

A pyrazine bis-adduct of a binuclear rhodium(II) carboxylate containing 3,4,5-triethoxybenzoate as the equatorial ligand

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Received 19 March 2002

Accepted 27 May 2002

Online 20 June 2002

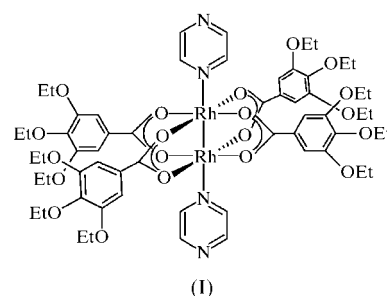
The title compound, tetrakis(μ -3,4,5-triethoxybenzoato- $\kappa^2O:O'$)bis[(pyrazine- κN)rhodium(II)]($Rh-Rh$), $[\text{Rh}_2(\text{C}_{13}\text{H}_{17}\text{O}_5)_4(\text{C}_4\text{H}_4\text{N}_2)_2]$, crystallizes on an inversion centre in the triclinic space group $P\bar{1}$. The equatorial carboxylate ligands bridge the two Rh^{II} atoms, giving a binuclear lantern-like structure. The pyrazine molecules occupy the two axial coordination sites. The phenyl rings are tilted by *ca* 10° with respect to the attached carboxylate groups. The pyrazine planes have a torsion angle of *ca* 19° around the $\text{Rh}-\text{N}$ bond with respect to the plane of the nearer carboxylate group and are not coplanar with the $\text{Rh}-\text{Rh}$ bond.

Comment

Lantern-type dirhodium carboxylates of the general formula $[\text{Rh}_2^{\text{II,II}}(\text{O}_2\text{CR})_4L_2]$ (L are axial ligands) have been the subject of numerous investigations focusing on their catalytic properties, antitumour activity, molecular and electronic structure, spectroscopic features and chemical reactivity (Norman *et al.*, 1979; Christoph & Koh, 1979; Boyar & Robinson, 1983; Cotton & Walton, 1992; Kitamura *et al.*, 2000). Moreover, their use as building blocks in the synthesis of advanced materials has received increasing attention (Marchon *et al.*, 1992; Barberá *et al.*, 1992; Bonar-Law *et al.*, 2000; Rusjan *et al.*, 2002). We have recently found that coordination polymers formed from dirhodium subunits linked by axial pyrazine ligands have interesting liquid-crystalline properties if the equatorial ligands are bulky carboxylates. We have suggested supramo-

lecular models to explain the structural features of the mesophases formed (Rusjan *et al.*, 2002).

Although molecular structures have been reported for many rhodium bis-adducts, they mainly involve aliphatic equatorial carboxylates (Christoph & Koh, 1979; Kitamura *et al.*, 2000). As far as we know, the only published structures of dirhodium tetrabenzoate *N*-heterocyclic bis-adducts are those of $[\text{Rh}_2(\text{O}_2\text{CPh})_4(\text{C}_5\text{H}_5\text{N})_2]$ (Mehmet & Tocher, 1991) and $[\text{Rh}_2(\text{TTB})_4(\text{C}_5\text{H}_5\text{N})_2]$, where TTB is 2,4,6-tri-*p*-tolylbenzoate (Callot *et al.*, 1989). Pyrazine bis-adducts of rhodium tetracarboxylates are rare, and only one aliphatic pyrazine derivative, $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\{2-(1\text{-pyrrolyl})\text{pyrazine}\}_2]$, has been published (Viossat *et al.*, 1993). In order to understand the liquid-crystalline properties better, the structure of the title compound, (I), has been determined.

