# Crystal and Molecular Structure of Bis(pyridine-2-thiolato)bis(triphenylphosphine)ruthenium(II)

By **S. R. Fletcher** and **A. C. Skapski,*** Chemical Crystallography Laboratory, Imperial College, London SW7 2AY

The structure of the title compound has been determined from three-dimensional *X*-ray diffractometer data. The crystals are orthorhombic, with unit-cell dimensions: $a = 27{\cdot}97$, $b = 11{\cdot}473$, and $c = 12{\cdot}358$ Å; space-group $Pna2_1$ and $Z = 4$. The structure was refined by least-squares to $R$ 0·038 for 2633 independent reflections.

The complex is monomeric, and the ruthenium atom has a highly distorted octahedral co-ordination. The triphenylphosphine groups are *cis*, and the pyridine-2-thiolato-ligands are both bidentate, co-ordinating through their nitrogen and sulphur atoms such that the sulphur atoms are *trans*. The Ru–P distances are 2·319 and 2·332 Å, Ru–N are 2·115 and 2·132 Å, while Ru–S distances are rather longer than usual (2·434 and 2·437 Å). The N–Ru–S angles are *ca.* 67°.

THE complex bis(pyridine-2-thiolato)bis(triphenylphosphine)ruthenium(II) was recently prepared [1] from blue solutions of ruthenium(II). Highly insoluble salts of univalent silver, copper, and mercury with pyridine-2-thiol had been previously reported [2] but no structural information about complexes with this ligand has hitherto been available. We have carried out an *X*-ray study of the title complex in order to find out whether pyridine-2-thiolate acts as a uni- or bi-dentate or a bridging ligand. We find that despite the unfavourable spatial arrangement of nitrogen and sulphur atoms the ligand is bidentate, and the geometry found suggests that the nitrogen atom is bound more strongly to the metal than is the sulphur.

## EXPERIMENTAL

The compound crystallises from chloroform as orange plates, many of which contained re-entrant angles indicative of twinning.

*Crystal Data:* $C_{46}H_{38}N_2P_2RuS_2$, $M = 846{\cdot}0$, Orthorhombic, $a = 27{\cdot}97$, $b = 11{\cdot}473$, $c = 12{\cdot}358$ Å, $U = 3966$ Å$^3$, $D_m$ (by flotation) $= 1{\cdot}45$, $Z = 4$, $D_c = 1{\cdot}45$, $F(000) = 1736$. Oscillation and Weissenberg photographs showed systematic absences: $h0l$, $h = 2n + 1$; and $0kl$, $k + l = 2n + 1$. These are consistent with space-groups $Pna2_1$ (No. 33) or $Pnam$ (No. 62); shown to be the former from the subsequent satisfactory solution and refinement of the structure. Cu-$K_\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu$(Cu-$K_\alpha$) $= 53{\cdot}6$ cm$^{-1}$. The unit-cell dimensions were determined by measuring some high-angle $\alpha_1$ and $\alpha_2$ reflections on a diffractometer.

Intensity data were collected for a crystal *ca.* $0{\cdot}25 \times 0{\cdot}25 \times 0{\cdot}03$ mm. (*a* perpendicular to plate) mounted on a Siemens off-line automatic four-circle diffractometer. Cu-$K_\alpha$ radiation at a take-off angle of 4·5°, a nickel $\beta$ filter and a Na(Tl)I scintillation counter were used. The $\theta$—$2\theta$ scan technique was employed, with a 'five-point' measuring procedure [3] to give 2633 independent reflections measured to $\theta$ 50°, of which 106 were judged to be unobserved.[3] The net count of the 940 reflection, measured as a reference every 25 reflections, did not vary significantly during the data collection (*ca.* 10 days). The data were scaled using the reference reflection and the Lorentz and polarisation corrections were applied.

*Solution and Refinement of the Structure.*—The structure was solved and refined by standard methods using the Crystal Structure Calculations System '*X*-Ray '63' described by J. M. Stewart in the University of Maryland Technical Report TR 64 6. Calculations were carried out on the Imperial College IBM 7094 and University of London CDC 6600 computers.

