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Low-temperature phase of diaqua(1,5-cyclooctadiene)rhodium(I) trifluoromethanesulfonate

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Crystals of the title compound, $[Rh(C_8H_{12})(H_2O)_2](CF_3SO_3)$, undergo a reversible phase transition at 215 (2) K. The high-temperature structure is disordered in space group $P2_1/m$ with $Z' = \frac{1}{2}$, while the twinned low-temperature structure is ordered in space group $P\overline{1}$ with $Z' = 2$.

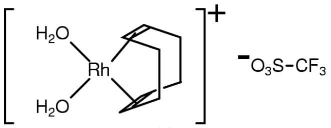
Key indicators

Single-crystal X-ray study
T = 152 K
Mean σ(C–C) = 0.009 Å
R factor = 0.055
wR factor = 0.140
Data-to-parameter ratio = 21.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The rhodium(I)-catalysed enantioselective enyne cyclization has recently attracted some attention (Lei *et al.*, 2002). Usually the Rh^I precursors for the catalyst contain chloride counterions which have to be removed by $AgSbF_6$ or $AgBF_4$, a problematic procedure with these highly hygroscopic silver salts. Now we have developed (I) as a pre-catalyst with easily exchangeable ligands only, which avoids the problematic silver salts and also gives active catalysts that lead to a high enantiomeric excess of the product (Hashmi *et al.*, 2003).



(I)

Crystals of (I) undergo a reversible phase transition at 215 (2) K. The high-temperature structure is monoclinic, space group $P2_1/m$ with $Z = 2$. The cell constants at 224 K are a = 6.3570 (7), b = 10.2477 (10), c = 10.5893 (14) Å and β = 91.236 (8)° (this study). Both the cation and anion have crystallographic m symmetry. The trifluoromethanesulfonate group is disordered over two orientations, while the cation shows large displacements of the ethylene C atoms in directions perpendicular to the eight-membered ring. Thus, this ring is found to be disordered over two symmetry-related conformations.

Below the phase transition temperature additional reflections occur, resulting in a doubling of the unit-cell volume. The low-temperature structure is triclinic, space group $P\overline{1}$ with Z = 4. The low-temperature cell is related to the high-temperature cell by the transformation: $\mathbf{a}_{low} = \mathbf{a}_{high} + \mathbf{b}_{high}$, $\mathbf{b}_{low} = \mathbf{a}_{high} - \mathbf{b}_{high}$ and $\mathbf{c}_{low} = -\mathbf{a}_{high} - \mathbf{c}_{high}$. The structure of the low-temperature modification of (I) has been determined at 152 (2) K. Splitting of the reflection profiles below the phase transition temperature showed the crystal to be twinned. The twinned cell is related to the high-temperature cell by the transformation: $\mathbf{a}_{twin} = -\mathbf{a}_{high} + \mathbf{b}_{high}$, $\mathbf{b}_{twin} = -\mathbf{a}_{high} - \mathbf{b}_{high}$ and $\mathbf{c}_{twin} = \mathbf{a}_{high} + \mathbf{c}_{high}$.

The structure contains two independent cation–anion pairs (Fig. 1). The dimensions of both cations and both anions are similar. The cyclooctadiene rings have twisted boat confor-

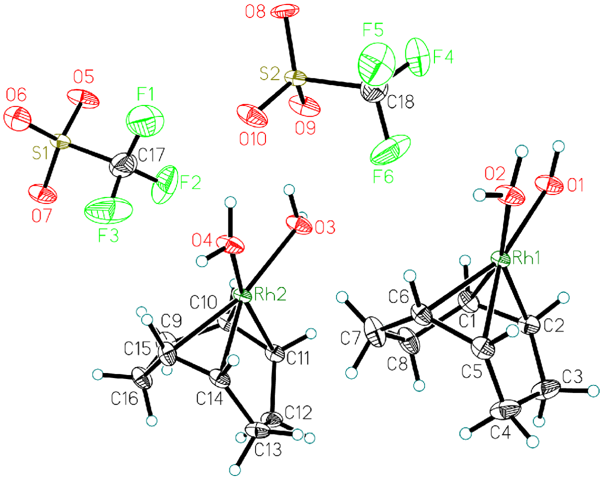


Figure 1
The structures of the two independent cations and two independent anions of (I) at 152 K, shown with 50% probability displacement ellipsoids. The H atoms are drawn as small spheres of arbitrary radius.

