# The Reaction of $WS_2Cl_2$ with Pyridine: Crystal Structure of Di-μ-sulphido-bis[chlorobis(pyridine)sulphidotungsten(V)]-Pyridine (1/2), $[W_2S_4Cl_2(py)_4]\cdot 2py$*

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Treatment of $WS_2Cl_2$ with pyridine (py) at room temperature leads to a redox reaction and the formation of a tungsten(V) species $[W_2S_4Cl_2(py)_4]\cdot 2py$ (**1**) which contains the $[(S)W(\mu\text{-}S)_2W(S)]^{2+}$ fragment and six-co-ordinate metal atoms. Crystals of (**1**) are monoclinic, space group $P2_1/c$, with $a = 10.636(8)$, $b = 23.180(15)$, $c = 14.529(12)$ Å, $\beta = 102.5(1)°$, and $Z = 4$. 1 245 Independent reflections above background were measured on a diffractometer and the structure refined to $R$ 0.079. The $[(S)W(\mu\text{-}S)_2W(S)]^{2+}$ fragment exists in the *syn* form with a W–W bond [2.844(4) Å] and two terminal W–S bonds [2.17(2), 2.13(2) Å].

The chemistry of the sulphido- and selenido-tungsten(VI) halides of formulation $WYX_4$ [Y = S or Se, X = Cl or Br] is well documented.[1,2] The structures of all four compounds have been examined by electron diffraction[3,4] and *X*-ray studies have been reported for both $WSCl_4$ and $WSBr_4$.[5] In contrast, although the species $WOSCl_2$, $WS_2Cl_2$, and $WSe_2Cl_2$ have been prepared[6] our efforts to ascertain the structures of these ternary compounds have so far failed. We have reported that the reaction of $WOSCl_2$ with $[AsPh_4]Cl$ in $CH_2Cl_2$ gave the dimeric tungsten(V) compound $[Cl_2(O)W(\mu\text{-}S)_2W(O)Cl_2]^{2-}$.[7] Few such dimeric tungsten(V) compounds have been reported, in contrast to the many reports of analogous molybdenum species. Continuing our studies on the compounds $WYY'Cl_2$ [Y = O or S, Y′ = O or S] we have studied the reaction of $WS_2Cl_2$ with pyridine and report the isolation of the tungsten(V) compound $[(py)_2Cl(S)W(\mu\text{-}S)_2W(S)Cl(py)_2]$.

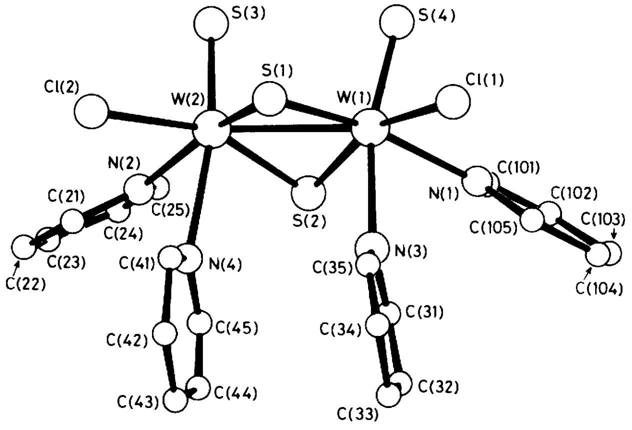

**Figure.** Molecular structure of $[W_2S_4Cl_2(py)_4]\cdot 2py$ showing the atom-numbering scheme

## Results and Discussion

The air- and moisture-sensitive compound $WS_2Cl_2$ dissolves completely in dry pyridine (py) to give a red-brown solution. Slow evaporation of the pyridine using the double-ampoule technique[8] gave approximately cubic, red-brown, extremely air-sensitive crystals, one of which was examined by single-crystal techniques. The asymmetric unit contains $[(py)_2Cl(S)W(\mu\text{-}S)_2W(S)Cl(py)_2]$ (**1**), together with two molecules of pyridine solvent. The atomic numbering scheme is given in the Figure; selected bond lengths and angles are in Table 1. The tungsten atoms are six-co-ordinate, which is unusual in Group 6A compounds containing the $[(Y)M(\mu\text{-}Y)_2M(Y)]^{2+}$ (M = Mo or W, Y = O or S) fragment, each being bound to two pyridine molecules, a chlorine atom, a terminally bound sulphur atom, and two sulphur atoms which form bridges between the two metal centres. The compound thus contains the $[(S)W(\mu\text{-}S)_2W(S)]^{2+}$ fragment for which only two structural determinations have been published, namely for $[W_4S_{12}]^{2-}$ [9] and $[W_2S_4(edt)_2]^{2-}$ (**2**) [$H_2edt$ = ethane-1,2-dithiol].[10] In these latter two compounds the tungsten atoms are five-co-ordinate with the site *trans* to the W–S multiple bond being vacant.

