Metal Complexes of Sulphur Ligands. Part VIII.[1] Crystal and Molecular Structure of *cis*-Bis(diethylphosphinodithioato)bis(dimethylphenylphosphine)ruthenium(II)

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The structure of $[Ru(S_2PEt_2)_2(PMe_2Ph)_2]$ has been determined by *X*-ray diffraction analysis. Reflections were collected from Weissenberg photographs along two axes, using a SAAB automatic film scanner. Crystals are orthorhombic, space group *Pbca*, with $Z = 8$ in a unit cell of dimensions: $a = 17{\cdot}88(4)$, $b = 20{\cdot}92(5)$, $c = 17{\cdot}31(3)$ Å. The structure was solved by standard methods, and refined to R 8·2% for 1387 observed reflections. The Ru–S bonds *trans* to phosphorus are significantly longer than the others.

THE structure of the title compound has been postulated on the basis of its spectroscopic and chemical properties, and shown to be structurally typical of a related series of compounds.[2] Furthermore, the observed temperature-dependent ^{1}H n.m.r. spectra which are exhibited by compounds of this type have been ascribed to facile interconversion of the two optical enantiomers possible for this *cis*-configuration. Consideration of various bond-rupture and -twist mechanisms for the inversion process strongly suggests that the mechanism involves a solvent-assisted cleavage of a ruthenium–sulphur bond *trans* to the tertiary phosphine.[1–3]

EXPERIMENTAL

Crystals of $[Ru(S_2PEt_2)_2(PMe_2Ph)_2]$ are air stable, dark red needles, which extinguish well about the needle axis under polarised light.

Crystal Data.—$C_{24}H_{42}P_4RuS_4$, $M = 683{\cdot}8$, Orthorhombic, $a = 17{\cdot}88(4)$, $b = 20{\cdot}92(5)$, $c = 17{\cdot}31(3)$ Å, $U = 6473{\cdot}5$ Å^3, $D_m = 1{\cdot}4$ g cm^{-3}, $Z = 8$, $D_c = 1{\cdot}4$ g cm^{-3}, $F(000) = 2832$. Space group *Pbca* (D_{2h}^{15}, No. 61). Cu-K_α radiation, Ni filter, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 82·82 cm^{-1}.

The crystals are naturally elongated along the *c* axis, so initially the *hk*0—6 layers were collected on Weissenberg films from a crystal with dimensions 0·162 × 0·267 × 0·794 mm. A second crystal, cut down from a larger crystal by use of solvent, had dimensions 0·210 × 0·227 × 0·307 and was used for collection of the layers *h*0—3*l*. Packs of five sheets of Ilford G *X*-ray film were used for each layer. Intensity values were obtained for each reflection using a SAAB automatic film scanner connected to a PDP 15 computer at the Edinburgh Regional Computer Centre. Processing of the raw data was carried out on the IBM 370.[4] Individual films of a pack were scaled together and equivalent reflections averaged and corrected for Lorentz-polarisation factors to give an intensity value for each reflection and an estimate of its error. Reflections occurring on two layers were used to put the whole data set on a common scale using a linear least-squares procedure. 3320 Reflections were obtained, of which 1387 (which could be seen by eye on the top film of a pack) were classed as observed. No absorption correction was applied.

Solution and Refinement of the Structure.—This was carried out on an IBM 370 by use of '*X*-Ray '72'.[5] Scattering factors and anomalous dispersion corrections were taken from ref. 6. The ruthenium atom was located from a three-dimensional Patterson function map and the rest of the non-hydrogen atoms by alternate least-squares refinements and difference-Fourier maps. The final R on F was 8·2% for the 1387 observed reflections. The final R on F^2 was 15·5% compared with a value of *ca*. 13% predicted from the agreement between equivalent reflections. A layer-by-layer analysis of the agreement confirms that the scaling of the layers was essentially correct.‡ Table 1 shows the final atomic parameters, together with their standard deviations calculated from the inverse matrix. Only the ruthenium, sulphur, and phosphorus atoms were given anisotropic temperature factors. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21062 (12 pp., 1 microfiche).§

