Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.106$
$S = 1.283$
1076 reflections
60 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0673P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.015$
$\Delta\rho_{\max} = 1.82$ e Å^{-3} (< 1.3 Å from Pt)
$\Delta\rho_{\min} = -3.05$ e Å^{-3} (< 1.3 Å from Pt)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Pt	0	0	1/2	0.0260 (2)
Cl11	−0.2011 (2)	0.03781 (8)	0.2642 (2)	0.0410 (3)
Cl12	−0.1139 (2)	−0.13918 (11)	1/2	0.0385 (4)
Cl2	0.0512 (4)	−0.3695 (2)	1/2	0.0610 (7)
N1	0.3991 (9)	−0.3520 (4)	1/2	0.046 (2)
C5	0.5245 (11)	−0.2872 (8)	1/2	0.047 (2)
C2	0.2438 (10)	−0.3162 (5)	1/2	0.037 (2)
N3	0.2619 (10)	−0.2335 (5)	1/2	0.057 (2)
C4	0.4368 (13)	−0.2125 (6)	1/2	0.046 (2)

Table 2. *Selected geometric parameters (Å, °)*

Pt—Cl11	2.319 (1)	N1—C5	1.385 (13)
Pt—Cl12	2.328 (2)	C5—C4	1.338 (14)
Cl2—C2	1.681 (8)	C2—N3	1.292 (10)
N1—C2	1.305 (10)	N3—C4	1.368 (12)
Cl11—Pt—Cl11$^{\rm i}$	89.80 (7)	N3—C2—Cl2	125.6 (7)
Cl11—Pt—Cl12	89.44 (5)	N1—C2—Cl2	125.2 (6)
C2—N1—C5	108.2 (7)	C2—N3—C4	109.9 (7)
C4—C5—N1	106.7 (8)	C5—C4—N3	106.1 (8)
N3—C2—N1	109.1 (8)		

Symmetry code: (i) $-x, -y, z$.

Data collection: local program (Zanotti, 1983). Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93 and *PARST*83 (Nardelli, 1983).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1347). Services for accessing these data are described at the back of the journal.

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Bis(acetylacetonato-*O*,*O*′)(η^4-*trans*-2,4-hexadiene)ruthenium(II) 1/6-Ethanol Solvate

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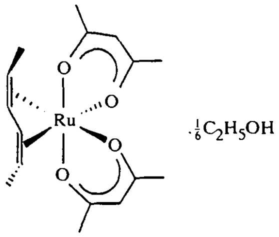
Abstract

The title compound, $[\mathrm{Ru(C_5H_7O_2)_2(C_6H_{10})}].1/6\mathrm{C_2H_6O}$, has a pseudo-octahedrally coordinated Ru$^{\rm II}$ center, where two coordination sites are occupied by a diene ligand. The diene ligand exhibits a η^4-*trans*-diene coordination mode. The compound crystallizes in space group $R\bar{3}$, incorporating disordered ethanol in cylindrical voids.

Comment

Current interest in transition metal diene complexes arises from their potential use as synthetic intermediates in the preparation of non-trivial products that are not readily accessible by conventional organic synthesis methods. The relationship between conformation and reactivity patterns of diene ligands attached to metal centers has been studied for many years. In fact, it has been demonstrated that there exist distinct reactivity profiles between a conjugated diene coordinated in a *cis versus* a *trans* conformation (Yasuda & Nakamura, 1987; Nakamura *et al.*, 1983).

While structural studies of metal complexes containing η^4-*cis*-dienes are extensive, structural data concerning η^4-*trans*-diene coordination are limited (Erker *et al.*, 1980, 1985; Kai *et al.*, 1982; Hunter *et al.*, 1985; Meléndez *et al.*, 1988, 1996; Ernst *et al.*, 1991; Sugaya *et al.*, 1996). As part of our research program aimed at the elucidation of structure and reactivity relationships of metal–diene complexes, we have carried out an X-ray single-crystal analysis of $Ru(acac)_2(\eta^4$-2,4-hexadiene).-1/6-ethanol, (1).



