

## Crystal and Molecular Structure of Thiocarbonyl-ethoxo(tetraphenylporphyrinato)-ruthenium(II), [Ru(TPP)(CS)(HOC<sub>2</sub>H<sub>5</sub>)]. A Case of Centrosymmetric–Noncentrosymmetric Ambiguity

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### Abstract

[Ru(TPP)(CS)(EtOH)] crystallizes in the triclinic system. Crystal data: C<sub>47</sub>H<sub>34</sub>N<sub>4</sub>ORuS,  $M_r = 803.91$ ,  $a = 10.607(3)$ ,  $b = 11.308(5)$ ,  $c = 17.699(2)$  Å,  $\alpha = 77.53(2)$ ,  $\beta = 73.17(1)$ ,  $\gamma = 69.85(3)^\circ$ ,  $V = 1891.6(10)$  Å<sup>3</sup>,  $P\bar{1}$  ( $C_i^1$ , no. 2),  $Z = 2$ ,  $F(000) = 824$ ,  $D_x = 1.410$ ,  $D_m = 1.39$  Mg m<sup>-3</sup> (by flotation in aqueous KI),  $\mu(\text{Mo } K\alpha) = 0.512$  mm<sup>-1</sup>,  $R = 0.094$ ,  $wR = 0.098$ ,  $S = 2.28$  for 4610 independent reflections with  $F_o > 5\sigma(F_o)$ . A second data set was collected using Cu  $K\alpha$  radiation. The structure was refined by standard least-squares and difference-Fourier methods in space groups  $P1$  and  $P\bar{1}$  using both the Mo  $K\alpha$  and Cu  $K\alpha$  data sets. Both data sets favor space group  $P\bar{1}$ , the Mo data giving a slightly better result than the Cu data. The two independent Ru atoms lie on the inversion centers  $\frac{1}{2}, 0, 0$  and  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  of space group  $P\bar{1}$ . Consequently, the two independent molecules have crystallographically imposed  $\bar{1}$  symmetry, the CS and EtOH axial groups are disordered and the RuN<sub>4</sub> portions of the molecules are planar. The deviations from planarity of the porphyrinato core are very small. The Ru—C—S groups are essentially linear with an average Ru—C—S bond angle of  $174(1)^\circ$ . The mean Ru—C(CS) and Ru—O (Et) bond lengths are 1.92 (4) and 2.15 (3) Å, respectively.

### 1. Introduction

The organometallic chemistry of metalloporphyrins is of special interest because of its relevance to the reaction of cytochrome P-450 with polyhalogenated compounds, widely used as solvents, insecticides and fungicides (Volf, Mansuy, Nastainczyk, Deutschman & Ullrich, 1977; Mansuy, Fontecave & Chottard, 1980; Arch, King, Nastainczyk & Ullrich, 1980). Comparison between carbonyl complexes of metalloporphyrins and those of the corresponding Fe hemes is of general interest. Since ruthenium is a third-row transition metal in the same group as iron, it has been considered as a suitable substitute for Fe, despite the marked differences shown by the chemistry of Ru and Fe porphyrins (Hoard,

1975). Interest in ruthenium porphyrin chemistry has also been stimulated by possible applications to energy conversion processes based on light-driven reactions and to the activation of small gaseous molecules of biological interest, such as O<sub>2</sub>, CO and N<sub>2</sub> (Farrell, Dolphin & James, 1978; James, Addison, Cairns, Dolphin, Farrell, Paulson & Walker, 1979; Young, Nagle, Meyer & Whitten, 1978; Hopf & Whitten, 1976; Collman, Barnes, Collins, Brothers, Gallucci & Ibers, 1981; Dolphin, Addison, Cairns, Dinello, Farrell, James, Paulson & Welborn, 1979; Paulson, Addison, Dolphin & James, 1979; Chow & Cohen, 1971). Ruthenium porphyrins have been shown to be competent catalysts in oxidation and decarbonylation processes (Domazetis, James, Tarpey & Dolphin, 1981; James, Mikkelsen, Leung, Williams & Wong, 1984; Groves & Quinn, 1985; Groves, Ahn & Quinn, 1988; Groves, Han & van Engelen, 1990).

