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.

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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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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33367 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

	x	y	z
Pd	5000	5000	5000
Cl	7013 (4)	4283 (2)	7734 (8)
S	3400 (4)	4147 (2)	2315 (7)
C(1)	4130 (17)	3309 (6)	3485 (32)
C(2)	2704 (15)	2765 (8)	2458 (30)
C(3)	1190 (16)	4136 (6)	3830 (28)
C(4)	208 (16)	3490 (7)	2802 (29)
O	1063 (13)	2891 (4)	3900 (20)
H(11)	5396	3208	2417
H(12)	4292	3292	5854
H(21)	2521	2833	63
H(22)	3188	2292	2958
H(31)	458	4583	3042
H(32)	1250	4167	6271
H(41)	−1104	3500	3627
H(42)	250	3458	417

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

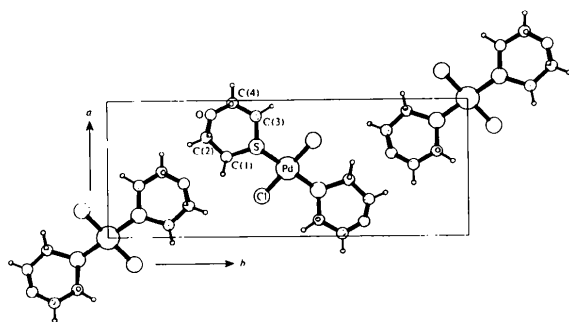| Pd—Cl	2·309 (3)	Cl—Pd—S	95·9 (1)
Pd—S	2·314 (3)	Pd—S—C(3)	104·9 (4)
S—C(3)	1·834 (12)	S—C(3)—C(4)	108·9 (8)
C(3)—C(4)	1·512 (18)	C(3)—C(4)—O	114·2 (10)
C(4)—O	1·401 (16)	C(4)—O—C(2)	111·4 (10)
O—C(2)	1·452 (15)	C(1)—C(2)—O	109·7 (11)
C(1)—C(2)	1·543 (19)	S—C(1)—C(2)	111·7 (9)
C(1)—S	1·790 (12)	C(1)—S—C(3)	98·2 (6)
		Pd—S—C(1)	112·9 (4)

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

Fig. 1 verifies that the ligand is in the *trans* square-planar configuration with the S atom equatorially bonded to the Pd. The thioxane ligands are in the chair conformation. The best plane through the Pd, Cl and S atoms makes an angle of 83·7° with the best plane through the four C atoms. The complete molecular geometry of the structure is shown in Table 2. The bond lengths and angles agree with the published values for other thioxane complexes.

Part of the reason for undertaking this study was to determine the relative Lewis basicity of N, S and O towards the Pd^{II} ion as Lewis acid. This, and the preceding two structural reports (Fowler & Griffiths, 1978a,b) have shown that coordination occurs *via* the S atom in the thioxane and thiomorpholinone compounds, and *via* the N atom for thiomorpholine. The modes of coordination in thiomorpholinone and thioxane compounds follow the HSAB principle (Pearson, 1963) and are in agreement with other structure determinations for complexes of thiomorpholin-3-one and thioxane with

soft Lewis acid ions (McEwen & Sim, 1967; Barnes, Hunter & Lown, 1977; Cannas, Carta, de Filippo, Marongiu & Trogu, 1974).

The mode of coordination *via* N in thiomorpholine confirms the predictions of Allen, Johnson, Rosevear & Wilkinson (1970) but, from the HSAB principle, coordination *via* S would be expected since Pd^{II} is classed as a soft Lewis acid. Thiomorpholine is known to form bridged species with simultaneous coordination *via* S and N to the Pd^{II} ion (Allen *et al.*, 1970) and thus it may be that there is little energy difference between the two modes of coordination, but in the absence of thermochemical data the question remains open. It is also known that addition of bulky alkyl substituents to a hard Lewis base has the effect of softening the donor atom (Jørgenson, 1964) and thus N in a heterocyclic ring may be softened sufficiently to act as a better Lewis base than S for the Pd^{II} ion.

The order of Lewis basicity of the three types of donor atom used has been shown to be N > S > O for dichloropalladium(II) as Lewis acid.

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