12. IR (KBr, cm^{-1}), 982 ν(C=S), 1195 ν (C–S), 1490 ν (C–N), 445 ν (Pd–S).

X-ray data collection and structure determination

A crystal of the complex was mounted on glass fiber. Diffraction data were recorded on a Bruker-AXS Smart Apex system equipped with a graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The data were collected using SMART.[9] The data integration was performed using SAINT.[10] An empirical absorption correction was carried out using SADABS.[11] The structure was solved with the direct methods and refined by full matrix least square methods based on F^2, using the structure determination and graphics package SHELXTL[12] based on SHELX 97.[13] Hydrogen atoms were included at calculated positions using a riding model. The final refinement gave a ratio of maximum/minimum residual density of 4.21 due to a positive residual density maximum of 1.255 eÅ^{-3} located at 0.918 Å from Pd1. The crystallographic data are given in Table 1. Selected bond lengths and angles are given in Table 2. Complete bond lengths and bond angles, anisotropic thermal parameters and calculated hydrogen coordinates are deposited as supplementary materials. The ORTEP atomic labeling Scheme is given in Fig. 1.

Table 1. Crystal Data and Structure Refinement

CCDC deposit no	295231
Empirical formula	$C_{14}H_{24}N_2PdS_4$
Formula weight	454.99
Temperature (K)	297
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	8.6491(8)
b (Å)	18.7305(16)
c (Å)	11.9933(10)
β (°)	107.074(1)
Volume (Å^3)	1857.3(3)
Z	4
Calculated density (g cm^{-3})	1.627
Absorption coefficient (mm^{-1})	1.444
$F(000)$	928
Crystal size (mm)	0.36 × 0.26 × 0.07
θ range for data collection (°)	2.08–28.38
Limiting indices	
	$-11 \le h \le 11$
	$-25 \le k \le 24$
	$-16 \le l \le 15$
Max and min transmission	$T_{min} = 0.6245$, $T_{max} = 0.9057$
Data/restraints/parameters	4497/0/192
Goodness-of-fit on F^2	1.078
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0414$, $wR_2 = 0.0944$
R indices (all data)	$R_1 = 0.0535$, $wR_2 = 0.0994$
Largest diff. Peak and hole (eÅ^{-3})	1.255 and -0.298

Table 2. Selected Bond Lengths (Å) and Bond Angles (°)

Bond lengths (Å)			
Pd(1)–S(1)	2.3096(9)	S(2)–C(1)	1.718(3)
Pd(1)–S(4)	2.3131(9)	S(3)–C(8)	1.713(3)
Pd(1)–S(3)	2.3179(9)	S(4)–C(8)	1.715(3)
Pd(1)–S(2)	2.3187(9)	N(1)–C(1)	1.310(4)
S(1)–C(1)	1.714(3)	N(2)–C(8)	1.314(4)
Bond angles (°)			
S(1)–Pd(1)–S(4)	103.77(3)	C(1)–S(1)–Pd(1)	86.84(11)
S(1)–Pd(1)–S(3)	176.53(4)	C(1)–S(2)–Pd(1)	86.47(11)
S(4)–Pd(1)–S(3)	75.40(3)	C(8)–S(3)–Pd(1)	86.37(11)
S(1)–Pd(1)–S(2)	75.28(3)	C(8)–S(4)–Pd(1)	86.47(11)
S(4)–Pd(1)–S(2)	174.18(4)	S(1)–C(1)–S(2)	110.91(19)
S(3)–Pd(1)–S(2)	105.19(3)	S(3)–C(8)–S(4)	111.40(19)