The geometry of the $[(S)W(\mu\text{-}S)_2W(S)]^{2+}$ unit in (**1**) is somewhat different from that in (**2**), although the bond lengths are comparable. Some variations in geometry are of course to be expected because whilst (**1**) contains six-co-ordinate tungsten and is neutral, (**2**) contains five-co-ordinate tungsten and carries a double negative charge.

The mean value of the two terminal W–S bond lengths [2.15(2) Å] is in agreement with that observed in (**2**) [2.144(2) Å]. The difference between these two bonds in (**1**) [2.17(2), 2.13(2) Å] is not significant. The angles subtended within the W–S–W–S ring [76.5(5)° at S(1), 76.0(4) at S(2), 100.7(5)° at W(1), 101.4(6)° at W(2)] are similar to those observed in (**2**) whereas the average length of the W–S bridging bonds [2.30(2) Å] is somewhat smaller than that observed in (**2**) [2.328(2) Å], although the difference is not significant. The W–W distances [2.844(4) Å in (**1**), 2.862(1) Å in (**2**)] are also similar but the angles between the $WS_2$ planes differ considerably, that in (**1**) [155.2(1)°] being much greater than in (**2**) [148.9(1)°].

In (**1**) the two tungsten atoms are displaced from their respective equatorial $S_2ClN$ planes towards the terminal sulphur atom by distances of 0.32(1) and 0.34(1) Å. These two $S_2ClN$ planes [maximum deviation of a contributing atom is 0.04 Å from the plane around W(1) and 0.05 Å from the plane around W(2)] intersect at a surprisingly small angle of 0.7

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* *Supplementary data available* (No. SUP 56602, 5 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

**Table 1.** Dimensions in the tungsten co-ordination spheres: distances (Å) and angles (°)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| W(1)–W(2) | 2.844(4) | W(1)–S(4) | 2.171(22) | W(2)–S(1) | 2.293(17) | W(2)–Cl(2) | 2.453(18) |
| W(1)–S(1) | 2.300(20) | W(1)–N(3) | 2.39(5) | W(2)–S(2) | 2.302(15) | W(2)–N(4) | 2.52(5) |
| W(1)–S(2) | 2.318(15) | W(1)–N(1) | 2.32(5) | W(2)–S(3) | 2.134(23) | W(2)–N(2) | 2.399(41) |
| W(1)–Cl(1) | 2.467(17) | | | | | | |
| W(2)–W(1)–S(1) | 51.63(43) | S(1)–W(1)–N(3) | 86.5(15) | W(1)–W(2)–S(2) | 52.25(39) | S(2)–W(2)–N(4) | 82.3(12) |
| W(2)–W(1)–S(2) | 51.75(38) | S(2)–W(1)–N(3) | 82.8(13) | S(1)–W(2)–S(2) | 101.4(6) | S(3)–W(2)–N(4) | 168.5(13) |
| S(1)–W(1)–S(2) | 100.7(5) | Cl(1)–W(1)–N(3) | 78.9(13) | W(1)–W(2)–S(3) | 95.5(5) | Cl(2)–W(2)–N(4) | 77.4(13) |
| W(2)–W(1)–Cl(1) | 137.7(5) | S(4)–W(1)–N(3) | 166.8(15) | S(1)–W(2)–S(3) | 102.1(7) | W(1)–W(2)–N(2) | 133.2(11) |
| S(1)–W(1)–Cl(1) | 86.1(6) | W(2)–W(1)–N(1) | 134.2(12) | S(2)–W(2)–S(3) | 102.3(7) | S(1)–W(2)–N(2) | 164.1(13) |
| S(2)–W(1)–Cl(1) | 160.1(6) | S(1)–W(1)–N(1) | 164.7(16) | W(1)–W(2)–Cl(2) | 138.84(44) | S(2)–W(2)–N(2) | 80.9(12) |
| W(2)–W(1)–S(4) | 97.1(5) | S(2)–W(1)–N(1) | 82.5(13) | S(1)–W(2)–Cl(2) | 87.1(6) | S(3)–W(2)–N(2) | 92.6(12) |
| S(1)–W(1)–S(4) | 104.7(6) | Cl(1)–W(1)–N(1) | 86.3(14) | S(2)–W(2)–Cl(2) | 157.6(6) | Cl(2)–W(2)–N(2) | 85.5(12) |
| S(2)–W(1)–S(4) | 101.6(7) | S(4)–W(1)–N(1) | 89.1(15) | S(3)–W(2)–Cl(2) | 96.0(7) | N(4)–W(2)–N(2) | 77.6(16) |
| Cl(1)–W(1)–S(4) | 94.7(6) | N(3)–W(1)–N(1) | 79.1(18) | W(1)–W(2)–N(4) | 95.6(12) | W(1)–S(1)–W(2) | 76.5(5) |
| W(2)–W(1)–N(3) | 95.4(13) | W(1)–W(2)–S(1) | 51.9(5) | S(1)–W(2)–N(4) | 87.1(12) | W(1)–S(2)–W(2) | 76.00(44) |