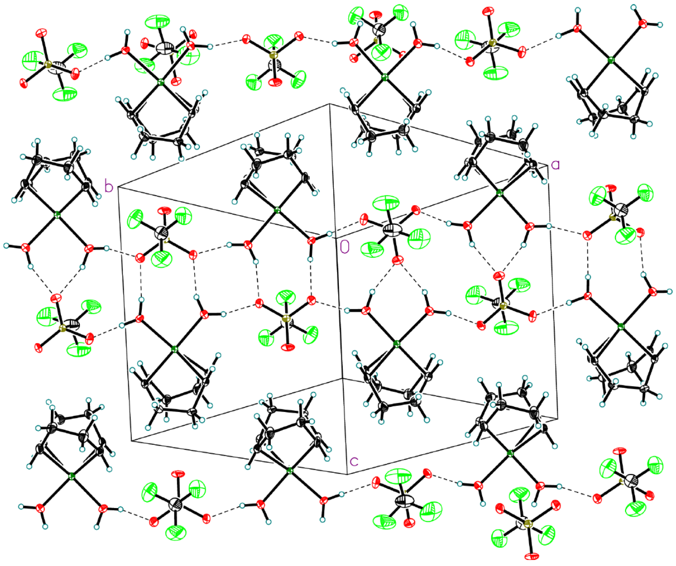


Figure 2
Crystal packing of (I) at 152 K, viewed down the [110] direction. The ellipsoids are as in Fig. 1.

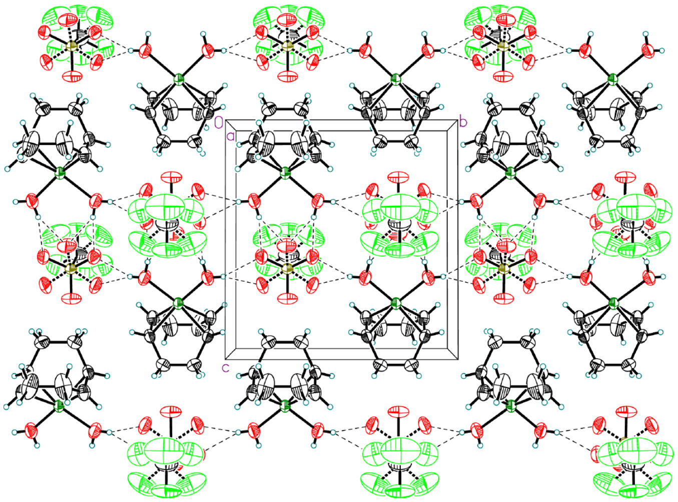


Figure 3
The crystal packing of (I) at 224 K, viewed down *a*. The ellipsoids are as in Fig. 1.

mations. The Rh atoms have square-planar configurations and are coordinated by two C=C double bonds and two water molecules. The Rh—C bond lengths range from 2.082 (5) to 2.108 (5) Å. The Rh—O bond lengths range from 2.125 (4) to 2.135 (4) Å. Similar dimensions have been reported for the corresponding 1,5-cyclooctadiene-aqua-*p*-tosyloxyrhodium(I) complex (Kölle *et al.*, 1995) and a (1,5-cyclooctadiene)bis(dimethylsulfoxide-*O*)rhodium(I) cation (Dorta *et al.*, 2002). The C=C double bonds have lengths between 1.385 (9) and 1.396 (9) Å and thus are considerably longer than the standard C=C double bond length of 1.33 Å. The cations and anions are connected by intermolecular O—H···O hydrogen bonds (Table 1), forming chains parallel to the [1$\overline{1}$0] direction (Fig. 2). Each cation donates hydrogen bonds to three different anions and each anion accepts hydrogen bonds from three different cations. Neighboring chains are connected by weak intermolecular C—H···O interactions. The crystal packing reveals seven different intermolecular C—H···O interactions, with H···O distances between 2.58 and 2.72 Å. The crystal packing shows only one weak intermolecular C—H···F contact, with an H···F distance of 2.72 Å, showing this type of interaction to be of minor importance compared to the C—H···O interactions.