DISCUSSION

Table 2 shows interatomic distances within the molecule and the shortest non-bonding contacts between molecules. The crystal structure consists of the packing of discrete monomeric molecules, the crystallographic *c* axis being almost perpendicular to the plane containing the ruthenium and phosphine phosphorus atoms, and the *a* axis almost parallel to the vector between these two phosphorus atoms. Figure 1 shows the molecular structure viewed down the latter.

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‡ Deposited with structure factors.

§ See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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TABLE 1

Positional (× 10^4) and thermal (× 10^3) parameters

Atom	x/a	y/b	z/c	$U/Å^2$
Ru	1264(1)	1696(1)	1447(1)	*
S(1)	1132(4)	1789(5)	58(4)	*
S(2)	1361(5)	1883(4)	2831(4)	*
S(3)	2155(4)	2662(3)	1514(5)	*
S(4)	184(4)	2515(4)	1308(4)	*
P(1)	514(4)	2569(5)	207(5)	*
P(2)	1823(6)	2719(4)	2605(5)	*
P(3)	415(4)	911(3)	1598(5)	*
P(4)	2243(3)	1016(3)	1357(5)	*
C(11)	−279(22)	2612(19)	−564(26)	102(13)
C(12)	−690(19)	2092(17)	−473(25)	87(12)
C(13)	1021(15)	3299(15)	−27(20)	53(8)
C(14)	607(21)	3897(19)	187(27)	95(13)
C(21)	2553(23)	2929(19)	3331(26)	98(13)
C(22)	3080(22)	2512(19)	3320(25)	96(13)
C(23)	1133(14)	3373(13)	2759(19)	49(8)
C(24)	1443(24)	4019(19)	2487(29)	107(15)
C(31)	68(18)	521(16)	690(22)	74(11)
C(32)	−479(17)	1180(16)	2042(21)	69(10)
C(33)	609(12)	251(12)	2209(17)	32(6)
C(34)	745(18)	331(17)	3030(22)	67(10)
C(35)	899(23)	−165(21)	3480(28)	108(14)
C(36)	904(20)	−845(17)	3208(25)	80(11)
C(37)	779(21)	−903(17)	2435(27)	85(13)
C(38)	605(17)	−378(16)	1907(21)	66(10)
C(41)	3124(16)	1362(14)	1013(20)	56(8)
C(42)	2575(16)	643(13)	2279(20)	53(8)
C(43)	2171(12)	343(12)	698(17)	33(7)
C(44)	2186(16)	−298(15)	995(20)	55(9)
C(45)	2137(17)	−825(15)	449(23)	65(10)
C(46)	2162(18)	−703(16)	−370(24)	73(11)
C(47)	2176(19)	−25(18)	−620(23)	79(11)
C(48)	2157(15)	479(15)	−154(22)	56(9)

* Anisotropic thermal parameters (× 10^3) in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	35(1)	49(1)	16(1)	−6(1)	1(1)	−3(2)
S(1)	51(4)	100(7)	18(3)	46(5)	−6(3)	−7(7)
S(2)	105(7)	51(5)	13(3)	−61(5)	−1(4)	3(6)
S(3)	50(4)	48(4)	30(4)	−15(3)	1(4)	23(6)
S(4)	44(3)	65(5)	24(4)	6(4)	0(3)	−14(8)
P(1)	50(4)	92(7)	24(4)	31(5)	−12(4)	−7(8)
P(2)	97(7)	68(6)	25(5)	−54(6)	−23(5)	13(7)
P(3)	33(3)	46(4)	35(5)	−13(3)	1(4)	−17(6)
P(4)	33(3)	47(4)	26(4)	−7(3)	3(3)	5(7)

