(Clegg & Wheatley, 1974), and the longest, 1·893 (4) Å, in Mn(CO)$_5$Cl (Greene & Bryan, 1971), not significantly longer than in {Mn(CO)$_4$}$_2$Cl$_2$. This effect can be attributed to the electron-withdrawing Cl ligands, which, by removing electron density from Mn, reduce overall Mn—CO π bonding.

The Mn—Cl lengths are slightly longer than those in Mn(CO)$_5$Cl, as expected for bridging ligands. Greene & Bryan (1971) also report an approximate value for Mn—Br in Mn(CO)$_5$Br of 2·50 (1) Å, which is slightly shorter than in {Mn(CO)$_4$}$_2$Br$_2$ (Dahl & Wei, 1963).

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Dichlorobis(thiomorpholine)palladium(II)

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Abstract. C$_8$H$_{18}$N$_2$S$_2$Cl$_2$Pd, $M_r = 383\cdot69$, triclinic, $P\bar{1}$, $a = 11\cdot31$ (1), $b = 5\cdot697$ (6), $c = 6\cdot731$ (8) Å, $\alpha = 116\cdot54$ (5), $\beta = 109\cdot14$ (6), $\gamma = 97\cdot3$ (1)°, $V = 363\cdot58$ Å^3, $Z = 1$, $D_o = 1\cdot834$ (2), $D_c = 1\cdot837$ (1) g cm^{-3}. The structure was refined to $R = 0\cdot068$ for 1997 unique non-zero reflexions. The coordination of the Pd atom is *trans* square-planar.

Introduction. Crystals were provided by Dr N. Johnson of the Chemistry Department, Portsmouth Polytechnic. 2016 unique reflexions (1997 non-zero) were measured with Mo $K\alpha$ radiation on a Stoe STADI-4, four-circle computer-controlled diffractometer. An $\omega/2\theta$ step scan was adopted and balanced filters were used for monochromatization. The intensities were corrected for Lorentz and polarization effects and those reflexions for which $I < 2\sigma(I)$ were given zero weight. The cell parameters were refined by least squares from 2θ values measured on the diffractometer for 10 reflexions. A Delauney reduction established that this was the reduced cell.

The structure was solved by Patterson and Fourier techniques. Refinement was by block-diagonal least squares minimizing $\sum (w\Delta^2) = \sum [w(K|F_o| - |F_c|)^2]$. Scattering factors were obtained from $f = A \exp(-ax^2) + B \exp(-bx^2) + C$ (Forsyth & Wells, 1959). Reflexions were rejected if $|F_o| \geq 3|F_c|$ and the weighting scheme was $w = 1$ for $|F_o| < F^*$ and $w = F^*/|F_o|$ if $|F_o| \geq F^*$. The value of F^* for the final cycles was 5·0. The H atoms were included at fixed calculated positions. The final R for 1997 non-zero reflexions was 0·068, when the shifts to the parameters were all <10% of their respective e.s.d.'s. The final parameters are listed in Table 1.‡

Discussion. The structure determination was carried out to support an IR spectroscopic study of the stereochemistry of transition-metal complexes, and, in par-

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‡ Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33365 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

	x	y	z
Pd	0	0	0
N	1513 (4)	2230 (8)	3505 (7)
Cl	1066 (1)	2232 (3)	−1385 (2)
S	4371 (2)	6487 (4)	7679 (3)
C(1)	1768 (5)	5243 (12)	4692 (10)
C(2)	2763 (6)	6853 (16)	7351 (10)
C(3)	2723 (6)	1432 (15)	3519 (10)
C(4)	3834 (7)	2776 (16)	6078 (12)
H(11)	2140	5912	3768
H(12)	924	5365	4534
H(21)	2834	8867	8089
H(22)	2433	6130	8260
H(31)	3049	2024	2523
H(32)	2477	633	2685
H(41)	4611	2137	5997
H(42)	3513	2190	7085
H(1)	1182	1590	4437

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

Pd—Cl	2·313 (1)	Cl—Pd—N	92·5 (1)
Pd—N	2·058 (4)	Pd—N—C(1)	113·5 (3)
N—C(1)	1·472 (7)	N—C(1)—C(2)	113·6 (5)
C(1)—C(2)	1·504 (8)	C(1)—C(2)—S	111·5 (4)
C(2)—S	1·810 (7)	C(2)—S—C(4)	96·4 (3)
S—C(4)	1·792 (8)	S—C(4)—C(3)	113·0 (5)
C(3)—C(4)	1·514 (9)	C(4)—C(3)—N	113·4 (5)
N—C(3)	1·494 (7)	C(3)—N—C(1)	113·1 (4)
		C(3)—N—Pd	110·5 (3)
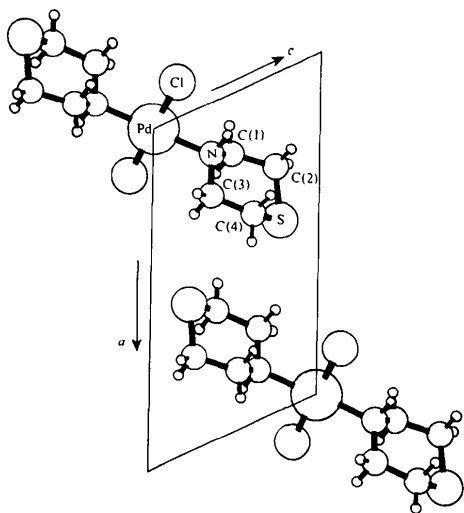
Fig. 1. The (010) projection showing the atom labelling.

that the complex contained a centre of symmetry. Further, on the basis of the assignment of IR stretching frequencies for the v(N—H) and v(C—S—C) modes it was postulated that the ligand was N-bonded to the Pd^{II} ion. Since bonding through S is also possible (because it is known that S is an effective base for the Pd^{II} ion), an X-ray structure determination would resolve any ambiguities.

Fig. 1 shows that the ligands are arranged in a *trans* square-planar configuration about the Pd ion. The thiomorpholine ligands are in the chair conformation with the N atom equatorially bonded to the Pd ion, thus confirming the spectroscopic conclusions. The best plane through the Pd, N and Cl atoms is inclined at an angle of 86·3° to that through the four C atoms in the thiomorpholine ring. The molecular geometry is given in Table 2.

It is believed that this study is the first X-ray determination performed for an organometallic complex containing a thiomorpholine ligand. A search of the Cambridge Crystallographic Data file has not indicated similar complexes for the comparison of bond lengths and angles.

ticular, to determine the relative Lewis basicity of N, S and O towards the Pd^{II} ion as Lewis acid (Allen, Johnson, Rosevear & Wilkinson, 1970). For the title compound, IR evidence suggested (Wilkinson, 1970)

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