Crystal and molecular structure of bis(N,N-diethyldithiocarbamato)palladium(II)

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Abstract

The crystal and molecular structure of bis(N,N-diethyldithiocarbamato)palladium(II), $\text{Pd}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2$, has been determined by a three-dimensional X-ray analysis. The compound crystallizes in the tetragonal space group $P4_2/n$ with unit cell dimensions $a = 16.439(8)$ Å and $c = 6.247(3)$ Å. The crystals are isomorphous with bis(N,N-diethyldithiocarbamato)platinum(II). Intensities were obtained with an automatic diffractometer. The structural parameters were refined by least-squares methods to a conventional R factor of 0.038 for 600 non-zero observed reflections. The palladium is in planar coordination with four sulphur atoms, the two non-equivalent Pd—S bond lengths being 2.317(3) and 2.315(3) Å.

Introduction

In connexion with our studies on dithiocarbamates, we investigated the crystal structure of the palladium salt. The crystals are isomorphous with the platinum salt (Amanov *et al.*, 1967).

Crystal data

Bis(N,N-diethyldithiocarbamato)palladium(II), $\text{Pd}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2$ ($=\text{Pd}(\text{dtc})_2$); FW 402.9. Yellow crystals, elongated along c ; crystal forms are {110} and {111}. Space group $P4_2/n$, from systematic absences. Unit cell dimensions: $a = 16.439(8)$ and $c = 6.247(3)$ Å; $V = 1688(2)$ Å³. $D_m = 1.58(1)$ g cm⁻³, $Z = 4$, $D_c = 1.590(2)$ g cm⁻³. Nickel-filtered copper radiation, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, was used. Linear absorption coefficient: $\mu = 84.7$ cm⁻¹.

The unit cell dimensions at 20°C were obtained from a platinum-calibrated Weissenberg photograph around (110). A crystal of approximate dimensions $0.1 \times 0.1 \times 0.15$ mm³ was mounted with c along the goniometer head axis for intensity measurements.

Structure factors

Intensity data were collected with an automatic Nonius diffractometer, using the moving counter-moving crystal method (scan speed 0.3°/min). Every 60 minutes, a reference reflexion was measured in order to detect fluctuations in the primary beam. Of the 1070 attainable symmetry-independent reflexions (up to $\sin \theta/\lambda = 0.53$ Å⁻¹), 602 reflexions were measured above background.

The observed intensities were corrected for fluctuations in the primary beam, Lorentz and polarization effects and absorption. The latter corrections were calculated according to the Busing and Levy (1957) scheme; $8 \times 8 \times 8$ volume fragments and seventeen bounding planes were taken into account. The unobserved reflexions were not used.

Table 1. Atomic parameters for $\text{Pd}(\text{dtc})_2$ with standard deviations

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0.5	0.0	0.0	0.00279(5)	0.00212(5)	0.0254(5)	0.00030(4)	0.0003(1)	-0.0008(1)
S(1)	0.5346(2)	0.0851(2)	0.2813(5)	0.0044(1)	0.0027(1)	0.025(1)	0.0008(1)	-0.0010(4)	-0.0011(3)
S(2)	0.4645(2)	0.1288(2)	-0.1169(6)	0.0056(2)	0.0027(1)	0.028(1)	0.0006(1)	-0.0008(4)	-0.0003(3)
N	0.4998(6)	0.2405(5)	0.183(2)	0.0051(5)	0.0022(4)	0.029(4)	-0.0004(3)	0.001(1)	-0.001(1)
C(1)	0.4997(6)	0.1638(6)	0.122(2)	0.0033(5)	0.0023(5)	0.030(5)	-0.0005(4)	-0.000(1)	-0.003(1)
C(2)	0.4641(9)	0.3045(7)	0.043(2)	0.0088(9)	0.0021(5)	0.028(6)	0.0004(5)	0.005(2)	0.001(1)
C(3)	0.534(1)	0.2670(7)	0.392(2)	0.0079(9)	0.0027(5)	0.032(6)	-0.0004(6)	-0.001(2)	-0.002(1)
C(4)	0.373(1)	0.3122(8)	0.081(3)	0.0070(8)	0.0042(6)	0.058(8)	0.0020(6)	0.005(2)	0.004(2)
C(5)	0.623(1)	0.290(1)	0.366(3)	0.0074(9)	0.0061(8)	0.064(9)	-0.0011(7)	-0.002(3)	-0.007(2)
H(21)	0.475	0.288	-0.126	$B = 5.2 \text{ \AA}^2$					
H(22)	0.494	0.362	0.070	5.2					
H(31)	0.528	0.219	0.511	5.5					
H(32)	0.499	0.319	0.456	5.5					
H(41)	0.362	0.324	0.254	7.1					
H(42)	0.341	0.256	0.035	7.1					
H(43)	0.346	0.363	-0.012	7.1					
H(51)	0.660	0.237	0.335	8.3					
H(52)	0.647	0.322	0.511	8.3					
H(53)	0.628	0.334	0.229	8.3					

The key to atom numbering is given in Fig. 1. The expression used for the temperature factor is:

$$\exp - [\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$$

The parameters of the hydrogen atoms have not been refined; the first figure of the numbering refers to the numbering of the concerning carbon atom.

Determination of the structure

The parameters of the isomorphous platinum compound were used as starting parameters for the least-squares refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The weight w for each reflexion was calculated according to $w = 1/(F_o + 40.0)$. The atomic scattering factor for Pd was corrected for anomalous scattering, using data from the International Tables (1962). After full-matrix least-squares refinement with anisotropic temperature factors ($R = 0.045$), a difference Fourier synthesis showed the position of the hydrogen atoms (of the eleven highest peaks, one was at the Pd position and ten were at the expected hydrogen positions).