compared to 27.7° in (**2**). There is a further difference in the structure of (**2**) in that the tungsten atoms are displaced by much larger distances (0.72, 0.72 Å) from these planes. A concomitant disparity in the S$_t$–W–X$_{eq}$ angles [t = terminal, eq. = equatorial; X = Cl, N, or S in (**1**), S in (**2**)] is observed with the values in (**1**) (range 89.1—104.7°) being smaller than those in (**2**) (range 101.5—111.8°). These differences are caused by the presence of the pyridine molecules *trans* to the terminal sulphur atoms in (**1**).

It is interesting to note that in (**2**) there are considerable differences in equivalent angles subtended at the metals which reduce molecular symmetry from $C_{2v}$ to $C_s$. These distortions have no obvious cause though they could arise from the effect of packing the two PPh$_4$ cations. In (**1**) there is no similar distortion.

The terminal sulphur atoms are bent away from the bridging (b) sulphur atoms [S$_t$–W–*S*$_b$ 101.6(7)—104.7(6)°] towards the chlorine atoms [S$_t$–W–Cl$_{eq}$ 94.7(6) and 96.0(7)°] and the nitrogen atoms [S$_t$–W–N$_{eq}$ 89.1(15) and 92.6(12)°]. It remains to be seen, when more structures of the W$_2$S$_4$ core have been studied, whether the distortion in (**1**) or (**2**) is the more typical.*

The axial metal–nitrogen bonds [W–N$_{ax}$] *trans* to W–S$_t$ terminal bonds [W(1)–N(3) 2.39(5), W(2)–N(4) 2.52(5) Å] are expected to be longer than the equatorial W–N$_{eq}$ bonds *cis* to W–S$_t$ bonds [W(1)–N(1) 2.32(5), W(2)–N(2) 2.40(4) Å]. Unfortunately the large standard deviations on the bond lengths mask any such effect in (**1**). The W–N$_{ax}$ bonds are bent away from the W–W vector by more than 90° [N(3)–W(1)–W(2) 95.4(13), N(4)–W(2)–W(1) 95.6(12)°] and as the W–S$_t$ bonds form similar angles with the W–W vector [S(4)–W(1)–W(2) 97.1(5), S(3)–W(2)–W(1) 95.5(5)°] the S$_t$–W–N$_{ax}$ angles are appreciably less than 180° [S(4)–W(1)–N(3) 166.8(15), S(3)–W(2)–N(4) 168.5(13)°]. The alignment of the pyridine rings in axial positions is such that steric interactions between the rings and the remaining atoms are minimised. Thus the two rings are approximately equidistant from their associated S$_2$NCl equatorial planes and the angle between the two planar rings is small at 13.5°. The equatorially bound pyridine rings are also disposed in such a manner as to minimise steric interactions, the rings being rotated out of the Cl–W–N$_{eq}$ plane by 26.7° [ring bound to W(1)], and 28.5° [ring bound to W(2)].

