

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

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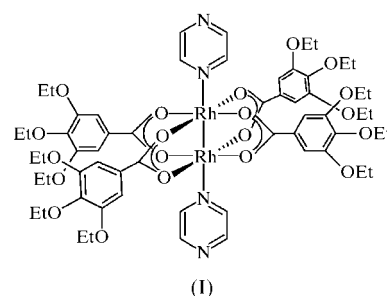
The title compound, tetrakis(μ -3,4,5-triethoxybenzoato- $\kappa^2O:O'$)bis[(pyrazine- κN)rhodium(II)]($Rh-Rh$), $[\text{Rh}_2(\text{C}_{13}\text{H}_{17}\text{O}_5)_4(\text{C}_4\text{H}_4\text{N}_2)_2]$, crystallizes on an inversion centre in the triclinic space group $P\bar{1}$. The equatorial carboxylate 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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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

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

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

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

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

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

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*.

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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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