The hydrogen atoms were placed at calculated positions (allowing rotation of the methyl groups so as to give the best fit with the difference Fourier synthesis) and were given isotropic temperature factors equal to the equivalent temperature factor of the attached carbon atom.

Anisotropic refinement with fixed hydrogen atom parameters gave $R = 0.037$. The final difference Fourier syntheses showed no significant electron density. A list of observed and calculated structure factors is available from the authors.

Computer programs. Calculations were performed on an IBM 360/50 computer using programs written by Busing *et al.* (1962), Johnson (1965), Ahmed & Pippy (1968), Beurskens *et al.* (1969) and Beurskens (1968).

Discussion

The structure is illustrated in Fig. 1 and a thermal-ellipsoid plot of the molecule is shown in Fig. 2. The atomic parameters are listed in Table 1 and distances and angles are given in Tables 2 and 3.

Table 2. Bond distances and angles in $\text{Pd}(\text{dtc})_2$ with standard deviations

Bond	Length (Å)	Bonds	Angle (deg.)
Pd—S(1)	2.317(3)	S(1)—Pd—S(2)	75.5(1)
Pd—S(2)	2.315(3)	Pd—S(1)—C(1)	86.1(4)
S(1)—C(1)	1.73(1)	Pd—S(2)—C(1)	87.0(4)
S(2)—C(1)	1.70(1)	S(1)—C(1)—S(2)	111.5(7)
C(1)—N	1.32(1)	S(1)—C(1)—N	123.1(9)
N—C(2)	1.49(2)	S(2)—C(1)—N	125.5(9)
N—C(3)	1.48(2)	C(1)—N—C(2)	120(1)
C(2)—C(4)	1.52(2)	C(1)—N—C(3)	123(1)
C(3)—C(5)	1.52(2)	C(2)—N—C(3)	117(1)
		N—C(2)—C(4)	111(1)
		N—C(3)—C(5)	110(1)

Table 3. Intermolecular distances (Å) less than 4 Å

Pd—C(3) II	3.93(2)	S(2)—C(4) III	3.83(2)
S(2)—S(1) I	3.997(5)	N—C(4) II	3.89(2)
S(1)'—C(2) III	3.69(1)	C(1)—C(4) II	3.65(2)
S(1)—C(4) II	3.82(1)	C(1)'—C(5) II	3.86(2)
S(1)'—C(5) II	3.92(2)	C(4)—C(4) II	3.83(2)
S(2)—C(3) I	3.98(1)		

Symmetry code: ' : $1 - x, -y, -z$ (molecule at $\frac{1}{2}00$). I: $x, y, z - 1$ (molecule at $\frac{1}{2}0\bar{1}$). II: $y, \frac{1}{2} - x, \frac{1}{2} - z$ (molecule at $00\frac{1}{2}$). III: $y, \frac{1}{2} - x, -\frac{1}{2} - z$ (molecule at $00\bar{\frac{1}{2}}$).

Fig. 1. Projection of $\text{Pd}(\text{dte})_2$ along c . Light molecules are at $z = 0$, dark molecules are at $z = \frac{1}{2}$; hydrogen atoms are omitted.

Fig. 2. Thermal ellipsoid plot of $\text{Pd}(\text{dte})_2$. Projection along c ; hydrogen atoms are omitted.

Table 4. Space groups and unit cell dimensions of $\text{Ni}(\text{dte})_2$, $\text{Pd}(\text{dte})_2$ and $\text{Pt}(\text{dte})_2$

	Space group	a (Å)	c (Å)	References
$\text{Ni}(\text{dte})_2$	$P2_1/c$	16.32*	6.19*	Bonamico <i>et al.</i> (1965)
$\text{Ni}(\text{dte})_2$ (β)	$P4/n$	16.18(2)	6.35(1)	Vaciago & Fasana (1958)
$\text{Ni}(\text{dte})_2$ (γ)	$P4/nmm$	16.35(4)	6.351(3)	Vaciago & Fasana (1968)
$\text{Pd}(\text{dte})_2$	$P4_2/n$	16.439(8)	6.247(3)	Present work
$\text{Pt}(\text{dte})_2$	$P4_2/n$	16.50	6.20	Amanov <i>et al.</i> (1967)

* Unit cell dimensions after transformation of the monoclinic cell to the pseudo-tetragonal cell: $(c \sin \beta + b) \frac{1}{2} \sqrt{2} = a$; $a = c$.

The palladium atom is in planar coordination with four sulphur atoms, the mean Pd—S distance being 2.316 Å. The equation of the coordination plane is $0.9135X + 0.1176Y - 0.3894Z - 7.5086 = 0$, with deviations from this plane for N: 0.02(1), C(1): 0.02(1), C(2): -0.05(2) and C(3): 0.07(2) Å. The geometry of the molecule is similar to that of the isostructural d^8 -complexes: Ni(dtc)₂ (Bonamico *et al.* 1965) and Pt(dtc)₂ (Amanov *et al.* 1967). Space groups and unit cell dimensions are compared in Table 4. The structure of the present complex is isomorphous with Pt(dtc)₂. (The published positional parameters of Pt(dtc)₂ may be transformed to the setting given in Table 1 by $\frac{1}{4} + x$, $\frac{1}{4} - y$, $\frac{3}{4} + z$.) From Table 4 it may be concluded that there exist four possible spatial arrangements of the molecules which give similar unit cell dimensions.

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