In a recent paper (Rachlewicz, Grzeszczuk & Latos-Grażyński, 1993) the synthesis and the chemical and electrochemical properties of the title complex ruthenium thiocarbonyl tetraphenylporphyrin (TPP = tetraphenylporphyrin) were reported. Thiocarbonyl and carbonyl ruthenium(II) complexes display similar chemical and electrochemical properties, with the exception of the internal reactivity of the thiocarbonyl ligand. In the present paper we report the molecular stereochemistry of the [Ru(TPP)(CS)(EtOH)] (1) complex and we compare it with [Ru(TPP)(CO)(EtOH)] (Bonnet, Eaton, Eaton, Holm & Ibers, 1973) and [Fe(OEP)(CS)] (Scheidt & Geiger, 1982) complexes, where OEP = octaethylporphyrin.

### 2. Experimental

Attempts to collect data at low temperature failed since three crystals in turn cracked upon cooling. The intensities were, therefore, measured at room temperature. The plate-shaped orange-red crystal used for data collection (0.16 × 0.44 × 0.64 mm mounted on a CAD-4 diffractometer, Mo  $K\alpha$  radiation) was obtained after an ethanol solution was allowed to evaporate slowly over

a period of months. The unit-cell dimensions and orientation matrix were obtained from 25 carefully centered reflections ( $\theta$  range 5–10°) in a standard manner. The Mo  $K\alpha$  data were corrected for absorption using  $\psi$  scans. The experimental details are given in Tables 1 and 2.†

The volume of the unit cell of [Ru(TPP)(CS)(EtOH)] is approximately twice as large as that of the carbonyl complex [Ru(TPP)(CO)(EtOH)] (Bonnet *et al.*, 1973). A comparison of the lattice constants is given in Table 1. Bonnet and co-workers (1973) commented on the difficulty of determining the space group of the carbonyl complex. They assumed the centrosymmetric space group  $P\bar{1}$ , so that with  $Z = 1$  their molecule has a crystallographically imposed center of symmetry and the Ru atom lies at (0,0,0). The CO and EtOH groups attached to Ru are disordered. They reported that a difference synthesis clearly revealed features interpretable as a superposition (because of  $\bar{1}$  symmetry) of a CO and an EtOH group (Bonnet *et al.*, 1973). They also considered the possibility that the space group was  $P1$ , in which case the CO and EtOH groups need not be disordered. They state that the structure-factor calculations based on the two possible enantiomorphs in  $P1$  indicated that the breakdown of Friedel's law would be undetectable for data collected with Mo  $K\alpha$  radiation and very difficult to detect [maximum differences between  $I(hkl)$  and  $I(\bar{h}\bar{k}\bar{l}) \sim 3\%$ ] with Cu  $K\alpha$  radiation. These calculations were based on the assumption that the only deviation from symmetry  $\bar{1}$  is brought about by the differences between CO and EtOH. In our case the corresponding difference between CS and EtOH groups would be more marked. Bonnet *et al.* (1973) also stated that 'presumably variations in Friedel pairs would be larger if the Ru(TPP) portion of the molecule was significantly noncentrosymmetric'. Refining the highly symmetrical porphyrin structure, distorted only by the presence of different axial CS and EtOH groups, was not expected to be straightforward. Marsh (1994, 1995) has pointed out that it is extremely difficult to decide by diffraction methods whether a crystal structure is centrosymmetric or only approximately so. If one cannot be entirely sure that a structure is noncentrosymmetric, 'one should opt for the centrosymmetric description with the implicit admission that diffraction data may well be unable to provide an unambiguous result' (Marsh, 1994). Recently Marsh (1995) has recommended nine procedures, based on Baur & Tillmanns (1986), to minimize the danger of error in such cases.

As an attempt to obtain improved data we collected a second set of data using the same crystal specimen on a KUMA-4 diffractometer with Cu  $K\alpha$  radiation. A comparison of the lattice constants obtained in the two