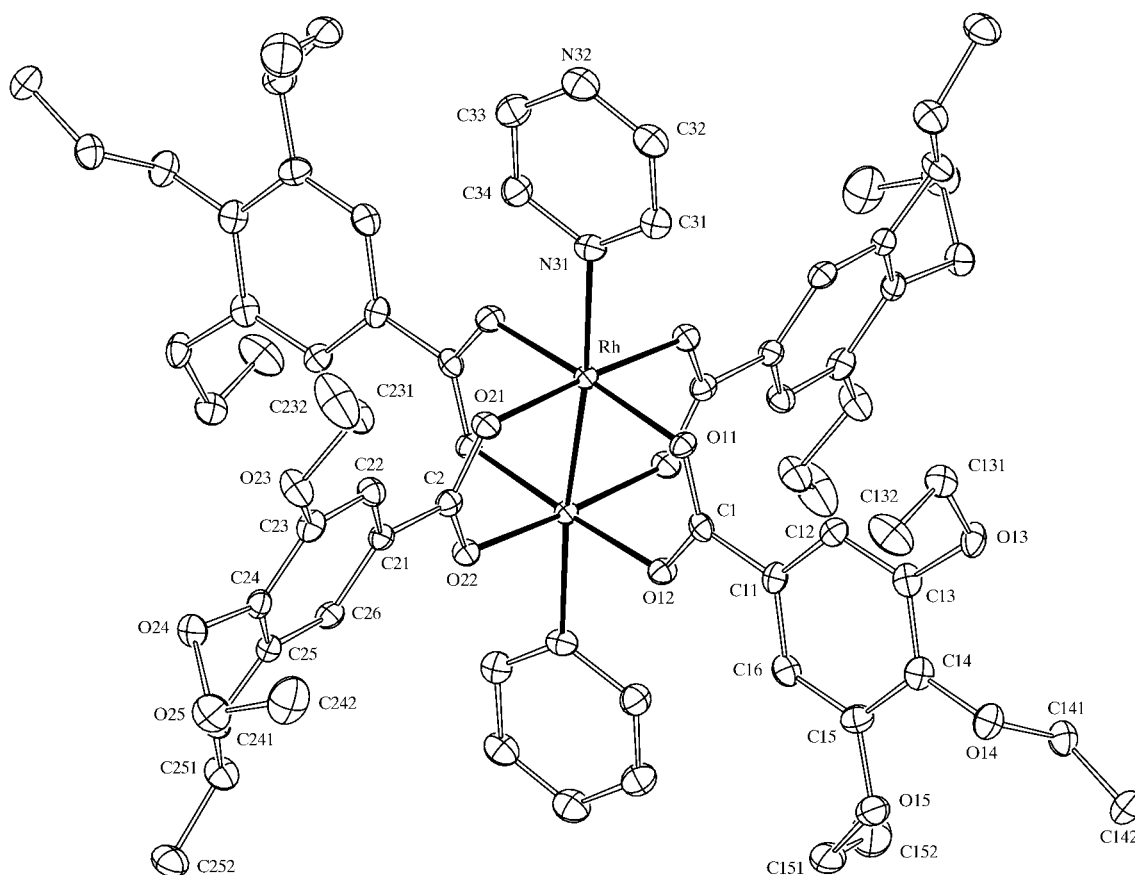


Complex (I) is located on a crystallographic inversion centre. Each Rh atom is in a slightly distorted octahedral environment (Fig. 1 and Table 1). The values of the $\text{Rh}-\text{Rh}$, $\text{Rh}-\text{N}31$ and mean $\text{Rh}-\text{O}$ bonds are typical for this kind of compound, and are very close to those found for $[\text{Rh}_2(\text{O}_2\text{CPh})_4(\text{C}_5\text{H}_5\text{N})_2]$ [2.402 (1), 2.247 (4) and 2.041 (3) Å, respectively; Mehmet & Tocher, 1991] and $[\text{Rh}_2(\text{TTB})_4(\text{C}_5\text{H}_5\text{N})_2]$ [2.374 (1), 2.25 (4) and 2.050 (8) Å, respectively; Callot *et al.*, 1989]. The distances and angles in (I) are also in the normal range for analogous amine bis-adducts (Cotton & Walton, 1992; Bonar-Law *et al.*, 2000; Kitamura *et al.*, 2000).

The phenyl rings of the equatorial ligands are tilted by *ca* 10° with respect to the planes of their carboxylate groups. Moreover, the ethoxy substituents have different conformations in the two independent benzoate groups. In one of them, the 3- and 5-alkoxy chains are in the plane of the phenyl ring, in a zigzag *trans* conformation [C23—O23—C231—C232 and C25—O25—C251—C252 torsion angles of 169.1 (3) and 169.0 (2)°, respectively], while the 4-alkoxy chain adopts a *gauche* conformation [C24—O24—C241—C242 torsion angle of 68.3 (3)°]. In the other benzoate ligand, the 3- and 5-alkoxy chains adopt *gauche* conformations [C13—O13—C131—C132 and C15—O15—C151—C152 torsion angles of 66.3 (3) and 73.6 (4)°, respectively], pointing towards opposite sides of the phenyl-ring plane, while the 4-substituent has a *trans* conformation [C14—O14—C141—C142 torsion angle of 168.5 (2)°].

The pyrazine (Pz) rings have a torsion angle of *ca* 18.5° around the $\text{Rh}-\text{N}31$ bond with respect to the plane of the nearer carboxylate group, and they are non-coplanar with the $\text{Rh}-\text{Rh}$ axis [$\text{Rh}-\text{Rh}-\text{N}31$ and $\text{Rh}-\text{N}31-\text{N}32$ angles of 174.57 (6) and 175.3 (1)°, respectively], as has already been observed for other related compounds (Mehmet & Tocher,

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Figure 1

A view of the title binuclear complex, (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Rh–ligand and Rh–Rh bonds are indicated by full lines.

