Dichlorobis(thiomorpholin-3-one)palladium(II)

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Abstract. $C_8H_{14}N_2O_2S_2Cl_2Pd$, $M_r = 411.66$, monoclinic, $P2_1/n$, $a = 12.166$ (2), $b = 8.425$ (4), $c = 6.595$ (3) Å, $\beta = 90.259$ (1)°, $V = 675.9$ Å^3, $Z = 2$, $D_o = 1.96$ (4), $D_c = 2.041$ (1) g cm^{-3}. The structure was refined to $R = 0.13$ for 1227 unique non-zero reflexions. The coordination of the Pd atom is *trans* square-planar, with the S atom attached axially.

Introduction. Crystals were supplied by Dr N. Johnson of the Chemistry Department, Portsmouth Polytechnic. 1948 unique structure amplitudes, of which 1227 were non-zero, were measured with graphite-mono-chromatized Mo $K\alpha$ radiation on a Stoe STADI-4, four-circle computer-controlled diffractometer. An $\omega/2\theta$ step scan was adopted, and the background measured with a stationary 30 s count at either end of the scanning range. The data were corrected for Lorentz and polarization effects and those reflexions with $I < 2\sigma(I)$ were given zero weight. The cell parameters were determined by least squares from the 2θ values measured on the diffractometer for 14 reflexions.

The structure was solved by Patterson and Fourier techniques. Refinement was by block-diagonal least squares, minimizing $\sum (w\Delta^2) = \sum [w(K|F_o| - |F_c|)^2]$.

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Scattering factors were obtained from $f = A \exp(-ax^2) + B \exp(-bx^2) + C$ (Forsyth & Wells, 1959). The H atoms were included in fixed calculated positions. Anomalous-dispersion corrections were applied for Pd, Cl and S. R for 1227 non-zero reflexions was 0.13, at which point the parameter shifts were $<10\%$ of their respective e.s.d.'s. The final R is higher than normally expected. An examination of possible reasons for this suggested that it was probably due to poor estimation of weak reflexions which constituted a significant proportion of the total. The final parameters are listed in Table 1.†

Discussion. Infrared investigations suggested that the complex contained a centre of symmetry (Allen, Johnson, Rosevear & Wilkinson, 1970). There was, however, some disagreement over the ligand coordination. Allen *et al.* (1970) preferred coordination to

Table 1. *Final fractional coordinates* ($\times 10^4$)

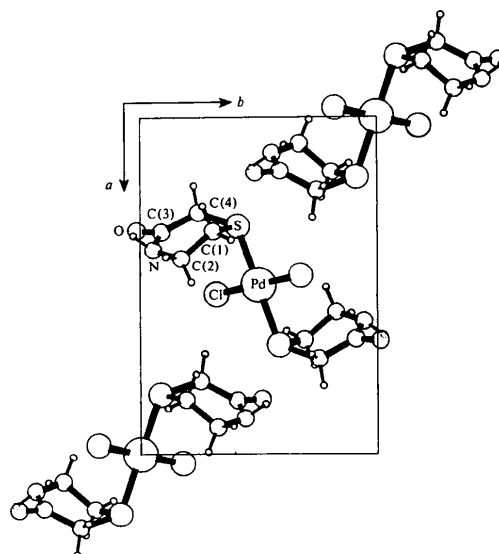|	x	y	z
Pd	5000	5000	5000
Cl	5275 (3)	3222 (5)	7591 (5)
S	3229 (3)	4129 (5)	4244 (5)
N	3936 (10)	5709 (16)	3683 (18)
O	3363 (11)	−140 (15)	6762 (17)
C(1)	3376 (12)	3078 (22)	1869 (19)
C(2)	4202 (13)	1737 (19)	2048 (21)
C(3)	3408 (13)	904 (22)	5463 (22)
C(4)	2830 (13)	2451 (21)	5742 (23)
H(11)	3632	3829	782
H(12)	2628	2650	1451
H(21)	4924	2153	2258
H(22)	4167	1091	728
H(41)	2941	2761	7210
H(42)	2031	2275	5498
H(5)	3515	−284	3039

Fig. 1. The (001) projection showing the atom labelling.

