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Bis[(*R*)-1-phenylethyl isocyanido]-(5,10,15,20-tetrakis{2,6-bis[(*S*)-2,2-dimethyl-1,3-dioxolan-4-ylmethyloxy]-phenyl}porphyrin)ruthenium(II) at 110 K

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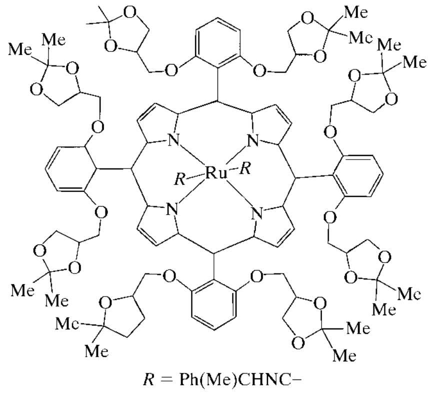
The geometry about the Ru atom in the title compound, $[Ru(C_9H_9N)_2(C_{92}H_{108}N_4O_{24})]$, is approximately tetragonal and the porphyrin ring is nearly planar, while the C—N—*R* angles [169.3 (3) and 163.9 (3)°] of the isocyanide ligands in the complex are different from the value of 180° expected in the free ligand.

Comment

During the past few years, we have been investigating the use of optically active ruthenium porphyrins in the chiral recognition of racemic phosphines (Le Maux *et al.*, 1991) and amino esters (Morice *et al.*, 1998). A few isocyanide derivatives of iron porphyrins (Jameson & Ibers, 1979) and ruthenium porphyrins (Geze *et al.*, 1995) have been described. However, no structural studies of ruthenium porphyrins bearing eight independent chiral pickets have been reported. The title compound, (I), was prepared as part of a chiral recognition study of racemic isocyanides with metalloporphyrins (Galardon *et al.*, 1999).

The porphyrin ring is nearly planar, with the Ru atom in the centre. The average Ru—N_p bond distance [2.054 (2) Å; N_p is an N atom of the porphyrin ring] falls within the range of distances reported for chiral porphyrin–Ru^{II} complexes (Le Maux *et al.*, 1995; Gross *et al.*, 1996; Lo *et al.*, 1997). This planarity is similar to that observed with (TPP)Fe^{II}(CN^{t}Bu)$_2$ (TPP is triphenylphosphine; Jameson & Ibers, 1979). The N_p—Ru—C_{CN} angles vary between 83.7 and 95.9° (C_{CN} is the isocyanide C atom), and the C_{CN}—Ru—C_{CN} angle is non-linear [175.02 (11)°]. A similar situation has been observed previously in (TPP)Fe(CN^{t}Bu)$_2$ (Jameson & Ibers, 1979) and was imputed to crystal-packing effects. The Ru—C_{CN} bonds [average 2.002 (3) Å] are longer than the Ru—CO [1.77 (2) (Bonnet *et al.*, 1973) and 1.79 (2) Å (Le Maux *et al.*, 1995)] or Ru=C [1.829 (9) Å; Galardon *et al.*, 1998] bonds of porphyrin–ruthenium complexes.



(I)

The C—N—*R* angles [169.3 (3) and 163.9 (3)°] of the isocyanide ligands in the complex are different from the value of 180° expected in the free ligand. This bending is close to that reported for (TPP)Fe(CN^{t}Bu)$_2$ (Jameson & Ibers, 1979). The phenyl groups of the isocyanide ligands are nearly perpendi-

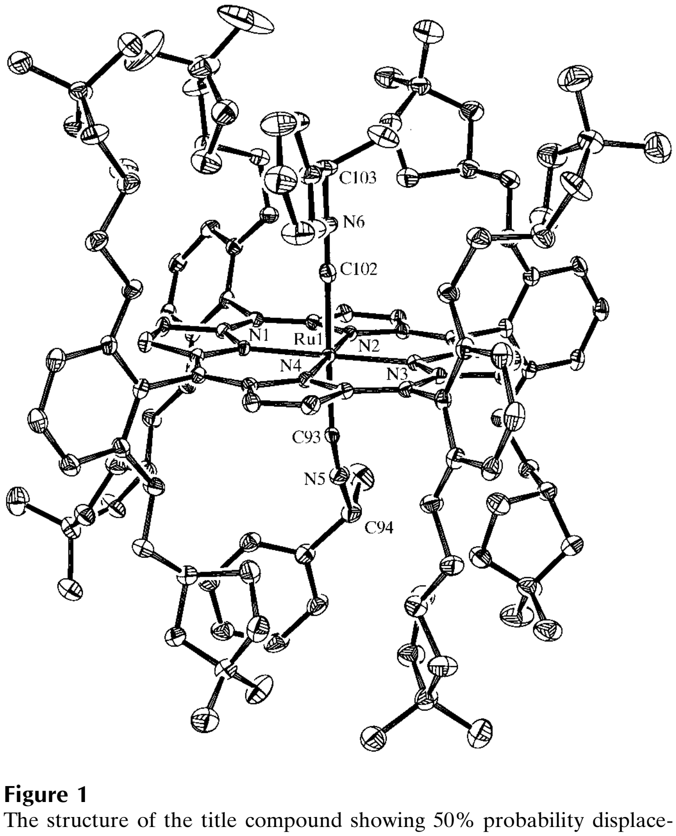


Figure 1
The structure of the title compound showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

cular to one another, probably because of crystal-packing effects.

