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The Structure of Bis(methyl 3-isopropylidenedithiocarbazato)palladium(II)

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Abstract

$C_{10}H_{18}N_4PdS_4$, $M_r = 428 \cdot 95$, is orthorhombic, space group $P2_12_12_1$, with $a = 25 \cdot 674$ (5), $b = 8 \cdot 299$ (3), $c = 7 \cdot 772$ (3) Å, $Z = 4$, $V = 1656 \cdot 0$ Å^3, $D_m = 1 \cdot 71$ (flotation), $D_c = 1 \cdot 72$ Mg m^{-3}, μ(Mo $K\alpha$) = $1 \cdot 57$ mm^{-1}. Final $R = 0 \cdot 065$ for 1560 counter reflexions. The coordination around Pd can be described as slightly distorted *cis*-planar with an angular distortion of $10 \cdot 73°$.

Introduction

Our recent X-ray studies of bis(methyl 3-isopropylidenedithiocarbazato)nickel(II) have shown that only the *cis* isomer is present in the solid state and that its complex plane is tetrahedrally distorted by $27 \cdot 71°$ (Głowiak & Ciszewska, 1978).

The reason for *cis*-complex formation as well as tetrahedral distortion is still not clear, so to obtain more information on both questions we have decided to study Pd^{II} and Pt^{II} complexes with the same ligand.

Both metal ions are characterized by a much stronger crystal-field stabilization energy which might affect the tetrahedral distortion.

In this paper the structure of the Pd^{II} complex is considered.

Experimental

The compound was prepared by the method described by Akbar Ali, Livingstone & Phillips (1971). Dark-orange needles suitable for X-ray studies were obtained by evaporation of an acetone solution. The crystal data are given in the *Abstract*.

The lattice parameters and orientation matrix were obtained by least squares from 15 reflexions. Intensities from a crystal $0 \cdot 08 \times 0 \cdot 08 \times 0 \cdot 18$ mm were collected with Mo $K\alpha$ radiation on a Syntex $P2_1$ four-circle diffractometer with a graphite monochromator. The θ–2θ scan technique was used to $2\theta = 60°$ and 2500 reflexions were measured, 1560 of which had $I > 1 \cdot 96\sigma(I)$. After each group of 15 reflexions the intensity of a standard was measured; no significant change was observed. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Structure determination

The structure was solved by the heavy-atom method. The coordinates of the Pd atom were deduced from a Patterson map, and the positions of a further 13 non-H atoms obtained from an electron density map phased on the contribution of the Pd atom. After full-matrix least-squares refinement a second electron-density map was calculated from which the positions of the five remaining non-H atoms were deduced. The atomic

parameters were refined with isotropic temperature factors to $R = 0.109$ and with anisotropic factors to $R = 0.065$. At this stage an attempt to find the H atoms from a difference map was not successful (distances and angles in the methylene groups differed consider-

Table 1. *Atomic coordinates with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{4}{3} \sum_i B_{ii}.$$

	x	y	z	B_{eq} (Å^2)
Pd	0.1843 (1)	0.0022 (2)	0.4081 (2)	2.26 (8)
S(1)	0.2642 (2)	−0.1091 (7)	0.3762 (9)	3.0 (5)
S(2)	0.3648 (2)	0.0447 (6)	0.4454 (8)	3.6 (5)
S(3)	0.1476 (2)	−0.2450 (6)	0.4285 (9)	3.4 (5)
S(4)	0.0395 (2)	−0.3356 (6)	0.3751 (10)	4.4 (6)
N(1)	0.2241 (6)	0.2150 (19)	0.3497 (20)	2.3 (14)
N(2)	0.2785 (6)	0.2153 (18)	0.3993 (28)	2.7 (15)
N(3)	0.1073 (6)	0.0778 (17)	0.4733 (22)	2.3 (13)
N(4)	0.0667 (5)	−0.0353 (19)	0.4335 (25)	3.1 (14)
C(1)	0.2982 (8)	0.0731 (22)	0.4015 (34)	3.0 (16)
C(2)	0.2090 (9)	0.3390 (23)	0.2580 (28)	3.0 (17)
C(3)	0.1539 (7)	0.3452 (24)	0.1890 (29)	2.6 (17)
C(4)	0.2492 (8)	0.4683 (21)	0.2116 (27)	3.2 (18)
C(5)	0.3897 (8)	0.2526 (28)	0.4240 (44)	5.5 (29)
C(6)	0.0841 (7)	−0.1838 (24)	0.4163 (35)	3.0 (17)
C(7)	0.0886 (10)	0.2012 (22)	0.5635 (26)	4.3 (21)
C(8)	0.1297 (7)	0.3203 (24)	0.6266 (31)	3.2 (18)
C(9)	0.0342 (7)	0.2197 (27)	0.6119 (37)	4.4 (21)
C(10)	−0.0225 (7)	−0.2338 (29)	0.3870 (37)	4.7 (22)