The two chlorine atoms, one bound to each tungsten atom, are *cis* to each other in the [W$_2$S$_4$Cl$_2$(py)$_4$] molecule, the bond lengths [W(1)–Cl(1) 2.467(17), W(2)–Cl(2) 2.453(18) Å] being similar to those observed in [Cl$_2$(O)W(μ-S)$_2$W(O)Cl$_2$]$^{2-}$ (2.42—2.48 Å).[6] There are no intermolecular contacts less than the sum of van der Waals radii between the molecules and the two pyridine solvent molecules.

In the preparation of (**1**) from WS$_2$Cl$_2$ and pyridine a reduction process has obviously taken place in which two atoms of chlorine have been lost for every molecule of (**1**) produced. We attempted to characterise the oxidation product by vacuum distilling the solvent from a WS$_2$Cl$_2$–pyridine mixture which had been allowed to react. This procedure yielded a red-brown oily material and a clear distillate. Treatment of this oil with CS$_2$ gave a red-brown solid. The chloride analysis suggests that the product could be a mixture of the tungsten(VI) compound [WS$_2$Cl$_2$(py)$_2$] and (**1**). However, the i.r. spectrum of the solid did not contain any bands between 520 and 550 cm$^{-1}$ which could be assigned to the vibrations of a *cis*-WS$_2$ group. Bands observed at 498 and 483 cm$^{-1}$ may be assigned to the two stretching modes of the W–S terminal bonds in the [(S)W(μ-S)$_2$W(S)]$^{2+}$ fragment. The i.r. spectrum did not contain any bands indicating the presence of the pyridinium ion. The $^1$H n.m.r. spectrum of the bulk sample in CD$_2$Cl$_2$ only contained resonances indicative of the presence of one type of co-ordinated pyridine molecule (*i.e.* a change in chemical shift of 0.15 to 0.53 p.p.m. from free pyridine). Thus the two sites occupied by pyridine in (**1**) must either be magnetically equivalent or there is rapid exchange between the two sites.

Having failed to determine the nature of the oxidation product from the solid species formed by the reaction of WS$_2$Cl$_2$ and pyridine we examined all the liquid products (*i.e.* the excess of pyridine and CS$_2$). In spite of extensive n.m.r. and g.l.c. studies in which searches were made for species such as chloropyridines and *N*-(4-pyridyl)pyridine [a compound said to be formed when niobium(V) halides are reduced with pyridine][12] we were unable to identify the oxidation product from the reaction of WS$_2$Cl$_2$ and pyridine. However, if a chloropyridine was produced it would only form approximately 0.7% of the total solvent volume and so it is unlikely that with the g.l.c. and n.m.r. equipment available to us we would have detected its presence. However, we can say from examination of i.r. and u.v. spectra that no *N*-(4-pyridyl)pyridine was formed.

From this study we believe that WS$_2$Cl$_2$ is a tungsten(VI) compound and that like WOSCl$_2$ it is reduced to tungsten(V) by loss of chlorine. This is in contrast to the situation with NbSCl$_3$ and NbSeBr$_3$ where reduction from niobium(V) to niobium(IV) takes place by the formation of Y$_2$$^{2-}$ from Y$^{2-}$ [Y = S or Se].[8,13]

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* We have recently determined two structures containing the [W$_2$S$_4$]$^{2+}$ core in which the metal atoms are five-co-ordinate: [W$_2$S$_4$(S$_2$CNEt$_2$)$_2$] and [W$_2$S$_4${S$_2$P(OEt)$_2$}$_2$].[11] The tungsten co-ordination spheres in these two compounds are symmetrical in a similar fashion to (**1**) and so the distortions in (**2**) are probably anomalous.