Table 1. *The lattice constants of [Ru(TPP)(CX)(EtOH)], X = S and O*

	[Ru(TPP)(CS)(EtOH)]		[Ru(TPP)(CO)(EtOH)]
	Present work	Bonnet <i>et al.</i> (1973)	
	Mo $K\alpha$ data		Cu $K\alpha$ data
Formula weight	803.93		787.89
Space group	$P1$ or $P\bar{1}$		$P\bar{1}$
$a$ (Å)	10.607 (3)	10.599 (5)	10.078 (4)
$b$ (Å)	11.308 (5)	11.301 (6)	11.819 (5)
$c$ (Å)	17.699 (2)	17.713 (5)	8.883 (4)
$\alpha$ (°)	77.53 (2)	77.55 (3)	101.37 (5)
$\beta$ (°)	73.17 (1)	73.15 (3)	106.12 (4)
$\gamma$ (°)	69.85 (3)	69.87 (4)	65.91 (3)
$V$ (Å <sup>3</sup> )	1891.6 (10)	1890.6 (14)	923.6
Wavelength (Å)	0.71073	1.54052	
$\mu$ (mm <sup>-1</sup> )	0.50	4.2	
$\rho$ (obs.)† (Mg m <sup>-3</sup> )	1.39		1.39
$\rho$ (calc.)	1.410		1.416
$Z$	2		1

† By flotation in aqueous K1.

Table 2. *Crystal data and details of refinement of (1) with Mo data*

	$P\bar{1}$	$P1$
Space group	$P\bar{1}$	$P1$
Crystal size (mm)	0.16 × 0.44 × 0.64	0.16 × 0.44 × 0.64
No. of parameters refined	477	907
Final $R$ indices (obs. data)		
$R$	0.094	0.086
$wR$	0.098	0.109
$R$ indices (all data)		
$R$	0.1840	0.1529
$wR$	0.1283	0.1311
Goodness-of-fit	2.28	1.44
Largest and mean $\Delta/\sigma$	0.64, 0.02	0.34, 0.04
Data-to-parameter ratio	9.7:1	6.0:1
Largest difference peak (e Å <sup>-3</sup> )	0.99	1.80
Largest difference hole (e Å <sup>-3</sup> )	-0.83	-1.02
$2\theta$ range (°)	2.5–55.9	2.5–55.9
Scan type	$2\theta - \theta$	$2\theta - \theta$
Index ranges	-13 → $h$ → 13 0 → $k$ → 14 -22 → $l$ → 32	-13 → $h$ → 13 0 → $k$ → 14 -22 → $l$ → 32
Measured reflections	9540	
Unique reflections	9429	
Observed reflections	4610 [ $F > 5\sigma(F)$ ]	5443 [ $F > 5\sigma(F)$ ]
Decomposition (%)	2	—
Absorption corrections	$\psi$ scans	Empirical (Walker & Stuart, 1983)
Transmission factors	0.779–0.999	—

experiments is given in Table 1. Statistical tests for the presence of a center of symmetry based on the mean value of  $|E^2 - 1|$  gave inconsistent results. For the Mo  $K\alpha$  data set, mean  $|E^2 - 1| = 0.849$ , almost exactly halfway between the expected values of 0.968 for a centrosymmetric and 0.739 for a noncentrosymmetric distribution. The *XPREP* procedure incorporated into the *SHELXTL/PC* system (Sheldrick, 1990) gave similar results. The Cu  $K\alpha$  data set seemed to indicate  $P1$  (mean  $|E^2 - 1| = 0.786$ ). Marsh (1995) has argued

† Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: MU0320). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

that such statistical tests can be very deceptive. Recommendations on how to refine almost centrosymmetric structures have recently been given by Watkin (1994) and Marsh (1995) recommends describing the structure in the centrosymmetric space group if at all possible, for the centrosymmetric refinement will not suffer from near-singularities and should converge normally. Further, 'if a centrosymmetric description – even one that involves disorder – provides adequate agreement between observed and calculated intensities, there is no profit in searching further'.

### 2.1. Solution of the structure of (1) in the space group $P\bar{1}$

The structure was solved easily by direct and Patterson methods using both sets of data. All but a few C atoms belonging to peripheral phenyl rings were revealed [XS program incorporated in the SHELXTL system (Sheldrick, 1990)]. Two Ru atoms were found in special positions of the space group  $P\bar{1}$ :  $d \frac{1}{2}, 0, 0$  and  $h \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ; both having site symmetry  $\bar{1}$  (Wyckoff's notation; *International Tables for Crystallography*, 1985, Vol. A).

### 2.2. Solution of the structure of (1) in the space group $P1$

The structure was also solved easily by direct and Patterson methods (Sheldrick, 1990) in  $P1$ , revealing two almost complete porphyrin rings which lack, however, most of the peripheral C phenyl ring atoms. In this case the CS and EtOH groups need not be disordered.