Table 2. *Bond lengths (Å) with their e.s.d.'s in parentheses*

Pd—S(1)	2.263 (6)	C(1)—N(2)	1.29 (2)
Pd—S(3)	2.263 (5)	C(6)—N(4)	1.32 (3)
Pd—N(1)	2.090 (16)	N(2)—N(1)	1.45 (2)
Pd—N(3)	2.135 (15)	N(4)—N(3)	1.44 (2)
S(1)—S(3)	3.224 (8)	N(1)—C(2)	1.31 (3)
S(1)—C(1)	1.758 (19)	N(3)—C(7)	1.33 (3)
S(3)—C(6)	1.710 (19)	C(2)—C(3)	1.51 (3)
S(2)—C(5)	1.85 (2)	C(2)—C(4)	1.53 (3)
S(4)—C(10)	1.80 (2)	C(7)—C(8)	1.53 (3)
C(1)—S(2)	1.76 (2)	C(7)—C(9)	1.46 (3)
C(6)—S(4)	1.73 (2)		

Table 3. *Bond angles (°) with their e.s.d.'s in parentheses*

S(1)—Pd—S(3)	90.9 (2)	C(6)—S(4)—C(10)	103.5 (11)
S(1)—Pd—N(3)	170.1 (5)	C(1)—N(2)—N(1)	112.5 (17)
N(1)—Pd—N(3)	104.8 (6)	C(6)—N(4)—N(3)	112.7 (16)
N(1)—Pd—S(3)	170.0 (5)	N(2)—N(1)—Pd	114.5 (11)
N(1)—Pd—S(1)	83.0 (5)	N(4)—N(3)—Pd	115.4 (11)
N(3)—Pd—S(3)	82.2 (4)	N(2)—N(1)—C(2)	115.4 (16)
Pd—S(1)—C(1)	95.0 (8)	N(4)—N(3)—C(7)	110.8 (16)
Pd—S(3)—C(6)	97.1 (8)	Pd—N(1)—C(2)	129.6 (14)
S(1)—C(1)—N(2)	126.4 (17)	Pd—N(3)—C(7)	133.2 (14)
S(2)—C(6)—N(4)	126.6 (17)	N(1)—C(2)—C(3)	119.7 (18)
S(1)—C(1)—S(2)	113.0 (12)	N(1)—C(2)—C(4)	118.6 (18)
S(3)—C(6)—S(4)	115.1 (13)	C(3)—C(2)—C(4)	121.5 (17)
S(2)—C(1)—N(2)	120.6 (17)	N(3)—C(7)—C(8)	114.8 (18)
S(4)—C(6)—N(4)	118.3 (16)	N(3)—C(7)—C(9)	124.3 (20)
C(1)—S(2)—C(5)	101.2 (11)	C(8)—C(7)—C(9)	120.8 (19)

Table 4. *Least-squares planes through various groups of atoms and the deviations (Å) of atoms from the planes*

(a) Plane through Pd, S(1), N(1)

$$-0.1829x - 0.1445y - 0.9724z + 3.9528 = 0$$

(b) Plane through Pd, S(3), N(3)

$$-0.2379x + 0.0343y - 0.9707z + 4.2041 = 0$$

(c) Plane through S(1), N(1), N(2), C(1)

$$0.2371x + 0.0214y - 0.9713z + 1.2491 = 0$$

S(1)	−0.002 (7)	C(1)	0.046 (26)
N(1)	0.012 (16)	Pd	−0.710 (2)
N(2)	−0.032 (21)		

(d) Plane through S(3), N(3), N(4), C(6)

$$0.1221x + 0.1725y - 0.9774z + 3.1439 = 0$$

S(3)	0.001 (7)	C(6)	−0.018 (27)
N(3)	−0.004 (17)	Pd	0.624 (2)
N(4)	0.010 (19)		

(e) Plane through C(2), C(3), C(4)

$$0.2816x - 0.5379y - 0.7946z + 1.5956 = 0$$

(f) Plane through C(7), C(8), C(9)

$$-0.1556x + 0.5669y - 0.8090z + 2.9505 = 0$$

Angles between planes (°) (e.s.d.'s 1–2°)