**Table 2.** Atomic co-ordinates ( × $10^4$) with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| W(1) | 9 906(3) | 1 580(1) | 3 918(2) | C(32) | 13 436(57) | 618(25) | 3 126(36) |
| W(2) | 7 887(3) | 972(1) | 2 698(2) | C(33) | 13 804(57) | 151(27) | 3 686(36) |
| S(1) | 8 790(20) | 784(9) | 4 250(11) | C(34) | 13 086(64) | 107(29) | 4 425(41) |
| S(2) | 9 432(16) | 1 553(8) | 2 285(11) | C(35) | 12 103(91) | 442(39) | 4 380(59) |
| Cl(1) | 1 140(18) | 1 505(9) | 5 560(11) | N(1) | 11 493(57) | 2 215(25) | 3 681(35) |
| S(3) | 6 414(21) | 1 577(10) | 2 808(13) | C(101) | 11 274(75) | 2 625(33) | 3 035(46) |
| Cl(2) | 6 570(18) | 106(8) | 2 723(11) | C(102) | 12 186(71) | 2 985(33) | 2 934(45) |
| S(4) | 8 764(19) | 2 311(9) | 4 190(12) | C(103) | 13 543(70) | 2 969(31) | 3 396(41) |
| C(1) | 11 877(64) | 1 103(30) | −102(41) | C(104) | 13 836(70) | 2 492(31) | 4 098(41) |
| C(2) | 13 150(59) | 1 058(28) | 232(37) | C(105) | 12 794(75) | 2 145(34) | 4 176(47) |
| C(3) | 13 683(79) | 1 381(34) | 908(48) | N(4) | 9 305(52) | 182(25) | 2 288(34) |
| N(5) | 12 917(67) | 1 890(29) | 1 073(41) | C(41) | 9 449(49) | −264(22) | 2 860(30) |
| C(5) | 11 562(83) | 1 962(38) | 679(51) | C(42) | 10 377(80) | −674(38) | 2 640(53) |
| C(6) | 11 133(93) | 1 540(43) | 174(56) | C(43) | 11 045(69) | −618(32) | 1 914(43) |
| N(6) | 5 767(60) | 3 407(31) | 2 067(40) | C(44) | 10 801(72) | −83(33) | 1 405(47) |
| C(8) | 6 853(121) | 3 032(52) | 2 068(87) | C(45) | 9 998(65) | 218(30) | 1 635(40) |
| C(9) | 7 081(129) | 3 097(56) | 1 179(84) | N(2) | 7 201(43) | 916(23) | 1 015(28) |
| C(10) | 6 582(75) | 3 455(36) | 482(49) | C(21) | 6 853(62) | 399(31) | 617(41) |
| C(11) | 5 546(88) | 3 699(38) | 481(58) | C(22) | 6 310(55) | 342(27) | −304(36) |
| C(12) | 5 043(90) | 3 647(37) | 1 282(58) | C(23) | 6 116(54) | 889(28) | −861(37) |
| N(3) | 11 566(54) | 923(27) | 3 742(35) | C(24) | 6 543(57) | 1 397(28) | −419(39) |
| C(31) | 12 289(63) | 1 004(34) | 3 050(42) | C(25) | 7 033(80) | 1 373(39) | 460(57) |

## Experimental

All preparations were carried out using an all-glass vacuum line. Solvents were rigorously dried and distilled on the vacuum line prior to use.

*Preparation of* $WS_2Cl_2$.—Tetrachlorosulphidotungsten(VI)[6] (*ca.* 0.03 mol) was quickly tipped under a stream of nitrogen into an ampoule (previously weighed) which contained a magnetic follower. The ampoule was rapidly evacuated and then filled with dry nitrogen and reweighed. A quantity of antimony(III) sulphide required to give a 3:1 molar ratio of $WSCl_4$ to $Sb_2S_3$ was taken and heated to 150 °C overnight while being pumped. The sulphide was allowed to cool and quickly poured under nitrogen onto the $WSCl_4$ in the ampoule. The ampoule was evacuated, cooled in liquid nitrogen, and dry $CS_2$ (50 $cm^3$) was distilled onto the mixture of solids. The ampoule was sealed, allowed to warm to room temperature, and the contents stirred for 7 d. The desired product formed as a solid. The ampoule was opened under dry nitrogen and the product isolated by vacuum-line filtration. The insoluble product was washed with fresh quantities of dry $CS_2$ (Found: Cl, 22.0; S, 19.7; W, 57.4. Calc. for $Cl_2S_2W$: Cl, 22.2; S, 20.1; W, 57.6%). In its i.r. spectrum (4 000—200 $cm^{-1}$) the compound has an absorption at 532 $cm^{-1}$ [ν(W=S) terminal stretch], a further strong band at 325 $cm^{-1}$, and weaker features at 357 and 280 $cm^{-1}$. The diffuse reflectance spectrum of the compound contained absorptions at 43 500, 36 000, 29 600, 18 600, and 6 800 $cm^{-1}$. An alternative route in which $B_2S_3$ was substituted for $Sb_2S_3$ was tried on a number of occasions. Although the reaction was faster with $B_2S_3$ the antimony route is preferred as $B_2S_3$ is air sensitive and difficult to obtain in a pure form. Analyses on all the products were in agreement with those required for $WS_2Cl_2$.