### 2.3. Refinement of the structure of (1)

All four models were completed by subsequent isotropic refinements followed by difference syntheses. The complete models were refined anisotropically using  $F^2$  (Cu data) or  $F$  (Mo data) values and full matrix least-squares (Sheldrick, 1992). Values of the atomic scattering factors and the anomalous terms were as incorporated in SHELXTL/PC or SHELXL92 (Sheldrick, 1992; *International Tables for Crystallography*, 1992, Vol. C). The H atoms were partly found in difference syntheses and partly idealized geometrically [C—H = 0.96 Å,  $U(H) = 1.2U(C)$  for aromatic, pyrrole —CH and methylene —CH<sub>2</sub>— groups and  $U(H) = 1.5U(C)$  for methyl groups]. The peripheral phenyl rings were treated as rigid groups with a C—C distance of 1.39 Å. The H atoms were allowed 'to ride' on the parent C atoms. No attempts have been made to locate the hydroxyl H atoms bonded to O(1) and O(2) atoms. The weighting scheme used was  $w = 1/[^2(F) + 0.00049F^2]$ . Ethanol molecules and the C(45) atom of the CS group were unstable during refinement. The C(45), C(46), C(47) and C(147) vibration tensors became nonpositive definite during refinement and these atoms, therefore, were treated isotropically. The bond lengths within ethanol molecules were constrained and refined, starting from values reported for EtOH in the CO complex by Bonnet *et al.* (1973). The  $P1$  model converged at  $R =$

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	$U_{eq}$
S(1)	0.8313 (7)	-0.0087 (10)	-0.0052 (5)	0.092 (4)
C(45)	0.6809 (25)	0.0034 (22)	-0.0044 (12)	0.034 (6)
Ru(1)	1/2	0.0	0.0	0.055 (1)
O(1)	0.3035 (23)	-0.0295 (19)	0.0112 (12)	0.071 (7)
C(46)	0.1996 (49)	0.0506 (46)	-0.0008 (26)	0.155 (22)
C(47)	0.1692 (25)	0.0944 (23)	-0.0834 (14)	0.092 (7)
N(21)	0.4134 (7)	0.1420 (5)	0.0707 (4)	0.042 (3)
N(22)	0.5215 (7)	-0.1309 (6)	0.0991 (4)	0.044 (3)
C(1)	0.3625 (9)	0.2717 (7)	0.0456 (5)	0.047 (4)
C(2)	0.3070 (9)	0.3380 (8)	0.1132 (6)	0.056 (4)
C(3)	0.3233 (9)	0.2519 (8)	0.1790 (6)	0.057 (4)
C(4)	0.3938 (9)	0.1291 (8)	0.1503 (5)	0.049 (4)
C(5)	0.4261 (9)	0.0137 (8)	0.2019 (5)	0.047 (4)