(a)–(b)	10.7	(d)–(f)	29.6
(c)–(d)	10.9	(e)–(f)	72.9
(c)–(e)	31.6		

ably from the values expected). The refinement was completed without H atoms at $R_1 = 0.065$ and $R_2 = 0.069$.* The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2$ (F). An anomalous-scattering factor was considered for the Pd atom (Templeton, 1962). Scattering factors for all atoms were taken from Cromer & Waber (1974). All calculations were carried out on a Nova 1200 minicomputer with a program supplied by Syntex. The final parameters are listed in Table 1, bond distances and angles in Tables 2 and 3. Least-squares-planes data are in Table 4.

Discussion

The configuration of the $[Pd^{II}\{(CH_3)_2CNNCSSCH_3\}_2]$ molecule projected on the (010) plane is presented in Fig. 1.

Two ligand molecules coordinate with the Pd^{II} ion through the S and N atoms, forming an inner tetrahedrally deformed planar *cis* complex as in the Ni^{II} compound (Głowiak & Ciszewska, 1978). The tetrahedral deformation of 10.73° in the complex under
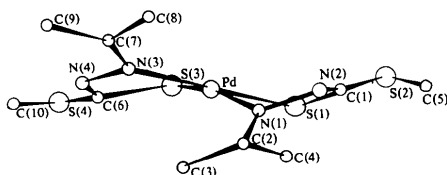
Fig. 1. Perspective view of the molecule viewed down **b**.

investigation, whose measure is the value of the interfacial angle θ between the planes intersecting Pd,S(1),N(1) and Pd,S(3),N(3), is considerably lower than that in the Ni^{II} complex (where $\theta = 27.71°$). This angle is $0°$ for a planar metal environment and $90°$ for a tetrahedron. Structural studies of *cis* and *trans* Ni^{II} complexes with thiosemicarbazide showed that the *trans* complexes are planar while the *cis* complex is slightly tetrahedrally deformed (Cavalca, Nardelli & Fava, 1962; Grønbæk & Rasmussen, 1962; Hazell, 1968). In other Ni^{II} *cis* complexes which have similar chelate systems, different degrees of tetrahedral deformation are observed depending on the type and size of the substituent at the donor N atom: $21.6°$ in bis[1-(α-methylbenzylidenehydrazono)ethanethiolato]-nickel(II) (Larsen, 1974), $27.71°$ in bis(methyl 3-isopropylidenedithiocarbazato)nickel(II) (Głowiak & Ciszewska, 1978), $22.0°$ in [Ni(nedc)$_2$] {nedc = methyl 3-[1-(2-naphthyl)ethylidene]dithiocarbazato} and $24.0°$ in [Ni(tedc)$_2$] {tedc = methyl 3-[1-(p-tolyl)ethylidene]dithiocarbazato} (Oniki, 1978). A decrease in the tetrahedral deformation found in the Pd^{II} complex may be due to a much higher crystal-field stabilization energy which counteracts tetrahedral deformation of the planar complex.

The five-membered chelate rings Pd,S(1),C(1), N(2),N(1) and Pd,S(3),C(6),N(4),N(3) show an envelope conformation with Pd deviating -0.710 (2) and 0.624 (2) Å from the respective mean planes through SCNN.

The Pd—S [2.263 (6), 2.263 (5) Å] and Pd—N [2.090 (16), 2.135 (15) Å] lengths are similar to the respective distances in other Pd^{II} complexes: 2.29, 2.25 and 2.05, 2.09 Å in [Pd(HN$_2$S$_2$)$_2$] (Weiss & Thewalt, 1968), 2.266 and 2.10 Å (mean values) in bis(4-methylazobenzene-2-thiolato)palladium(II) (Dyachenko, Atovmyan, Aldoshin, Kogan, Koshin & Osipov, 1976). The remaining bonds in the chelate rings are similar to those in the analogous Ni^{II} complex.

There are only van der Waals interactions between adjacent molecules. The shortest distances between atoms of neighbouring molecules are: S(1)$\cdots$C(2)(0.5 $- x, - y, 0.5 + z$) 3.59 (2), N(2)$\cdots$C(4)(0.5 $- x$, 1 $- y, 0.5 + z$) 3.65 (3), C(3)$\cdots$C(10)($-x, 0.5 + y, 0.5 - z$) 3.49 (3) Å.

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