A three-dimensional Patterson synthesis revealed the position of the ruthenium atom, and also tentatively the positions of one sulphur and one phosphorus atom. Least-squares refinement on these three atoms gave $R$ 0·325. A difference Fourier synthesis showed the positions of the other sulphur and phosphorus atoms ($R$ 0·172), and the inclusion in least squares of the two nitrogen atoms which complete the octahedral co-ordination about ruthenium gave $R$ 0·158 with all atoms having thermal parameters of the expected magnitude. The 46 carbon atoms in the molecule were now located and this allowed the sulphur and phosphorus atoms to be unambiguously distinguished by their environment. The original assignment in fact proved to be correct. Block-diagonal refinement of all the non-hydrogen atoms with isotropic temperature factors gave $R$ 0·075.

At this stage the data were corrected for absorption effects according to the method of ref. 4 using a $10 \times 10 \times 6$ grid, with crystal path-lengths determined by the vector

---

[1] J. D. Gilbert, D. Rose, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 2765.

[2] 'The Chemistry of Heterocyclic Compounds,' Part IV, ed. A. Weissberger, Interscience, New York, 1964, p. 353.

[3] A. C. Skapski and P. G. H. Troughton, *Acta Cryst.*, 1970, **B26**, 716.

[4] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

analysis procedure of ref. 5. Refinement as before reduced $R$ to 0·063. All atoms were now allowed to refine anisotropically and an anomalous dispersion correction for ruthenium was applied to give $R$ 0·039. When the hydrogen atoms were included as a ' fixed contribution ' with isotropic temperature factors of their parent atoms, $R$ fell to 0·038. In the final stages of refinement Hughes' weighting scheme [6] was used, where $w = 1$ for $F < F^*$, and $\sqrt{w} = F^*/F$ for $F \geqslant F^*$, with $F^* = 70$. Refinement was terminated with $R$ unchanged at 0·038 and standard deviations slightly lower. The scattering form factors were taken from ref. 7, and the correction for the real and imaginary parts of the anomalous dispersion for ruthenium from ref. 8. A final difference Fourier synthesis was

TABLE 1

Fractional co-ordinates with estimated standard deviations in parentheses

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| (a) ($\times 10^5$) | | | |
| Ru | 09089(2) | 20578(5) | 0 |
| P(1) | 16112(7) | 10644(17) | −03782(17) |
| P(2) | 10213(7) | 21960(18) | 18655(18) |
| S(1) | 03018(7) | 05918(19) | 03706(20) |
| S(2) | 12241(8) | 38089(19) | 08587(19) |
| (b) ($\times 10^4$) | | | |
| N(1) | 0210(2) | 2753(6) | 0121(7) |
| C(11) | −0056(3) | 1821(8) | 0287(7) |
| C(12) | −0568(3) | 1892(10) | 0359(9) |
| C(13) | −0760(3) | 3003(10) | 0177(12) |
| C(14) | −0487(3) | 3961(8) | −0049(11) |
| C(15) | 0004(3) | 3833(8) | −0067(10) |
| N(2) | 0739(2) | 2143(6) | −1672(6) |
| C(21) | 0938(3) | 3181(7) | −1972(7) |
| C(22) | 0894(3) | 3596(9) | −3040(8) |
| C(23) | 0616(4) | 2943(9) | −3751(8) |
| C(24) | 0403(3) | 1908(9) | −3440(8) |
| C(25) | 0478(3) | 1522(8) | −2358(7) |
| C(31) | 1794(3) | 1283(7) | −1810(6) |
| C(32) | 2127(3) | 2111(8) | −2114(8) |
| C(33) | 2225(3) | 2275(9) | −3237(9) |
| C(34) | 1987(4) | 1648(9) | −4010(8) |
| C(35) | 1653(3) | 0815(9) | −3712(8) |
| C(36) | 1554(3) | 0628(7) | −2605(7) |
| C(41) | 2157(3) | 1463(8) | 0362(6) |
| C(42) | 2267(3) | 2664(9) | 0467(8) |
| C(43) | 2677(4) | 3007(11) | 1037(10) |
| C(44) | 2973(3) | 2170(11) | 1508(8) |
| C(45) | 2869(4) | 0991(11) | 1419(9) |
| C(46) | 2447(3) | 0631(9) | 0854(8) |
| C(51) | 1640(3) | −0538(7) | −0337(6) |
| C(52) | 1311(3) | −1154(7) | 0262(7) |
| C(53) | 1331(4) | −2380(8) | 0341(8) |
| C(54) | 1697(4) | −2958(8) | −0184(9) |
| C(55) | 2027(4) | −2365(9) | −0802(8) |
| C(56) | 2005(3) | −1137(8) | −0874(7) |
| C(61) | 1261(3) | 0907(7) | 2544(7) |
| C(62) | 0994(3) | −0120(8) | 2630(8) |
| C(63) | 1199(4) | −1135(9) | 3103(9) |
| C(64) | 1670(4) | −1110(10) | 3463(9) |
| C(65) | 1941(4) | −0110(10) | 3351(9) |
| C(66) | 1747(3) | 0898(9) | 2906(8) |
| C(71) | 1371(3) | 3390(7) | 2488(7) |
| C(72) | 1526(3) | 4335(8) | 1889(8) |
| C(73) | 1742(4) | 5291(9) | 2430(9) |
| C(74) | 1800(3) | 5283(9) | 3533(9) |
| C(75) | 1647(3) | 4334(8) | 4135(8) |
| C(76) | 1431(3) | 3382(9) | 3631(8) |
| C(81) | 0453(3) | 2539(8) | 2569(7) |
| C(82) | 0299(3) | 3686(9) | 2424(8) |
| C(83) | −0142(4) | 4044(10) | 2889(9) |
| C(84) | −0413(4) | 3282(11) | 3487(10) |
| C(85) | −0251(4) | 2142(11) | 3670(11) |
| C(86) | 0194(3) | 1786(9) | 3211(9) |