Although the molecule has no crystallographically-imposed symmetry, it has an approximate two-fold axis through the ruthenium atom, between the two phosphine groups, bisecting the P–Ru–P angle. Figure 2 shows a view of one enantiomorph down this ' axis '. Since the space group is centrosymmetric, the unit cell will contain equal numbers of both enantiomorphs, which suggests that the solution from which the crystals were deposited probably contains both optical isomers, as would be required by the postulated mechanism for the temperature dependence of the ^1H n.m.r. spectra.[2,3]

TABLE 2

Selected interatomic distances (Å) and angles (°)

(*a*) Distances			
Ru–S(1)	2·423(7)	P(1)–C(11)	1·95(4)
Ru–S(2)	2·433(8)	P(1)–C(13)	1·82(3)
Ru–S(3)	2·575(7)	P(2)–C(21)	1·86(4)
Ru–S(4)	2·592(8)	P(2)–C(23)	1·86(3)
Ru–P(3)	2·251(7)	P(3)–C(31)	1·87(4)
Ru–P(4)	2·262(7)	P(3)–C(32)	1·86(3)
S(1)–P(1)	1·986(13)	P(3)–C(33)	1·77(3)
S(4)–P(1)	1·999(11)	P(4)–C(41)	1·83(3)
S(2)–P(2)	1·973(13)	P(4)–C(42)	1·87(3)
S(3)–P(2)	1·983(12)	P(4)–C(43)	1·81(3)
Mean C–C(Ph)	1·43(6)	Mean C–C(Et)	1·42(12)
(*b*) Angles			
S(1)–Ru–S(4)	77·4(3)	P(2)–S(2)–Ru	88·7(4)
S(2)–Ru–S(3)	77·6(3)	P(2)–S(3)–Ru	84·5(4)
P(1)–S(1)–Ru	89·5(4)	S(1)–P(1)–S(4)	104·0(5)
P(1)–S(4)–Ru	84·6(4)	S(2)–P(2)–S(3)	105·1(5)
(*c*) Non-bonded contacts between molecules			
C(31) · · · C(31)	3·24(5)	C(12) · · · C(45)	3·70(5)
C(11) · · · C(41)	3·66(5)	C(23) · · · C(37)	3·75(5)

The ruthenium atom is in a distorted octahedral environment (Figure 2). The S–Ru–S angles of the bidentate ligands (77·5°) are smaller than 90° owing to the ' bite ' of the phosphinodithioato-groups which are 3·14 Å compared with other mean S · · · S distances of 3·6 Å.

The Ru–P distances [mean 2·257(7) Å] are at the

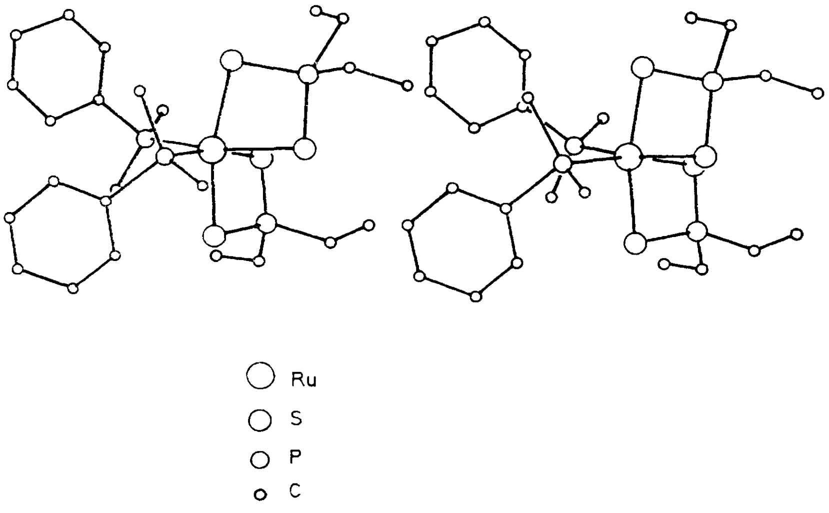


FIGURE 1 Stereopair showing the molecular structure

shorter end of the range (2·2—2·4 Å) found in other Ru^{II}, complexes.[7,8] The shortest distance reported is in the $RuCl_2(PPh_3)_3$ complex,[7] where one octahedral site on the metal is sterically blocked by the bulky phosphine groups. The short Ru–P (2·230 Å) bond is *trans* to this site.