(1)

The X-ray analysis of (1) shows that the Ru center has pseudo-octahedral coordination geometry, two coordination sites being occupied by the diene ligand, which adopts the less common η^4-*trans*-diene coordination mode. The intraligand (*cis*) Ru–acac angles [O2—Ru—O1 92.6 (2) and O3—Ru—O4 92.83 (14)°] are slightly larger than expected (90°). On the other hand, the interligand *cis* and *trans* angles deviate substantially, showing contractions, from the ideal values of 180 and 90°; the *trans* O2—Ru—O4 angle is 176.06 (15), while the *cis* angles are O2—Ru—O3 83.82 (14), O1—Ru—O3 83.02 (15) and O1—Ru—O4 85.0 (2)°.

The diene ligand is non-planar with a C12—C13—C14—C15 torsion angle of 124 (1)°, which is similar to the typical torsion angles for η^4-*trans* diene coordination [122–127° (Kai *et al.*, 1982; Hunter *et al.*, 1985; Meléndez *et al.*, 1988, 1996; Ernst *et al.*, 1991; Erker *et al.*, 1985)]. The C—C bond distances within the diene follow a short–long–short pattern. The Ru—C bond distances of the Ru–diene interaction reveal a pattern of Ru—C(internal) < Ru—C(terminal). Interestingly, even though the diene is attached in the *trans* conformation, it has similar C—C and Ru—C bonding patterns to those of the η^4-*cis*-diene coordination of a previously reported $Ru(acac)_2$(1,3-cyclohexadiene) complex (Ernst *et al.*, 1991).

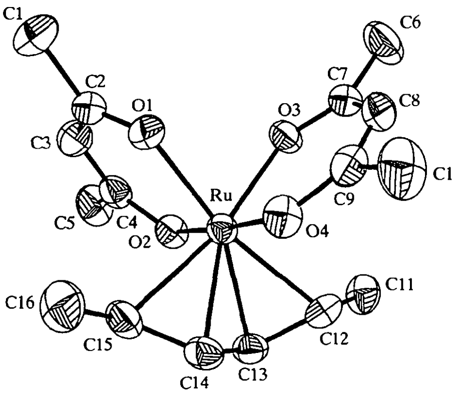


Fig. 1. The solid-state structure of $Ru(acac)_2(\eta^4$-*trans*-2,4-hexadiene) drawn with 35% probability displacement ellipsoids. H atoms and co-crystallized solvent have been omitted for clarity.

In the packing of the unit cell, circular arrays of six complex molecules are stacked throughout the crystal lattice, thus creating cylindrical void spaces. This void volume in the lattice is occupied by co-crystallized ethanol, disordered both rotationally along its axis and end-for-end with the methyl C atom located at an inversion point.

Experimental

The title compound was prepared according to a published procedure (Ernst *et al.*, 1991), substituting anhydrous ethanol by 95% ethanol. After crystallization in hexane at 268 K for 24 h, orange single crystals suitable for X-ray diffraction were obtained. Spectroscopic data are identical to those published previously (Ernst *et al.*, 1991).

Crystal data

$[Ru(C_5H_7O_2)_2(C_6H_{10})]$.-
$1/6C_2H_6O$
$M_r = 389.10$
Trigonal
$R\bar{3}$
$a = 31.877\ (7)$ Å
$c = 9.6140\ (10)$ Å
$V = 8460\ (3)$ Å^3
$Z = 18$
$D_x = 1.375$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 10$–12°
$\mu = 0.847$ mm^{-1}
$T = 296\ (2)$ K
Prism
0.40 × 0.30 × 0.30 mm
Orange

Data collection

Siemens *P*4 diffractometer
θ–2θ scans
Absorption correction:
ψ scan (North *et al.*, 1968)
$T_{min} = 0.647$, $T_{max} = 0.776$
6446 measured reflections
4311 independent reflections
2687 reflections with $I > 2\sigma(I)$

$R_{int} = 0.048$
$\theta_{max} = 27.50°$
$h = -35 \rightarrow 32$
$k = -41 \rightarrow 0$
$l = 0 \rightarrow 12$
3 standard reflections
every 197 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.126$
$S = 1.018$
4306 reflections
198 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 3.3198P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.498$ e Å^{-3}
$\Delta\rho_{min} = -0.470$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (*Å*^{2})

