

Bis[μ -4-(ethylammoniomethyl)-3,5-dimethylpyrazolato- $\kappa^2 N^1:N^2$]bis[(η^4 -1,5-cyclooctadiene)rhodium(I)] dichloride dichloromethane methanol solvate

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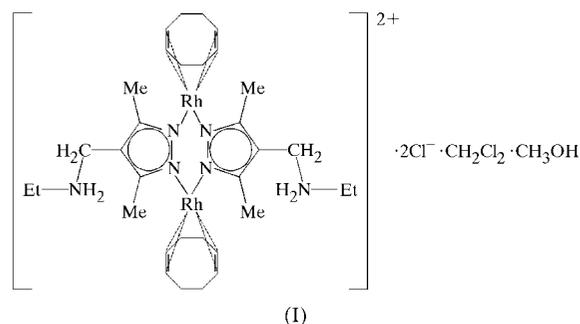
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In the title compound, $[\text{Rh}_2(\text{C}_8\text{H}_{15}\text{N}_3)_2(\text{C}_8\text{H}_{12})_2]\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{CH}_3\text{OH}$, the dinuclear Rh^{I} complex has C_2 symmetry and the two pyrazolato ligands act as μ -bridges. The coordination of each Rh^{I} cation is completed by one cyclooctadiene (COD) ligand. It is shown that the average $\text{Rh}-\text{C}(\text{COD})$ distance is linearly dependent on the $\text{Rh}-\text{N}(\text{pyrazole})$ distance in this type of compound, and this is ascribed to the steric hindrance produced by the packing.

Comment

Research into the coordination chemistry of pyrazole-derived ligands has progressed rapidly over the last two decades. Mukherjee (2000) published an extensive review, completing those presented by La Monica & Ardizzioia (1997) and Trofimenko (1972, 1986, 1993). Only four structures of dinuclear rhodium(I) complexes with pyrazole bridges and



cyclooctadiene ligands (cod) (Louie *et al.*, 1984; Cano *et al.*, 1997; Esquiús *et al.*, 2000) are present in the Cambridge Structural Database (CSD, release of November 2001; Allen & Kennard, 1993). A feature of these compounds is the

variation of the $\text{Rh}-\text{C}$ and $\text{Rh}-\text{N}$ bond distances without a clear reason. In order to increase understanding of this distance variation, the title compound, (I), was prepared, which is similar to those previously published by Esquiús *et al.* (2000).

The molecular structure of (I) is shown in Fig. 1 and selected geometric details are given in Table 1. The structure of (I) consists of discrete molecules separated by van der Waals interactions and weak hydrogen bonds (Table 2).

The methanol molecules were located as disordered, and atom O1 seems to form a hydrogen bond with a Cl^- anion [$\text{O1} \cdots \text{Cl1}^{\text{i}}$ 3.118 (4) Å; symmetry code (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$]. Each Rh atom is linked to four C atoms of a cyclooctadiene ligand and two N atoms of two different pyrazole units. The pyrazole acts as a μ - N,N' -bridge between two Rh atoms. The

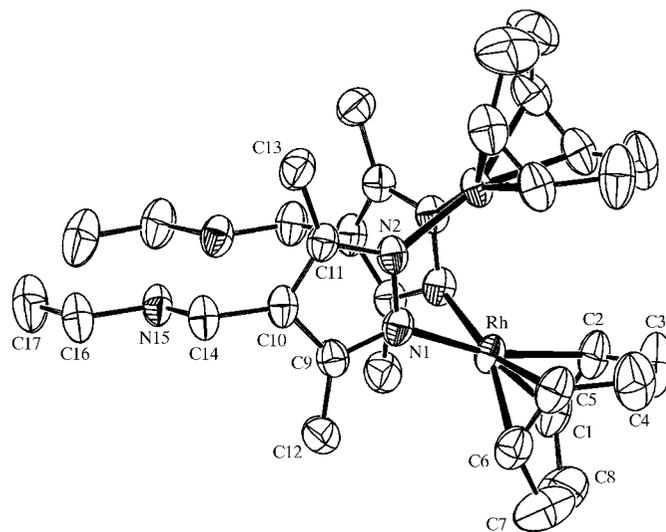


Figure 1

A view of the molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. The H atoms, the Cl^- anions and the dichloromethane and methanol solvent molecules have been omitted for clarity.