Carbon atoms are numbered C(*mn*) where *m* is the ring number and *n* the atom number in the ring. For $m = 1$ and 2 the carbon atoms are members of the pyridine rings containing N(1) and N(2) respectively. For $m = 3$—8, the carbon atoms are members of phenyl rings with C(*m*1) bonded to a phosphorus atom and other atoms are numbered in sequence such that C(*m*4) is *para* to C(*m*1).

TABLE 2

Anisotropic thermal parameters *

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| (a) ($\times 10^5$) | | | | | | |
| Ru | 66(1) | 461(4) | 412(3) | −9(2) | 1(2) | 0(5) |
| P(1) | 63(2) | 512(16) | 366(14) | 4(5) | 17(5) | 22(12) |
| P(2) | 68(3) | 540(17) | 371(14) | −3(5) | 9(5) | 9(14) |
| S(1) | 90(3) | 610(17) | 689(19) | −66(6) | 13(6) | 33(15) |
| S(2) | 101(3) | 557(17) | 530(16) | −40(6) | −21(6) | 27(15) |
| (b) ($\times 10^4$) | | | | | | |
| C(11) | 7(1) | 99(8) | 53(8) | −4(2) | 2(2) | −6(6) |
| C(12) | 10(1) | 146(12) | 94(11) | −2(3) | −2(3) | −20(9) |
| C(13) | 10(1) | 146(11) | 106(12) | 14(3) | −3(4) | −11(10) |
| C(14) | 11(1) | 111(9) | 87(8) | 11(3) | −1(3) | −9(10) |
| C(15) | 15(1) | 85(8) | 73(7) | 13(3) | −7(3) | −5(9) |
| N(1) | 7(1) | 81(6) | 48(5) | 1(2) | −1(2) | −1(6) |
| N(2) | 7(1) | 58(6) | 48(5) | 4(2) | −1(2) | −1(5) |
| C(21) | 11(1) | 60(7) | 52(6) | 0(2) | 1(2) | 3(6) |
| C(22) | 16(2) | 85(9) | 62(7) | 4(3) | −1(3) | 4(7) |
| C(23) | 15(1) | 109(10) | 50(7) | −1(3) | −7(3) | 6(7) |
| C(24) | 13(1) | 101(10) | 66(8) | −1(3) | −7(3) | −3(7) |
| C(25) | 10(1) | 82(8) | 69(8) | −1(3) | −2(3) | −13(7) |
| C(31) | 8(1) | 76(8) | 37(6) | 6(2) | 2(2) | 7(6) |
| C(32) | 11(1) | 92(9) | 63(7) | 3(3) | 5(3) | 16(7) |
| C(33) | 14(1) | 100(10) | 69(8) | 6(3) | 12(3) | 25(8) |
| C(34) | 17(2) | 122(10) | 45(6) | 11(3) | −3(3) | 13(8) |
| C(35) | 14(1) | 116(10) | 53(7) | 9(3) | −3(3) | −4(7) |
| C(36) | 13(1) | 65(7) | 51(6) | 4(3) | 2(2) | −8(6) |
| C(41) | 6(1) | 92(8) | 44(6) | −2(2) | 5(2) | −1(6) |
| C(42) | 10(1) | 105(9) | 74(7) | −13(3) | 3(3) | −12(7) |