*Reaction of* $WS_2Cl_2$ *with Pyridine*.—Dichlorodisulphidotungsten(VI) (2 × $10^{-3}$ mol) was placed under dry nitrogen in a dry glass ampoule that contained a magnetic stirrer. The ampoule was evacuated and cooled with liquid nitrogen. Pyridine (25 $cm^3$), which had been dried over potassium mirrors, was distilled onto the solid. The ampoule was sealed and after the contents had been allowed to rise to room temperature they were stirred for 7 d at room temperature. A red-brown solution was formed. The ampoule was opened under nitrogen and the contents subjected to vacuum filtration. There was no solid product. The liquid products were removed by vacuum distillation and a brown sticky solid was deposited. Treatment of this with dry $CS_2$ gave a dark brown crystalline solid which was kept under a dynamic vacuum for 24 h [Found: C, 25.7; H, 2.2; Cl, 13.5; N, 5.9. $WS_2Cl_2(py)_2$ ($C_{10}H_{10}Cl_2N_2S_2W$) requires C, 25.2; H, 2.1; Cl, 14.9; N, 5.9%. $W_2S_4Cl_2(py)_4$ ($C_{20}H_{20}Cl_2N_4S_4W_2$) requires C, 27.2; H, 2.3; Cl, 8.0; N, 6.3%]. Recrystallisation of the solid from neat pyridine gave (**1**) in high yield.

The analyses of the brown solid were repeated a number of times on each sample that was prepared and the figures quoted are an average. Although for each sample we were able to obtain repeatable chlorine analyses we never succeeded in obtaining consistent tungsten analyses on any of the samples using the 'Oxine' method.

*Crystal Structure Determination*.—A sample of $WS_2Cl_2$ in a double ampoule was treated with an excess of pyridine by the procedure given above. The solvent was slowly removed and a crystalline mass obtained. A thorough inspection of the available crystals showed that nearly all were twinned. We did find one untwinned crystal (of approximate size 0.3 × 0.3 × 0.35 mm) but this was stuck to a smaller one (of approximate size 0.1 × 0.1 × 0.1 mm). In view of the extreme instability of the compound it was decided not to attempt to separate the crystals but to measure the intensities of the larger sample.

*Crystal data*. $C_{30}H_{30}Cl_2N_6S_4W_2$, $M$ = 1 041.47, monoclinic, space group $P2_1/c$, $a$ = 10.636(8), $b$ = 23.180(15), $c$ = 14.529(12) Å, $\beta$ = 102.5(1)°, $U$ = 3 497.0 $Å^3$, $Z$ = 4, $D_c$ = 1.98 g $cm^{-3}$, $F(000)$ = 1 992, $\mu$ = 73.7 $cm^{-1}$, Mo-$K_\alpha$ radiation, $\lambda$ = 0.7107 Å.

The crystal was set up to rotate about $c$ on a Stoe STADI2 diffractometer. 2 616 Independent reflections were measured with $2\theta_{max.}$ of 40° using an ω scan of width (1.5 + sinμ/tanθ) and rate 0.033 ° $s^{-1}$. The background count was 20 s. 1 245 Data with $I > 3\sigma(I)$ were used in subsequent calculations. An empirical absorption correction was applied. The structure was solved by the usual heavy-atom methods. Tungsten, sulphur, and chlorine atoms were refined anisotropically, nitrogen and carbon isotropically. There was no clear identification of the nitrogen atom of the solvent pyridine rings. All six atoms in each ring were refined as carbon and the atom with the lowest thermal parameter was fixed to be nitrogen. Hydrogen atoms were placed in trigonal positions and those in the same ring were given an equivalent thermal parameter (subsequently refined). After refinement to convergence a number of reflections with $F_o \gg F_c$ were removed from the data because it was thought that these abnormal intensities were caused by the smaller crystal. The refinement was repeated to give a final $R$ of 0.079 ($R'$ 0.080). In the final cycle of refinement, no shift was $>0.10\sigma$. Final atomic co-ordinates are given in Table 2. Calculations were carried out using SHELX 76[14] and our own programs on the Amdahl V7.

## Acknowledgements

We thank the S.E.R.C. for financial support (to N. T.) and provision of the diffractometer, and Mr. A. Johans for his help in the collection of the *X*-ray data.

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*Received* 13*th September* 1985; *Paper* 5/1583