C(22)	0.4641 (7)	0.0855 (6)	0.3140 (4)	0.072 (5)
C(23)	0.4344	0.0982	0.3945	0.093 (7)
C(24)	0.3376	0.0458	0.4495	0.094 (7)
C(25)	0.2704	-0.0194	0.4240	0.081 (6)
C(26)	0.3000	-0.0321	0.3435	0.066 (5)
C(21)	0.3969	0.0203	0.2885	0.050 (4)
C(6)	0.4842 (9)	-0.1068 (8)	0.1762 (5)	0.048 (4)
C(7)	0.5277 (10)	-0.2237 (8)	0.2275 (6)	0.062 (5)
C(8)	0.5824 (11)	-0.3168 (9)	0.1803 (6)	0.065 (5)
C(9)	0.5795 (8)	-0.2605 (7)	0.0988 (5)	0.045 (4)
C(10)	0.6333 (9)	-0.3226 (7)	0.0340 (5)	0.048 (4)
C(28)	0.6160 (5)	-0.5483 (5)	0.0637 (4)	0.063 (5)
C(29)	0.6772	-0.6795	0.0750	0.072 (5)
C(30)	0.8188	-0.7292	0.0702	0.097 (7)
C(31)	0.8993	-0.6477	0.0541	0.161 (11)
C(32)	0.8381	-0.5165	0.0428	0.145 (10)
C(27)	0.6964	-0.4668	0.0476	0.052 (4)
S(2)	0.6457 (9)	0.7452 (7)	0.4131 (5)	0.082 (4)
C(145)	0.5728 (52)	0.6409 (36)	0.4505 (31)	0.040 (11)
Ru(2)	1/2	1/2	1/2	0.068 (1)
O(2)	0.4438 (45)	0.3364 (37)	0.5661 (27)	0.095 (16)
C(146)	0.3201 (61)	0.3261 (41)	0.5609 (31)	0.266 (43)
C(147)	0.2833 (39)	0.2244 (34)	0.6157 (22)	0.148 (16)
N(121)	0.3029 (7)	0.6114 (7)	0.4985 (5)	0.056 (3)
N(122)	0.5172 (8)	0.4457 (7)	0.3941 (4)	0.057 (4)
C(101)	0.2108 (10)	0.6886 (8)	0.5558 (5)	0.059 (4)
C(102)	0.0822 (10)	0.7509 (9)	0.5337 (6)	0.063 (5)
C(103)	0.0934 (11)	0.7114 (10)	0.4643 (6)	0.069 (5)
C(104)	0.2330 (10)	0.6258 (8)	0.4413 (6)	0.055 (4)
C(105)	0.2819 (10)	0.5651 (8)	0.3732 (5)	0.057 (4)
C(122)	0.2100 (7)	0.6564 (7)	0.2451 (5)	0.077 (6)
C(123)	0.1251	0.6710	0.1944	0.096 (7)
C(124)	0.0180	0.6163	0.2191	0.117 (10)
C(125)	-0.0043	0.5470	0.2945	0.129 (11)
C(126)	0.0805	0.5324	0.3453	0.103 (8)
C(121)	0.1877	0.5871	0.3206	0.069 (5)
C(106)	0.4180 (11)	0.4815 (8)	0.3518 (5)	0.057 (5)
C(107)	0.4699 (11)	0.4171 (8)	0.2828 (6)	0.058 (5)
C(108)	0.5994 (10)	0.3443 (8)	0.2829 (5)	0.054 (4)
C(109)	0.6331 (11)	0.3589 (9)	0.3515 (6)	0.058 (5)
C(110)	0.7544 (10)	0.2950 (8)	0.3775 (5)	0.056 (4)
C(128)	0.8470 (9)	0.0761 (6)	0.3411 (4)	0.123 (8)
C(129)	0.9373	-0.0147	0.2922	0.137 (9)
C(130)	1.0374	0.0178	0.2279	0.088 (6)
C(131)	1.0472	0.1410	0.2124	0.102 (7)
C(132)	0.9570	0.2317	0.2613	0.091 (7)
C(127)	0.8569	0.1993	0.3257	0.060 (4)