| C(43) | 16(2) | 164(14) | 74(9) | −17(4) | 0(3) | −24(10) |
| C(44) | 11(1) | 185(14) | 56(7) | −9(4) | 7(3) | −38(9) |
| C(45) | 12(1) | 175(14) | 60(7) | 4(4) | −6(3) | −33(9) |
| C(46) | 11(1) | 134(11) | 45(6) | 9(3) | −3(2) | −22(7) |
| C(51) | 9(1) | 65(7) | 43(6) | 0(2) | −6(2) | −5(5) |
| C(52) | 12(1) | 74(7) | 58(8) | −2(2) | 1(2) | 10(6) |
| C(53) | 18(2) | 70(8) | 76(9) | −1(3) | −3(3) | 11(6) |
| C(54) | 21(2) | 67(7) | 72(10) | 2(3) | −15(3) | −1(7) |
| C(55) | 18(2) | 81(8) | 52(7) | 17(3) | −5(3) | −6(7) |
| C(56) | 13(1) | 73(8) | 48(6) | 8(3) | −4(2) | −6(6) |
| C(61) | 14(1) | 69(8) | 37(6) | 3(3) | 2(2) | −5(6) |
| C(62) | 17(2) | 69(8) | 52(7) | 0(3) | −2(3) | −5(6) |
| C(63) | 25(2) | 84(9) | 66(8) | 1(4) | −4(4) | −1(8) |
| C(64) | 20(2) | 118(11) | 74(9) | 15(4) | 3(3) | −13(8) |
| C(65) | 19(2) | 111(11) | 73(9) | 14(4) | 2(3) | −3(8) |
| C(66) | 12(1) | 98(9) | 66(7) | 8(3) | −2(3) | −4(7) |
| C(71) | 8(1) | 70(7) | 52(6) | 1(2) | 2(2) | −9(6) |
| C(72) | 15(1) | 73(8) | 69(8) | −9(3) | −4(3) | 9(7) |
| C(73) | 17(2) | 91(9) | 79(8) | −10(3) | −6(3) | 5(8) |
| C(74) | 12(1) | 88(9) | 89(9) | 0(3) | −11(3) | −13(8) |
| C(75) | 11(1) | 87(8) | 64(7) | −2(3) | −3(3) | −15(7) |
| C(76) | 12(1) | 110(10) | 46(6) | 2(3) | −2(3) | −12(7) |
| C(81) | 7(1) | 73(7) | 57(7) | 0(2) | 3(2) | 1(6) |
| C(82) | 13(1) | 89(9) | 58(7) | 10(3) | 3(3) | −1(7) |
| C(83) | 18(2) | 110(10) | 73(8) | 11(4) | 4(3) | −7(8) |
| C(84) | 14(2) | 147(13) | 95(10) | 9(4) | 13(3) | 3(9) |
| C(85) | 15(2) | 137(13) | 105(10) | 14(4) | 15(4) | 15(10) |
| C(86) | 11(1) | 95(9) | 84(9) | 5(3) | 9(3) | 3(8) |

* In the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

---

[5] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[6] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

[7] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[8] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

featureless except for a few peaks of *ca.* 0·5—0·7 eÅ$^{-3}$ in the immediate vicinity of the ruthenium atom.