1991; Cotton *et al.*, 1992; Miyasaka *et al.*, 2001), but not seen for Viossat's pyrazine-derivative bis-adduct (Viossat *et al.*, 1993). No comparisons can be made with the $[\text{Rh}_2(\text{TTB})_4(\text{C}_5\text{H}_5\text{N})_2]$ compound, where the axial pyridines are highly disordered (Callot *et al.*, 1989). The deviation from linearity of the Rh–Rh–N31 angle is comparable with that found in other systems exhibiting hydrogen bonds (Kitamura *et al.*, 2000) or H– π interactions (Bonar-Law *et al.*, 2000). However, no evidence of such interactions has been found in (I). Nevertheless, it supports the hypothesis suggested for the mesophase of the long-chain polymeric analogues, where non-linear Rh–Pz–Rh arrangements were proposed. The explanation of these features still remains open.

Experimental

The precursor compound, $[\text{Rh}_2(\text{O}_2\text{CC}_6\text{H}_2(\text{OC}_2\text{H}_5)_3)_4]$, was synthesized from commercial $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4]$ by a metathesis reaction in a twofold excess of the molten ligand for 4 h under an N_2 atmosphere. The compound was purified by washing with hot methanol, and then by dissolution in CHCl_3 and addition of methanol until precipitation of the light-blue methanolic bis-adduct occurred. Finally, the precipitate was dried under vacuum at 353 K until a green solid was obtained, due to the release of the axial ligands. When an excess of pyrazine was added to a solution of the complex in acetone, the

solution immediately turned red. Red crystals of (I) were obtained by slow evaporation of the solvent and were kept in contact with the mother liquor in order to prevent loss of pyrazine and subsequent degradation. This instability made other physicochemical assays difficult.

Crystal data

$[\text{Rh}_2(\text{C}_{13}\text{H}_{17}\text{O}_5)_4(\text{C}_4\text{H}_4\text{N}_2)_2]$
 $M_r = 1379.07$
 Triclinic, $P\bar{1}$
 $a = 7.780$ (1) Å
 $b = 13.056$ (1) Å
 $c = 15.245$ (1) Å
 $\alpha = 97.04$ (1)°
 $\beta = 93.48$ (1)°
 $\gamma = 94.23$ (1)°
 $V = 1528.9$ (3) Å³

$Z = 1$
 $D_x = 1.498$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 21 034 reflections
 $\theta = 1.0$ – 27.5°
 $\mu = 0.62$ mm⁻¹
 $T = 100$ (2) K
 Prism, red
 0.10 × 0.05 × 0.04 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: numerical (Coppens *et al.*, 1965)
 $T_{\min} = 0.930$, $T_{\max} = 0.979$
 19 184 measured reflections
 5375 independent reflections

4778 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.090$
 $\theta_{\text{max}} = 25^\circ$
 $h = -9 \rightarrow 9$
 $k = -15 \rightarrow 15$
 $l = -18 \rightarrow 18$
 Intensity decay: <2%

Table 1

Selected geometric parameters (Å, °).

Rh—O12 ⁱ	2.026 (2)	Rh—O11	2.056 (2)
Rh—O21	2.035 (2)	Rh—N31	2.252 (2)
Rh—O22 ⁱ	2.049 (2)	Rh—Rh ⁱ	2.4037 (4)
O12 ⁱ —Rh—O21	90.31 (8)	O22 ⁱ —Rh—N31	95.10 (8)
O12 ⁱ —Rh—O22 ⁱ	89.98 (7)	O11—Rh—N31	95.11 (8)
O21—Rh—O22 ⁱ	176.08 (7)	O12 ⁱ —Rh—Rh ⁱ	86.44 (5)
O12 ⁱ —Rh—O11	175.91 (7)	O21—Rh—Rh ⁱ	88.30 (5)
O21—Rh—O11	89.93 (8)	O22 ⁱ —Rh—Rh ⁱ	87.82 (5)
O22 ⁱ —Rh—O11	89.51 (7)	O11—Rh—Rh ⁱ	89.48 (5)
O12 ⁱ —Rh—N31	88.98 (8)	N31—Rh—Rh ⁱ	174.57 (6)
O21—Rh—N31	88.82 (8)		

Symmetry code: (i) 1 - x, 1 - y, 1 - z.

RefinementRefinement on F^2 $R(F) = 0.034$ $wR(F^2) = 0.087$ $S = 1.06$

5375 reflections

394 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 1.2037P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.016$$

$$\Delta\rho_{\max} = 0.73 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -1.24 \text{ e } \text{Å}^{-3}$$

All H atoms were located among the first 45 peaks of a difference Fourier map, but were positioned stereochemically and refined with a riding model, with C—H distances in the range 0.95–0.99 Å. Methyl H atoms were treated as rigid bodies and were allowed to rotate around the corresponding C—C bond. The largest peak and trough of the final difference map were located 1.23 and 0.94 Å, respectively, from the Rh atom.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

This work was supported by CONICET and the University of Buenos Aires (AX27), Argentina, and by FAPESP and

CNPq, Brazil. MR acknowledges CONICET for a PhD fellowship. FDC and OEP are members of the scientific staff of CONICET. The authors also thank the Cambridge Structural Database (Allen & Kennard, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1651). Services for accessing these data are described at the back of the journal.

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