Table 2. *Bond lengths* (Å) *and angles* (°)

Pd—Cl	2·296 (4)	Cl—Pd—S	95·0 (1)
Pd—S	2·327 (4)	Pd—S—C(4)	112·4 (5)
S—C(4)	1·790 (17)	S—C(4)—C(3)	119·2 (11)
C(4)—C(3)	1·489 (25)	C(4)—C(3)—O	120·9 (14)
C(3)—O	1·329 (21)	O—C(3)—N	118·5 (16)
C(3)—N	1·372 (20)	C(4)—C(3)—N	120·5 (14)
N—C(2)	1·495 (19)	C(3)—N—C(2)	126·2 (13)
C(1)—C(2)	1·513 (23)	N—C(2)—C(1)	113·5 (12)
S—C(1)	1·811 (15)	C(2)—C(1)—S	111·3 (9)
		C(1)—S—C(4)	97·2 (8)
		C(1)—S—Pd	104·1 (5)

Pd through the N atom while de Filippo & Preti (1969) proposed coordination through S. Coordination via the O atom was not indicated.

Fig. 1 shows the expected square-planar configuration about the Pd atom which is at a centre of symmetry. The thiomorpholinone ligands are S-bonded to the Pd atom and exhibit a distorted chair confor-

mation, the region containing the N, C(3), C(4) and O atoms being approximately planar. The S atom is axially coordinated. This is unusual in that S is usually found to coordinate equatorially, in contrast to Se in which the axial isomer predominates (Barnes, Hunter & Lown, 1977).

The molecular geometry is given in Table 2, and the bond lengths and angles agree with literature values for similar thiomorpholin-3-one complexes.

References

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Dichlorobis(1,4-thioxane)palladium(II)

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Abstract. $C_8H_{16}O_2S_2Cl_2Pd$, $M_r = 385·96$, monoclinic, $P2_1/n$, $a = 7·442$ (6), $b = 19·62$ (1), $c = 4·413$ (3) Å, $\beta = 95·52$ (4)°, $V = 641·4$ Å^3, $Z = 2$, $D_o = 1·97$ (2), $D_c = 2·015$ (7) g cm^{-3}. The structure was refined to $R = 0·074$ for 420 unique non-zero reflexions. The S atom is bonded equatorially to Pd, which has a *trans* square-planar configuration.

Introduction. Crystals were supplied by Dr N. Johnson of the Chemistry Department, Portsmouth Polytechnic. The intensities were collected with Mo $K\alpha_1$ radiation obtained from a graphite monochromator on a Stoe STADI-4 four-circle computer-controlled diffractometer. An $\omega/2\theta$ step scan was performed and the background measured for 30 s at each end of the scanning range. Only 420 unique non-zero reflexions were available, with few reflexions of measurable intensity above $2\theta = 40°$. The intensities were corrected for Lorentz and polarization effects, and those reflexions for which $I < 2\sigma(I)$ excluded. The cell parameters were

refined by least squares from the 2θ angles measured on the diffractometer for 12 reflexions.

The structure was solved by Patterson methods and refinement was by block-diagonal least squares, minimizing $\sum(w\Delta^2) = \sum [w(K|F_o| - |F_c|)^2]$. Scattering factors were obtained from $f = A \exp(-ax^2) + B \exp(-bx^2) + C$ (Forsyth & Wells, 1959). The non-hydrogen atoms were refined with anisotropic thermal parameters while the H atoms were placed at fixed calculated positions. The final R was 0·074 for 420 unique non-zero reflexions. The final parameters are listed in Table 1.†

Discussion. Infrared investigations (Wilkinson, 1970) suggested that the thioxane ligands were in the *trans* square-planar configuration about the Pd ion and were S-bonded to the Pd. Bonding to the Pd *via* the O atom was not favoured.

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