Tables 1 and 2 list the final co-ordinates of the non-hydrogen atoms and the coefficients for the anisotropic temperature factors. The standard deviations have been estimated from block-diagonal matrix refinement and are, therefore, a slight underestimate of the true deviations. The co-ordinates of the hydrogen atoms are given in Table 3. The observed and calculated structure factors are listed in Supplementary Publication No. SUP 20291 (7 pp., 1 microfiche).*

TABLE 3

Fractional co-ordinates ($\times 10^3$) of the hydrogen atoms, numbered according to the carbon atoms to which they are bonded

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| H(12) | −078 | 117 | 052 |
| H(13) | −114 | 309 | 020 |
| H(14) | −065 | 477 | −024 |
| H(15) | 023 | 457 | −024 |
| H(22) | 107 | 438 | −333 |
| H(23) | 057 | 323 | −461 |
| H(24) | 020 | 140 | −404 |
| H(25) | 031 | 072 | −213 |
| H(32) | 227 | 248 | −286 |
| H(33) | 232 | 255 | −252 |
| H(34) | 208 | 178 | −487 |
| H(35) | 150 | 047 | −305 |
| H(36) | 145 | 036 | −341 |
| H(42) | 204 | 330 | 006 |
| H(43) | 277 | 390 | 111 |
| H(44) | 329 | 241 | 189 |
| H(45) | 309 | 034 | 178 |
| H(46) | 238 | −028 | 073 |
| H(52) | 104 | −071 | 064 |
| H(53) | 107 | −285 | 075 |
| H(54) | 170 | −387 | −016 |
| H(55) | 231 | −282 | −120 |
| H(56) | 224 | −068 | −140 |
| H(62) | 068 | 039 | 252 |
| H(63) | 099 | −192 | 312 |
| H(64) | 181 | −183 | 381 |
| H(65) | 230 | −013 | 360 |
| H(66) | 144 | 144 | 286 |
| H(72) | 146 | 436 | 102 |
| H(73) | 190 | 613 | 235 |
| H(74) | 195 | 608 | 326 |
| H(75) | 165 | 410 | 494 |
| H(76) | 129 | 256 | 389 |
| H(82) | 051 | 430 | 197 |
| H(83) | −026 | 491 | 276 |
| H(84) | −075 | 355 | 376 |
| H(85) | −045 | 158 | 415 |
| H(86) | 031 | 092 | 332 |

DISCUSSION

*Description of The Structure.*—The molecular structure is shown in Figure 1. The complex is monomeric and the bulky triphenylphosphine groups are *cis*. The pyridine-2-thiolato-ligands are both bidentate, co-ordinating through their nitrogen and sulphur atoms such that the sulphur atoms are *trans*. Thus the co-ordination about the central ruthenium atom is highly distorted octahedral. The more important bond lengths and bond angles are shown in Tables 4 and 5 respectively. In each of three bond types in the co-ordination sphere (Figure 2) pairs of like bond lengths are not significantly different, and mean values will, therefore, be used throughout the discussion.

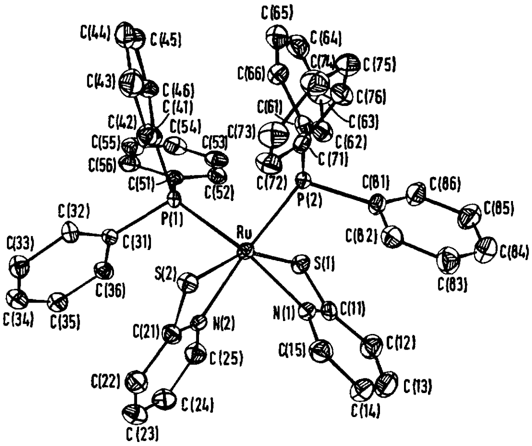

FIGURE 1 The molecular structure showing thermal vibration ellipsoids scaled to enclose 30% probability

TABLE 4

Selected bond lengths (Å) with standard deviations in parentheses

| | | | |
|---|---|---|---|
| Ru–S(1) | 2·434(2) | Ru–S(2) | 2·437(2) |
| Ru–N(1) | 2·115(6) | Ru–N(2) | 2·132(7) |
| Ru–P(1) | 2·319(2) | Ru–P(2) | 2·332(2) |
| P(1)–C(31) | 1·859(8) | P(2)–C(61) | 1·827(9) |
| P(1)–C(41) | 1·838(8) | P(2)–C(71) | 1·851(9) |
| P(1)–C(51) | 1·841(8) | P(2)–C(81) | 1·854(8) |
| | Mean P–C 1·845 | | |
| | Phenyl ring, mean C–C 1·399 | | |
| S(1)–C(11) | 1·732(9) | S(2)–C(21) | 1·747(9) |
| | Pyridine ring, mean C–C 1·400 | | |
| | Pyridine ring, mean C–N 1·347 | | |