0.086,  $wR = 0.1088$  and  $S = 1.44$ . However, 11 atoms from various parts of the molecule had nonpositive definite ADP's (anisotropic displacement parameters). During both refinements correlation matrix elements greater than 0.5 were present. The refinements of the two models are compared in Table 2. The Cu data gave

Table 4. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

S(1)—C(45)	1.55 (3)	S(2)—C(145)	1.56 (5)
C(45)—Ru(1)	1.91 (3)	C(145)—Ru(2)	1.94 (5)
Ru(1)—O(1)	2.17 (3)	Ru(2)—O(2)	2.14 (4)
Ru(1)—N(21)	2.043 (7)	Ru(2)—N(121)	2.040 (7)
Ru(1)—N(22)	2.049 (6)	Ru(2)—N(122)	2.036 (8)
O(1)—C(46)	1.20 (5)	O(2)—C(146)	1.39 (9)
C(46)—C(47)	1.53 (5)	C(146)—C(147)	1.42 (6)
N(21)—C(1)	1.397 (9)	N(121)—C(101)	1.401 (11)
N(21)—C(4)	1.346 (12)	N(121)—C(104)	1.373 (15)
N(22)—C(6)	1.365 (11)	N(122)—C(106)	1.365 (15)
N(22)—C(9)	1.380 (10)	N(122)—C(109)	1.413 (11)
C(1)—C(2)	1.420 (14)	C(101)—C(102)	1.427 (15)
C(2)—C(3)	1.359 (13)	C(102)—C(103)	1.357 (17)
C(3)—C(4)	1.455 (12)	C(103)—C(104)	1.460 (12)
C(4)—C(5)	1.419 (11)	C(104)—C(105)	1.393 (14)
C(5)—C(21)	1.487 (11)	C(105)—C(121)	1.483 (15)
C(5)—C(6)	1.403 (12)	C(105)—C(106)	1.422 (12)
C(6)—C(7)	1.445 (11)	C(106)—C(107)	1.429 (14)
C(7)—C(8)	1.350 (14)	C(107)—C(108)	1.336 (14)
C(8)—C(9)	1.450 (13)	C(108)—C(109)	1.417 (17)
C(9)—C(10)	1.352 (13)	C(109)—C(110)	1.396 (15)
C(10)—C(27)	1.529 (9)	C(110)—C(127)	1.494 (11)
S(1)—C(45)—Ru(1)	174.1 (16)	S(2)—C(145)—Ru(2)	174 (4)
C(45)—Ru(1)—O(1)	172.6 (8)	C(145)—Ru(2)—O(2)	171 (2)
C(45)—Ru(1)—N(21)	90.7 (8)	C(145)—Ru(2)—N(121)	91.7 (14)
O(1)—Ru(1)—N(21)	93.2 (6)	O(2)—Ru(2)—N(121)	95.5 (12)
C(45)—Ru(1)—N(22)	86.0 (7)	C(145)—Ru(2)—N(122)	93.7 (17)
O(1)—Ru(1)—N(22)	87.8 (5)	O(2)—Ru(2)—N(122)	92.3 (14)
N(21)—Ru(1)—N(22)	89.6 (3)	N(121)—Ru(2)—N(122)	89.4 (3)
Ru(1)—O(1)—C(46)	126 (3)	Ru(2)—O(2)—C(146)	117 (3)
O(1)—C(46)—C(47)	123 (3)	O(2)—C(146)—C(147)	112 (4)
Ru(1)—N(21)—C(1)	126.5 (6)	Ru(2)—N(121)—C(101)	127.2 (7)
Ru(1)—N(21)—C(4)	126.9 (5)	Ru(2)—N(121)—C(104)	127.0 (6)
C(1)—N(21)—C(4)	106.6 (7)	C(101)—N(121)—C(104)	105.8 (7)
Ru(1)—N(22)—C(6)	126.9 (5)	Ru(2)—N(122)—C(106)	127.2 (5)
Ru(1)—N(22)—C(9)	125.2 (6)	Ru(2)—N(122)—C(109)	126.5 (7)
C(6)—N(22)—C(9)	107.9 (6)	C(106)—N(122)—C(109)	106.3 (8)
N(21)—C(1)—C(2)	109.0 (7)	N(121)—C(101)—C(102)	110.4 (9)
C(1)—C(2)—C(3)	108.2 (8)	C(101)—C(102)—C(103)	106.9 (8)
C(2)—C(3)—C(4)	105.9 (9)	C(102)—C(103)—C(104)	107.5 (10)
N(21)—C(4)—C(3)	110.3 (7)	N(121)—C(104)—C(103)	109.3 (9)
N(21)—C(4)—C(5)	126.7 (8)	N(121)—C(104)—C(105)	126.7 (8)
C(3)—C(4)—C(5)	122.9 (8)	C(103)—C(104)—C(105)	123.9 (10)
C(4)—C(5)—C(21)	118.2 (8)	C(104)—C(105)—C(121)	118.9 (8)
C(4)—C(5)—C(6)	124.0 (8)	C(104)—C(105)—C(106)	123.3 (10)
C(21)—C(5)—C(6)	117.8 (7)	C(121)—C(105)—C(106)	117.8 (9)
C(5)—C(21)—C(22)	118.6 (5)	C(105)—C(121)—C(122)	120.4 (5)
C(5)—C(21)—C(26)	121.3 (5)	C(105)—C(121)—C(126)	119.5 (5)
N(22)—C(6)—C(5)	125.9 (7)	N(122)—C(106)—C(105)	126.3 (9)
N(22)—C(6)—C(7)	109.6 (7)	N(122)—C(106)—C(107)	109.3 (8)
C(5)—C(6)—C(7)	124.1 (8)	C(105)—C(106)—C(107)	124.3 (11)
C(6)—C(7)—C(8)	106.1 (8)	C(106)—C(107)—C(108)	107.8 (10)
C(7)—C(8)—C(9)	108.8 (8)	C(107)—C(108)—C(109)	108.5 (8)
N(22)—C(9)—C(8)	107.3 (8)	N(122)—C(109)—C(108)	108.1 (9)
N(22)—C(9)—C(10)	126.4 (7)	N(122)—C(109)—C(110)	124.1 (10)
C(8)—C(9)—C(10)	126.1 (7)	C(108)—C(109)—C(110)	127.7 (8)
C(9)—C(10)—C(27)	117.5 (7)	C(109)—C(110)—C(127)	113.9 (9)
C(10)—C(27)—C(28)	121.5 (4)	C(110)—C(127)—C(128)	118.2 (5)
C(10)—C(27)—C(32)	118.5 (4)	C(110)—C(127)—C(132)	121.7 (5)