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

	x	y	z	U_{eq}
Ru	0.440237 (14)	0.121027 (14)	0.61647 (4)	0.03826 (14)
O1	0.49816 (13)	0.15941 (13)	0.4853 (4)	0.0553 (10)
O2	0.46300 (13)	0.07303 (12)	0.6680 (4)	0.0475 (9)
O3	0.48904 (12)	0.16375 (13)	0.7663 (4)	0.0492 (9)
O4	0.42223 (14)	0.17271 (13)	0.5682 (4)	0.0515 (9)
C1	0.5672 (2)	0.1783 (3)	0.3541 (8)	0.094 (3)
C2	0.5287 (2)	0.1454 (2)	0.4572 (6)	0.059 (2)
C3	0.5289 (2)	0.1049 (2)	0.5114 (7)	0.066 (2)
C4	0.4991 (2)	0.0732 (2)	0.6116 (6)	0.0534 (15)
C5	0.5087 (2)	0.0342 (2)	0.6653 (7)	0.077 (2)
C6	0.5284 (3)	0.2286 (2)	0.9222 (7)	0.085 (2)
C7	0.4936 (2)	0.2041 (2)	0.8052 (6)	0.0549 (15)
C8	0.4686 (2)	0.2260 (2)	0.7495 (7)	0.059 (2)
C9	0.4366 (2)	0.2110 (2)	0.6385 (6)	0.0527 (14)
C10	0.4155 (3)	0.2422 (2)	0.5959 (8)	0.085 (2)
C11	0.3923 (2)	0.0904 (2)	0.9246 (6)	0.061 (2)
C12	0.3817 (2)	0.0967 (2)	0.7774 (6)	0.0509 (14)
C13	0.3726 (2)	0.0625 (2)	0.6754 (6)	0.0489 (13)
C14	0.3708 (2)	0.0754 (2)	0.5341 (6)	0.0512 (14)
C15	0.4012 (2)	0.0718 (2)	0.4395 (6)	0.0566 (15)
C16	0.4085 (3)	0.0903 (3)	0.2932 (6)	0.083 (2)
O91†	0	0	0.2812 (5)	0.25 (1)
C92†	0	0	1.854 (8)	0.27 (5)
C93	0	0	0	0.26 (3)

† Site occupancy = 0.50.

Table 2. *Selected geometric parameters (Å, °)*

Ru—O4	2.051 (3)	Ru—C12	2.242 (5)
Ru—O2	2.055 (3)	C9—C10	1.509 (8)
Ru—O3	2.057 (3)	C11—C12	1.491 (7)
Ru—O1	2.058 (4)	C12—C13	1.385 (7)
Ru—C14	2.104 (5)	C13—C14	1.429 (7)
Ru—C13	2.104 (5)	C14—C15	1.376 (7)
Ru—C15	2.226 (5)	C15—C16	1.498 (8)
O4—Ru—O2	176.06 (15)	O3—Ru—O1	83.02 (15)
O4—Ru—O3	92.83 (14)	C13—C12—C11	122.6 (5)
O2—Ru—O3	83.82 (14)	C12—C13—C14	118.0 (5)
O4—Ru—O1	85.0 (2)	C15—C14—C13	118.2 (5)
O2—Ru—O1	92.6 (2)	C14—C15—C16	124.3 (6)

Three peaks in the penultimate difference map not associated with the complex were found in a cylindrical void along the threefold axis having an approximate diameter of 5 Å, each peak with an electron density of 1.4 e Å^{-3}. These peaks were assigned as a disordered co-crystallized ethanol molecule of solvation. The disordered solvent molecule was refined without H atoms. All non-H atoms were refined with anisotropic displacement parameters. The remaining H atoms were treated as idealized contributions constrained to the attached non-H atom using a riding model.

All software and sources of the scattering factors are contained in the *SHELXTL* (5.03) program library (Sheldrick, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1341). Services for accessing these data are described at the back of the journal.

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catena-Poly[[(di-2-pyridyl-*N*-amine)(propionato-*O*,*O*′)copper(II)]-μ-nitrato-*O*:*O*′]

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Abstract

The title compound, [Cu(NO$_3$)(C$_3$H$_5$O$_2$)(C$_{10}$H$_9$N$_3$)], contains infinite chains of a six-coordinate CuN$_2$O$_2$O$'_2$ chromophore. The molecular chromophore has a distorted octahedral structure, with symmetrically bonding di-2-pyridylamine (dpyam) and bidentate propionate groups defining an equatorial O$_2$N$_2$ plane, and axial O

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