In the high-temperature phase (Fig. 3), the trifluoromethanesulfonate group is statistically distributed over two orientations, which are related by a 60° rotation about the S—C axis. The hydrogen-bonding system of the high-temperature phase is a superposition of two possible patterns. Below the phase transition temperature the trifluoromethanesulfonate groups are ordered, resulting in an ordered hydrogen-bonding system.

Experimental

Compound (I) was prepared as described in a patent (Rivas Nass, 2003). Orange blocks were obtained by crystallization from chloroform.

Crystal data

$[Rh(C_8H_{12})(H_2O)_2](CF_3O_3S)$
$M_r = 396.19$
Triclinic, $P\overline{1}$
$a = 11.9569\ (11)$ Å
$b = 12.0716\ (17)$ Å
$c = 12.1417\ (17)$ Å
$\alpha = 104.944\ (12)^\circ$
$\beta = 105.414\ (10)^\circ$
$\gamma = 116.683\ (10)^\circ$
$V = 1357.1\ (4)$ Å^3

$Z = 4$
$D_x = 1.939$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 177 reflections
$\theta = 3$–23°
$\mu = 1.46$ mm^{-1}
$T = 152\ (2)$ K
Block, orange
0.50 × 0.48 × 0.12 mm

Data collection

Siemens SMART 1K CCD diffractometer
ω scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1996)
$T_{min} = 0.414$, $T_{max} = 0.872$
17620 measured reflections

7851 independent reflections
7426 reflections with $I > 2\sigma(I)$
$R_{int} = 0.089$
$\theta_{max} = 30.2^\circ$
$h = -14 \rightarrow 17$
$k = -14 \rightarrow 17$
$l = -18 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.140$
$S = 1.08$
7851 reflections
369 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 5P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 3.79$ e Å^{-3}
$\Delta\rho_{\min} = -3.26$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0052 (7)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H01A···O7$^{\rm i}$	0.89 (7)	1.92 (9)	2.749 (8)	153 (13)
O1—H01B···O5$^{\rm ii}$	0.88 (10)	1.84 (10)	2.710 (10)	168 (8)
O2—H02A···O7$^{\rm i}$	0.90 (7)	1.90 (10)	2.743 (9)	155 (11)
O2—H02B···O10$^{\rm iii}$	0.90 (13)	1.93 (12)	2.766 (10)	155 (8)
O3—H03A···O9	0.88 (8)	1.96 (7)	2.774 (7)	154 (8)
O3—H03B···O9$^{\rm ii}$	0.90 (11)	1.89 (11)	2.773 (10)	167 (8)
O4—H04A···O10	0.88 (4)	1.92 (6)	2.748 (7)	154 (9)
O4—H04B···O6$^{\rm iv}$	0.89 (12)	1.86 (12)	2.732 (11)	165 (11)

Symmetry codes: (i) $1+x, 1+y, z$; (ii) $1-x, -y, 1-z$; (iii) $1-x, 1-y, 1-z$; (iv) $-x, -y, 1-z$.

H atoms on the cyclooctadiene rings were geometrically positioned and refined as riding, using fixed distances; Csp^2—H = 0.95 Å and Csp^3—H = 0.99 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The positions of the H atoms of the water molecules were calculated to produce linear hydrogen bonds, and were refined using an O—H distance restraint of 0.90 (3) Å, an H···H distance restraint of 1.45 (3) Å within each water molecule and a fixed isotropic displacement parameter, $U_{\rm iso}$(H) = 0.045 Å^2. The crystal was twinned. Each reflection hkl approximately coincides with a reflection $\overline{khl}$ of the second domain. A large peak width was used for the integration of the reflection profiles to account for both the main and the twin peak. The twin fraction refined to 0.3753 (15). The largest residual density was found within 0.9 Å of the Rh atoms.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

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