similar but less reliable results and were rejected from further considerations. All calculations were performed on a PC486 personal computer compatible with IBM PC using *SHELXTL/PC* (Sheldrick, 1990) or *SHELXL92* (Sheldrick, 1992) for final refinements.

### 3. Results and discussion

Atomic coordinates are given in Table 3, and selected bond lengths and angles together with their standard

deviations in Table 4. Figs. 1(a) and 1(b) display the numbering schemes. Figs. 2(a) and 2(b) are diagrams of the independent molecules showing the orientations of the axial CS groups and EtOH molecules.

The course of refinements described above has led to the conclusion that the structure is best described in the centrosymmetric space group  $P\bar{1}$ . A detailed discussion of the EtOH–Ru–CS geometry is not justified in view of the likely systematic errors. The average value of the C—S bond length is 1.56(4)  $\text{\AA}$ , almost identical to the value of 1.559(3)  $\text{\AA}$  found for the C—S bond

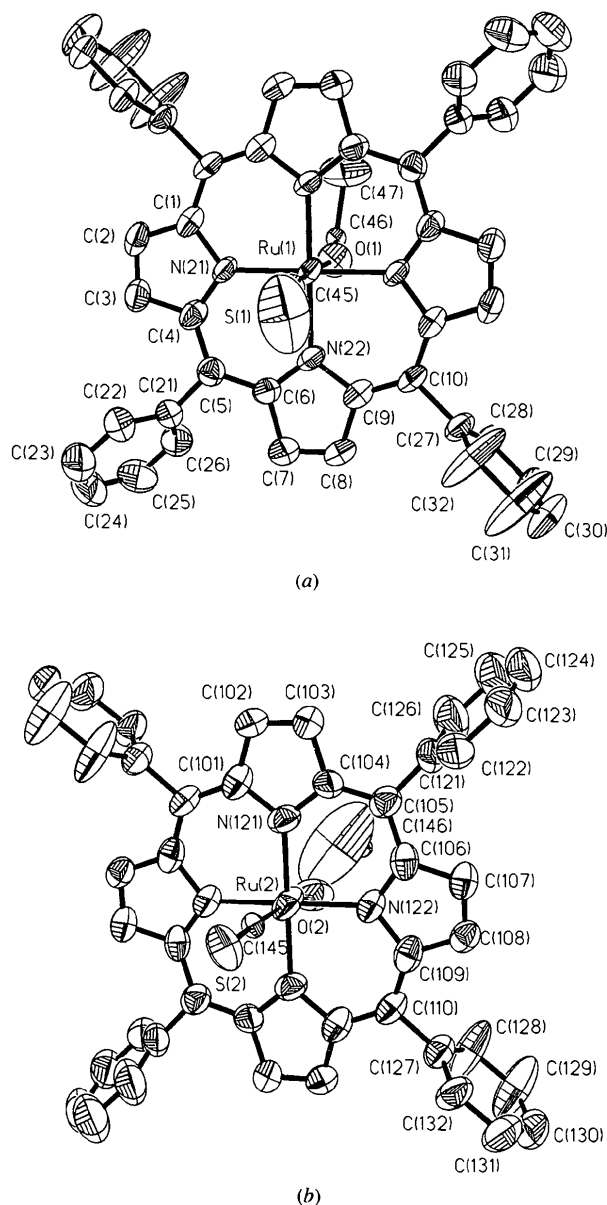


Fig. 1. Diagrams of two independent  $[\text{Ru}(\text{TPP})(\text{CS})\text{Et}(\text{OH})]$  molecules showing numbering schemes with H atoms omitted for clarity. The atoms are drawn as 50% probability ellipsoids.

length in Fe(OEP)(CS) by Scheidt & Geiger (1982). The Ru—C(CS) mean distance of 1.92 (4) Å is longer than the 1.77 (2) Å found in the carbonyl complex (Bonnet *et al.*, 1973) and the Fe—C(CS) bond length of 1.662 (3) Å found by Scheidt & Geiger (1982). The Ru—C—S group is almost linear (Figs. 2a and 2b), with an average 174 (2)°.