TABLE 5

Selected bond angles (°) with standard deviations in parentheses

| | | | |
|---|---|---|---|
| N(1)–Ru–S(2) | 93·1(2) | N(2)–Ru–S(1) | 93·3(2) |
| N(1)–Ru–S(1) | 66·6(2) | N(2)–Ru–S(2) | 67·7(2) |
| N(1)–Ru–P(2) | 91·8(2) | N(2)–Ru–P(1) | 91·0(2) |
| N(1)–Ru–N(2) | 80·9(3) | P(1)–Ru–P(2) | 96·8(1) |
| S(1)–Ru–P(1) | 106·8(1) | S(2)–Ru–P(2) | 109·0(1) |
| S(1)–Ru–P(2) | 87·4(1) | S(2)–Ru–P(1) | 90·6(1) |
| P(1)–Ru–N(1) | 169·0(2) | P(2)–Ru–N(1) | 171·6(2) |
| | S(1)–Ru–S(2) | 154·7(1) | |
| Ru–S(1)–C(11) | 80·1(3) | Ru–S(2)–C(21) | 80·6(3) |
| S(1)–C(11)–N(1) | 110·1(6) | S(2)–C(21)–N(2) | 109·8(6) |
| Ru–N(1)–C(11) | 103·1(6) | Ru–N(2)–C(21) | 101·8(5) |
| Ru–P(1)–C(31) | 111·0(3) | Ru–P(2)–C(61) | 116·6(3) |
| Ru–P(1)–C(41) | 118·8(3) | Ru–P(2)–C(71) | 122·2(3) |
| Ru–P(1)–C(51) | 121·5(3) | Ru–P(2)–C(81) | 111·2(3) |

The Ru–P distances of 2·326 Å fall roughly in the middle of the range found in other structures, *viz.* 2·2—2·4 Å. They are most closely similar to those found in $Ru_2Cl_5(PBu_3)_4$ [9] (2·329) and in $Ru_3Cl_6(PPhEt_2)$ [10] (2·318 Å) where the phosphorus atoms are *trans* to bridging chlorine atoms. The Ru–N distances

---

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[9] G. Chioccola, J. J. Daly, and J. K. Nicholson, *Angew. Chem. Internat. Edn.*, 1968, **7**, 131.

[10] K. A. Raspin, *J. Chem. Soc.* (*A*), 1969, 461.

(2·124 Å) are slightly longer than the sum of Pauling's covalent radii,[11] but are in good agreement with those reported previously *e.g.* $[Ru(NH_3)_5Cl]Cl_2$ [12] and $[Ru(NH_3)_5N_2]Cl_2$ [13] mean 2·10, and $[Ru(NH_3)_4(SO_2)Br]Br$ [14] 2·127 Å. The normality of the Ru–N distances in the present complex may be contrasted with the situation found in $RuH(AcO)(PPh_3)_3$,[15] another complex with a highly distorted octahedral co-ordination, where the Ru–O(AcO) distances *trans* to $PPh_3$ and H are con-considerably greater (2·208 and 2·256 Å respectively).

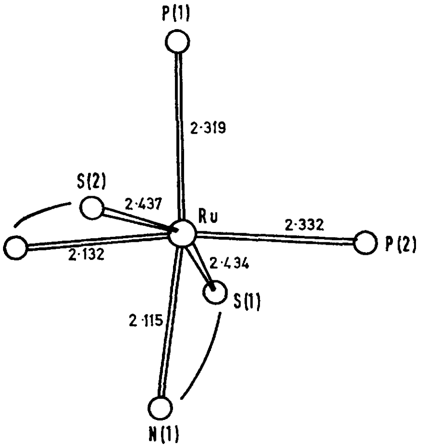

FIGURE 2 Co-ordination about the ruthenium atom.