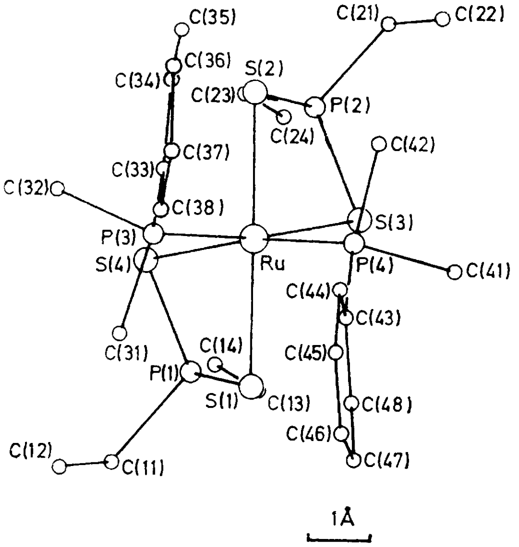


FIGURE 2 The molecule viewed down the approximate two-fold axis

The Ru–S bonds *trans* to Ru–P bonds have a mean distance of 2·584(9) Å, while the mean of those *trans* to other Ru–S bonds is 2·428(7) Å. The difference between the two is $>16\sigma$. The longer bonds would be expected to be weaker, and this supports the mechanism for interconversion of optical isomers,[3] the first step of which is seen as the breaking of a Ru–S bond, *trans* to a tertiary phosphine group.

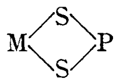
Many structures containing bidentate phosphinodithioate and dithiophosphate groups co-ordinated to transition metals are found to have a planar grouping for the  atoms.[9] There are also several structures where the atoms are definitely non-coplanar.[10,11] The reasons for this deviation are usually steric effects from the crystal packing or crowding of bulky ligands around the central metal atom. The planes in the present structure and the deviations from them are shown in Table 3.

TABLE 3

Least-squares planes and deviations (Å) from them; x,y,z are co-ordinates in fractions of the cell edge

Plane (1): $12·963x + 14·275y + 1·627z = 4·184$
Ru 0·11, S(1) −0·15, S(4) −0·14, P(1) 0·18
Plane (2): $14·825x - 11·372y + 2·274z = 0·378$
Ru −0·10, S(2) 0·14, S(3) 0·13, P(2) −0·17
Plane (3): $17·473x + 1·879y - 3·348z = 0·361$
P(3) 0, C(33) 0·01, C(34) −0·01, C(35) 0·01, C(36) −0·02, C(37) 0·02, C(38) −0·01
Plane (4): $17·877x - 0·522y - 0·291z = 3·881$
P(4) 0·04, C(43) −0·04, C(44) 0·01, C(45) −0·03, C(46) 0·03, C(47) 0·03, C(48) −0·04

The phosphorus atoms are removed from the planes so as to increase their distances from the tertiary phosphine groups and it would seem that steric factors are responsible for this. The possibility of hydrogen bonds to sulphur from phenyl or ethyl hydrogens was discounted when the positions of the hydrogen atoms were calculated; none were found to be closer to sulphur than 2·65 Å, with an angle at the hydrogen atom of 125°. This compares with a distance of 2·35 Å and near-linear N–H · · · S bonds in thiourea,[12] which is known to contain hydrogen bonds to sulphur.

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