Results and discussion

The reaction of 4-methyl-1-piperidine dithiocarbamic acid with palladium(II) chloride resulted in the deprotonation of the former by Pd(II) to afford the title complex. The palladium (II) ion is bonded to four sulfur atoms belonging to two dithiocarbamate ligands and the PdS_4 core exhibits a distorted square planar geometry. The Pd(II) ion is displaced from the least square plane defined by the four sulfur atoms by 0.0926(5) Å. The four Pd–S bond distances are not equal and are in the range 2.3096(9)–2.3187(9) Å. The S–Pd–S bond angles in the two strained four-membered chelate rings average to 75.34(3)°. The remaining S–Pd–S bond angles are 105.19(3)° and 103.77(3)° respectively. These values are in agreement with those reported for other bis(N,N-dialkyldithiocarbamato)-palladium(II) complexes.[14–15] The N–C bonds of the two NCS_2 moieties, N1–C1 1.310(4) Å and N2–C8 1.314(4) Å, are shorter than a single N–C bond hence suggesting a partial double bond character. The four S–C bond distances show no significant difference and average to 1.715(3) Å, indicating also a partial double bond character. These data suggest a pronounced electronic delocalization in the NCS_2 moiety. The two piperidyl rings adopt a chair conformation with the methyl groups taking equatorial positions. The two methyl substituents are anti and the torsional angle for C5 C4 C11 and C12 is −169.1(7)°. The shortest Pd. . .Pd

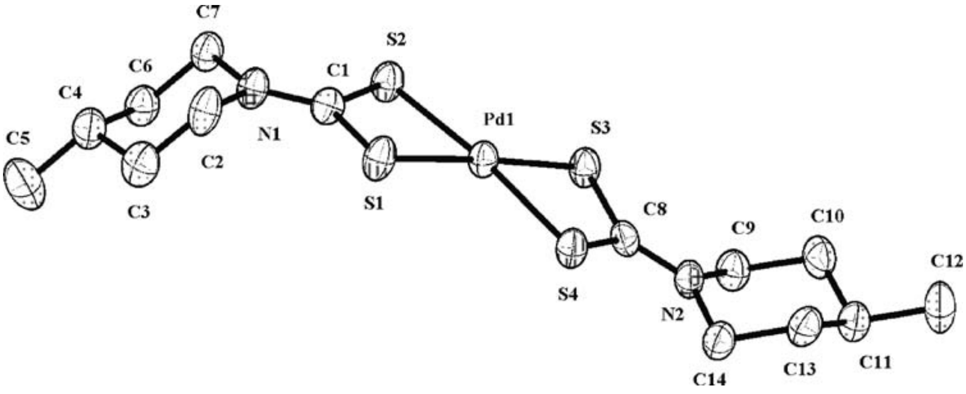


Fig. 1. Molecular structure of bis(4-methylpiperidine-dithiocarbamato-S,S′)-palladium(II). Thermal ellipsoids have been drawn with 30% probability. Hydrogen atoms have been omitted for clarity.

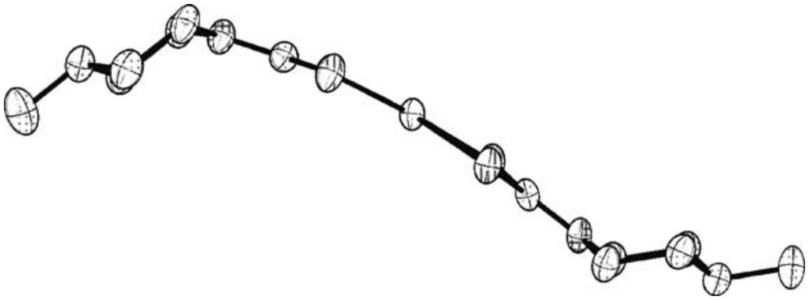


Fig. 2. Side view of the molecular structure of bis(4-methylpiperidine-dithiocarbamato-S,S′)-palladium(II). Thermal ellipsoids have been drawn with 30% probability. Hydrogen atoms have been omitted for clarity.

distance is 6.244 Å, ruling out any metal-metal interaction. One intermolecular S3–S3″ distance (3.566 Å) is significantly less than the some of the Van der Waals radii, indicating intermolecular interactions through sulfur atoms.

Supplementary materials The supplementary X-ray data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition No 295231.

Acknowledgements

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