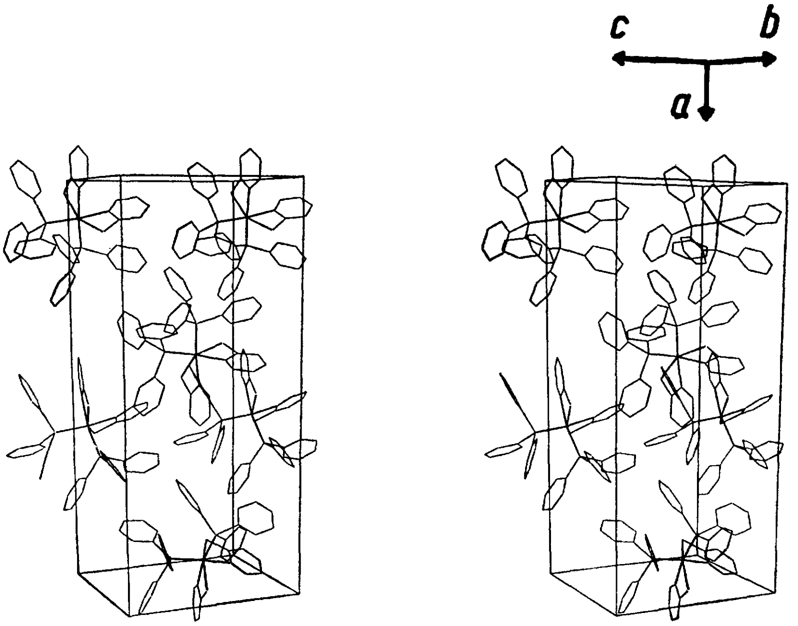

FIGURE 3 A stereoscopic view of the packing

There are few reported Ru–S distances with which to compare those found in the present structure, 2·436 Å. In $[Ru(NH_3)_4(SO_2)Br]Br$,[14] the Ru–S bond length is 2·07 Å, but clearly multiple bonding to the $SO_2$ ligand is involved. In $RuS_2$ [16] the distance is 2·35 Å, appreciably shorter than our value.

It can be seen that the drive to achieve octahedral co-ordination for ruthenium(II) tolerates considerable strain in pyridine-2-thiolate. Thus the Ru–N–C and N–C–S angles are distorted from the 120° expected for $sp^2$ hybridised atoms to 102 and 110° respectively. The Ru–S–C angles are 80°, as compared with 90° expected if the sulphur bonded using pure *p* orbitals, and 100—110° more usually found.

The angles about ruthenium which show the greatest departure from ideal octahedral co-ordination geometry are the two N–Ru–S angles of *ca.* 67°. It is interesting to consider which of the co-ordinating atoms is most out of its ideal position. The two N–Ru–P angles are *ca.* 170° while the S–Ru–S angle is *ca.* 155°. The sulphur atoms are the most displaced, and this taken together with the acute bond angles at the sulphur suggests that 'bent bonds'[17] with their consequent inferior orbital overlaps may be involved here. This is consistent with the rather long Ru–S distances, and suggests that the nitrogen is the more strongly bonded of the co-ordinating atoms in the pyridine-2-thiolato-ligand.

Figure 3 is a stereoscopic view [18] of the three-dimensional packing of the molecules, and Table 6 shows the

---

[11] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 246.

[12] C. K. Prout and H. M. Powell, *J. Chem. Soc.*, 1962, 137.

[13] F. Bottomley and S. C. Nyburg, *Acta Cryst.*, 1968, **B24**, 1289.

[14] L. H. Vogt, J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, 1965, **4**, 1157.

[15] A. C. Skapski and F. A. Stephens, *Chem. Comm.*, 1969, 1008.

[16] V. J. Sutarno, O. Knop, and K. J. J. Reid, *Canad. J. Chem.*, 1967, **45**, 1391.

[17] E. R. Corey and L. F. Dahl, *Inorg. Chem.*, 1962, **1**, 521.

[18] C. K. Johnson, ORTEP thermal ellipsoid plotting program, Oak Ridge National Laboratory, 1965, ORNL 3794.

shortest intra- and inter-molecular non-bonded interactions. The intramolecular overcrowding is the greater, and may be largely responsible for the non-coincidence of the ruthenium, phosphorus, and sulphur atoms with the planes of the aromatic ring systems to which they are bonded. Table 7 shows that while the rings are satisfactorily planar the associated heavy atoms lie significantly out of most of these planes. The greatest deviation occurs for P(2) which is 0·203 Å out of the plane of ring C(7*n*); this corresponds to a P–C(*m*1)–C(*m*4) angle of *ca.* 174°.