The rather high values of the displacement parameters of the chiral groups attached to the phenyl ring suggest a large motion of these groups (very large at room temperature, see below), as can also be seen in the crystal structure (Fig. 1); a relatively large cavity results since the chiral groups extend far above the porphyrin mean plane. Contrary to our expectations, only weak steric effects are present and this may also explain the weak chiral recognition (Galardon *et al.*, 1999).

Experimental

The title compound was prepared from the chiral ruthenium porphyrin precursor and eight equivalents of (*R*)-1-phenylethyl isocyanide, as previously reported for the racemic ligands (Galardon *et al.*, 1999). Crystals suitable for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2–hexane solution in the presence of a small excess of isocyanide.

Crystal data

$[Ru(C_9H_9N)_2(C_{92}H_{108}N_4O_{24})]$
$M_r = 2017.24$
Monoclinic, $P2_1$
$a = 18.5099$ (2) Å
$b = 15.0831$ (2) Å
$c = 18.5766$ (2) Å
$\beta = 90.5023$ (6)°
$V = 5186.14$ (10) Å^3
$Z = 2$
$D_x = 1.292$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 157 703 reflections
$\theta = 1.00$–27.88°
$\mu = 0.227$ mm^{-1}
$T = 110$ (2) K
Block, purple
0.38 × 0.28 × 0.25 mm

Data collection

Enraf–Nonius KappaCCD diffractometer
Area-detector scans (see text)
Absorption correction: analytical (de Meulenaer & Tompa, 1965; Alcock, 1970)
$T_{\min} = 0.895$, $T_{\max} = 0.932$
82 451 measured reflections
12 855 independent reflections (plus 11 880 Friedel-related reflections)
22 116 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 27.87°$
$h = -24 \rightarrow 24$
$k = -19 \rightarrow 19$
$l = -24 \rightarrow 24$

Table 1
Selected geometric parameters (Å, °).

Ru1—C102	1.998 (3)	Ru1—N3	2.0581 (15)
Ru1—C93	2.006 (2)	N5—C93	1.163 (3)
Ru1—N2	2.051 (2)	N5—C94	1.451 (3)
Ru1—N4	2.0522 (19)	N6—C102	1.157 (3)
Ru1—N1	2.0549 (15)	N6—C103	1.440 (3)
C102—Ru1—C93	175.02 (11)	C102—Ru1—N3	90.59 (9)
C102—Ru1—N2	91.39 (9)	C93—Ru1—N3	88.73 (8)
C93—Ru1—N2	83.69 (9)	N2—Ru1—N3	90.21 (8)
C102—Ru1—N4	88.98 (9)	N4—Ru1—N3	89.86 (8)
C93—Ru1—N4	95.95 (9)	N1—Ru1—N3	179.29 (7)
N2—Ru1—N4	179.62 (9)	C93—N5—C94	163.9 (3)
C102—Ru1—N1	88.81 (9)	C102—N6—C103	169.3 (3)
C93—Ru1—N1	91.90 (8)	N5—C93—Ru1	167.0 (2)
N2—Ru1—N1	90.17 (8)	N6—C102—Ru1	178.2 (2)
N4—Ru1—N1	89.76 (8)		

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.103$
$S = 1.025$
24 735 reflections
1270 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 1.5527P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.78$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.039 (12)

In a previous study at room temperature, due to their large thermal expansion, some difficulties were encountered in localizing the dimethyldioxolane pickets. So, in the further refinement calculations, it was necessary to set bond and angle restraints for these groups. This method leads to high values for *R* and the s.u.'s, and a too low *r*/*p* ratio. In this situation, the use of the CCD technique at low temperature results in a decrease in the thermal motion and a significant increase in the *r*/*p* ratio. Most of the H atoms were found in a difference Fourier map (except for the dimethyldioxolane pickets). These were treated as riding [using the *AFIX* x3 command in *SHELXL*97 (Sheldrick, 1997)]. It was also possible to confirm unambiguously the absolute configuration using the Friedel pairs and to obtain good geometrical data.

Data collection: *KappaCCD Software* (Nonius, 1999); cell refinement: *HKL Scalepack* (Otwinowski & Minor, 1997); data reduction: *HKL Denzo* and *Scalepack* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1998); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1094). Services for accessing these data are described at the back of the journal.

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