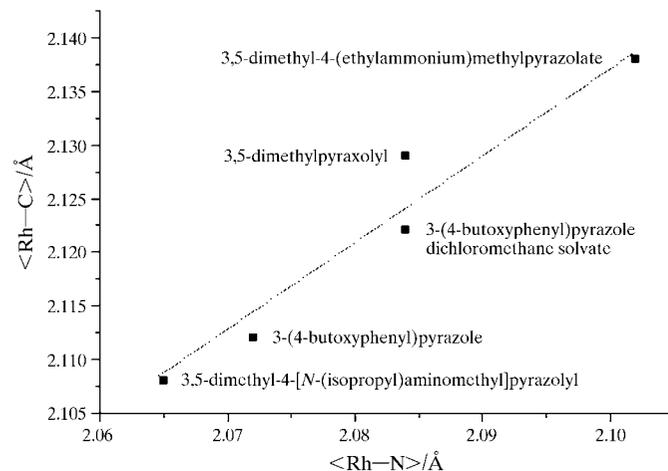


Figure 2

A graph of average $\text{Rh}-\text{C}$ versus average $\text{Rh}-\text{N}$ bond lengths in μ -pyrazole- $[\text{Rh}(\text{COD})_2]$ units.

Rh—N1—N2—Rhⁱ torsion angle is 2.43 (19)°. The planarity of this moiety is similar to that observed when the pyrazole lacks a bulky substituent in position 4 (Louie *et al.*, 1984; Esquiús *et al.*, 2000). The dihedral angle between the Rh/N1/N2/Rhⁱ and pyrazole planes is 20.17 (10)°. The ethylammoniomethyl moiety is planar and twisted by 87.0 (2)° with respect to the pyrazole plane.

If the average Rh—C(COD) and Rh—N(pyrazole) lengths are compared, it is observed that <Rh—C> increases when <Rh—N> increases (Fig. 2), while the N—N and C—C lengths remain practically constant [average values in the five structures are 1.360 (7) and 1.375 (12) Å, respectively]. This suggests that the bond lengths involving the Rh atom are more affected by the steric hindrance of the packing than by electronic effects. This is corroborated by the two electronically more similar pyrazole ligands, 3,5-dimethyl-4-[N-(isopropyl)aminomethyl]pyrazolyl and 3,5-dimethyl-4-(ethylammonium)methylpyrazolate, presenting the upper and lower limiting values.

Experimental

To prepare (I), [RhCl(COD)]₂ (0.08 g, 0.16 mmol) dissolved in CH₂Cl₂ (5 ml) was added to a solution of 3,5-dimethyl-4-(ethylamino)methylpyrazole (0.08 g, 0.32 mmol) in CH₂Cl₂ (5 ml) and the mixture stirred for 15 h. The solvent was evaporated to dryness *in vacuo* and the residue was washed with Et₂O and dissolved in a minimum amount of CH₂Cl₂. The title complex was precipitated by adding hexane to the solution. A yellow–orange solid was filtered off and dried *in vacuo*. Crystals of (I) were obtained by evaporation of a methanol solution.