TABLE 6

Selected non-bonded distances (Å)

| | | | |
|---|---|---|---|
| (i) Intramolecular | | | |
| N(1) · · · C(81) | 3·12 | N(2) · · · C(31) | 3·12 |
| N(1) · · · C(82) | 3·06 | N(2) · · · C(36) | 3·09 |
| C(11) · · · C(81) | 3·27 | C(21) · · · C(31) | 3·24 |
| C(42) · · · C(72) | 3·33 | | |
| (ii) Intermolecular | | | |
| H(34) · · · H($55^{I}$) | 2·41 | C(44) · · · C($55^{I}$) | 3·37 |
| H(14) · · · H($23^{II}$) | 2·44 | C(12) · · · C($63^{III}$) | 3·41 |

Superscripts refer to atoms in the following positions:

I $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$

II $-x, 1 - y, \frac{1}{2} + z$

III $x - 1, y, z - 1$

TABLE 7

Deviations (Å) of atoms from the least-squares planes of the aromatic rings

| Plane | Deviation * | | Bonded atoms | Distance from plane |
|---|---|---|---|---|
| | Mean | Max. | | |
| Py, N(1), C(1*n*) | 0·013 | 0·024 | Ru | 0·186(16) |
| | | | S(1) | 0·141(16) |
| Py, N(2), C(2*n*) | 0·011 | 0·021 | Ru | 0·135(13) |
| | | | S(2) | 0·113(13) |
| Ph, C(3*n*) | 0·004 | 0·010 | P(1) | 0·125(6) |
| Ph, C(4*n*) | 0·007 | 0·015 | P(1) | 0·017(10) |
| Ph, C(5*n*) | 0·005 | 0·011 | P(1) | 0·073(7) |
| Ph, C(6*n*) | 0·007 | 0·012 | P(2) | 0·103(10) |
| Ph, C(7*n*) | 0·001 | 0·002 | P(2) | 0·203(2) |
| Ph, C(8*n*) | 0·013 | 0·025 | P(2) | 0·079(16) |

* Deviation of atoms defining plane.

The differences between the pyridine-2-thiolato-ligand here and free pyridine-2-thiol as reported by Penfold [19] are compared in Figure 4. Penfold found that the C–S bond length was 1·68 Å, which he considered was due to a degree of double-bond character resulting from the contribution of a third tautomeric form of the molecule, that of α-thiopyridone. This also explained the large variations in the C–C bond lengths which he found within the ring. By calculating the degree of resonance contribution of this tautomer which led to the best agreement between observed and calculated bond lengths, Penfold was able to deduce that the C–S bond had a double-bond character of *ca.* 65%. In the ligand in the present molecule, however, the C–S bond is longer and the C–C bond lengths are very similar. In addition, the C–S bond is not strictly in the plane defined by the ring. These facts indicate that in the pyridine-2-thiolato-ligand the α-thiopyridone tautomer makes little contribution to the resonance form.

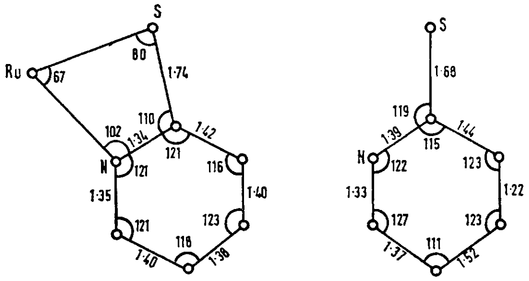

FIGURE 4 A comparison of (mean) bond lengths and angles in the pyridine-2-thiolato-ligand with those in pyridine-2-thiol (ref. 19)

We thank Dr. D. Rose and Professor G. Wilkinson for providing the crystals and for discussions, Professor D. Rogers for the use of a diffractometer, Mr. D. J. Williams for assistance in collecting the diffractometer data, and the S.R.C. for a Research Studentship (to S. R. F.).

[1/1578 *Received*, 1*st September*, 1971]

---

[19] B. R. Penfold, *Acta Cryst.*, 1953, **6**, 707.