The displacement of a metal atom from the N<sub>4</sub> porphinato plane is a function of the spin state of the metal, the number of axial ligands (one or two) and their relative bonding strengths (Scheidt & Geiger, 1982). The

Ru<sup>II</sup> ion in our structure is forced to be in the plane of the macrocycle by the imposed crystallographic symmetry.

The geometries of the porphyrin rings are very similar to those found in other ruthenium complexes. The average Ru—N<sub>av</sub> or Ct··N [Ct = geometrical center of the macroring (Hoard, 1975)] distance observed is 2.042 (7) Å. Corresponding distances are 2.049 (5) Å in the carbonyl complex (Bonnet *et al.*, 1973), 2.052 (6) and 2.037 (7) Å in ruthenium 'picnic-basket' porphyrin complexes (Collman, Brauman, Fitzgerald, Hampton, Naruta, Sparapany & Ibers, 1988; Collman, Brauman, Fitzgerald, Sparapany & Ibers, 1988), 2.052 (9) Å in Ru(CO)(py)(TPP) (Little & Ibers, 1973), 2.050 (3) Å in an adduct of styrene oxide and tetra(2,6-dichlorophenyl)porphyrinato(carbonyl)ruthenium(II), and, significantly longer, 2.144 (4) Å in [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> (Stynes & Ibers, 1971). All but the last distance are within the range 1.960–2.099 Å discussed by Hoard (1975), who summarized the geometries of the porphyrin core in a number of metalloporphyrins. The average distances N—C 1.38 (1), C<sub>a</sub>—C<sub>b</sub> 1.44 (12) and C<sub>b</sub>—C<sub>b</sub> 1.35 (1) Å also fall within the ranges described by Hoard (1975). Finally, it should be noted that atoms C(30), C(31), C(32), C(130), C(131) and C(132) show highly anisotropic displacement parameters which may indicate slight departure from inversion symmetry.

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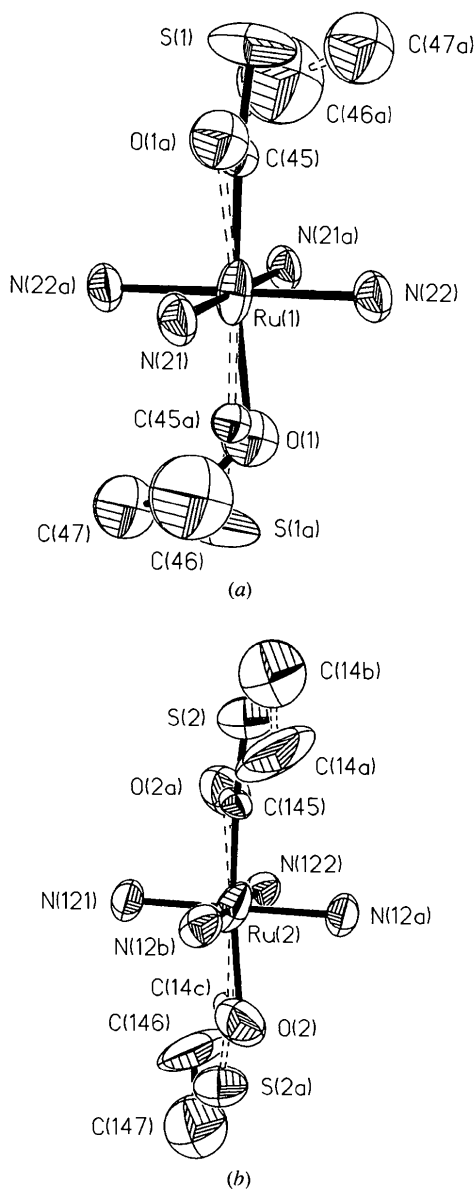


Fig. 2. Drawings of two independent molecules of (1) showing the orientations of axial thiocarbonyl and EtOH groups. The atoms are drawn as 50% probability ellipsoids.

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