Crystal data

| | |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|
| [Rh ₂ (C ₈ H ₁₅ N ₃) ₂ (C ₈ H ₁₂) ₂]Cl ₂ ·CH ₂ Cl ₂ ·CH ₄ O | <i>D_x</i> = 1.492 Mg m ⁻³ |
| <i>M_r</i> = 916.52 | Mo <i>K</i> α radiation |
| Monoclinic, <i>C</i> ₂ / <i>c</i> | Cell parameters from 25 reflections |
| <i>a</i> = 12.587 (3) Å | <i>θ</i> = 12–21° |
| <i>b</i> = 25.762 (9) Å | <i>μ</i> = 1.11 mm ⁻¹ |
| <i>c</i> = 13.240 (13) Å | <i>T</i> = 293 (2) K |
| <i>β</i> = 108.24 (3)° | Prism, yellow–orange |
| <i>V</i> = 4078 (4) Å ³ | 0.2 × 0.1 × 0.1 mm |
| <i>Z</i> = 4 | |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|------------------------|-------------|------------------------|-------------|
| Rh—N ²ⁱ | 2.095 (2) | Rh—C1 | 2.142 (3) |
| Rh—N1 | 2.104 (2) | Rh—C5 | 2.144 (3) |
| Rh—C6 | 2.129 (3) | Rh—Rh ⁱ | 3.1579 (9) |
| Rh—C2 | 2.137 (2) | N1—N2 | 1.377 (3) |
| N2 ⁱ —Rh—N1 | 83.15 (9) | N2 ⁱ —Rh—C5 | 161.91 (10) |
| N2 ⁱ —Rh—C6 | 160.26 (10) | N1—Rh—C5 | 94.84 (10) |
| N1—Rh—C6 | 92.33 (10) | C6—Rh—C5 | 37.37 (11) |
| N2 ⁱ —Rh—C2 | 95.28 (11) | C2—Rh—C5 | 81.97 (12) |
| N1—Rh—C2 | 164.91 (10) | C1—Rh—C5 | 94.66 (12) |
| C6—Rh—C2 | 93.91 (12) | C9—N1—Rh | 130.93 (15) |
| N2 ⁱ —Rh—C1 | 93.74 (11) | N2—N1—Rh | 116.59 (13) |
| N1—Rh—C1 | 157.72 (10) | C11—N2—Rh ⁱ | 133.54 (16) |
| C6—Rh—C1 | 83.17 (13) | N1—N2—Rh ⁱ | 113.59 (13) |
| C2—Rh—C1 | 37.17 (11) | | |

Symmetry code: (i) 1 - *x*, *y*, $\frac{1}{2}$ - *z*.

Table 2

Hydrogen-bonding geometry (Å, °).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| N15—H15...Cl1 | 0.90 (2) | 2.45 (2) | 3.286 (4) | 154 (3) |
| N15—H15A...Cl1 ⁱ | 0.90 (2) | 2.29 (2) | 3.188 (4) | 175 (2) |

Symmetry code: (i) 1 - *x*, *y*, $\frac{1}{2}$ - *z*.

Data collection

| | |
|-------------------------------------------------|-------------------------------|
| Enraf–Nonius CAD-4 diffractometer | <i>θ</i> _{max} = 30° |
| <i>ω</i> / <i>2θ</i> scans | <i>h</i> = -17 → 16 |
| 6120 measured reflections | <i>k</i> = 0 → 36 |
| 5860 independent reflections | <i>l</i> = 0 → 18 |
| 4234 reflections with <i>I</i> > 2σ(<i>I</i>) | 3 standard reflections |
| <i>R</i> _{int} = 0.061 | frequency: 120 min |
| | intensity decay: none |

Refinement

| | |
|-------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|
| Refinement on <i>F</i> ² | H atoms: see below |
| <i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.028 | <i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0406 <i>P</i>) ²] |
| <i>wR</i> (<i>F</i> ²) = 0.079 | where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3 |
| <i>S</i> = 0.98 | (Δ/σ) _{max} = 0.001 |
| 5860 reflections | Δρ _{max} = 0.58 e Å ⁻³ |
| 222 parameters | Δρ _{min} = -0.35 e Å ⁻³ |

Methanol atoms O1 and C19 were located from a difference Fourier synthesis. Their occupancy factor of 0.5 was assigned according to the peak heights. The molar ratio with respect to the remaining formula was confirmed by elemental analysis. The H atoms on N15 were refined freely. The positions of 27 H atoms were geometrically computed (C—H = 0.93–0.97 Å) and refined using a riding model, with *U*_{iso}(H) = 1.2*U*_{eq}(C). Dichloromethane H atoms were located from a difference Fourier synthesis, while methanol H atoms were not located.

Data collection: *CAD-4/PC* (Kretschmar, 1996); cell refinement: *CAD-4/PC*; data reduction: *CFEO* (Solans, 1978); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3.2* (Brueggemann & Schmid, 1990); software used to prepare material for publication: *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1049). Services for accessing these data are described at the back of the journal.

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