

catena-Poly[[[tetrakis(μ -acetato- κ^2 O:O')dirhodium(II)]- μ -[1,3-bis-(dimethylamino)propan-2-ol- κ^2 N:N']] tetrahydrofuran hemisolvate]

Andrej Pevc,^a Alojz Demšar,^a Katsuyuki Aoki^b and Iztok Turel^{a*}

^aFaculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, PO Box 537, 1000 Ljubljana, Slovenia, and ^bDepartment of Materials Science, Faculty of Engineering, Toyohashi University of Technology, 1-1 Hibarigaoka, Tempakucho, Toyohashi-shi, Aichi 441-8580, Japan
Correspondence e-mail: iztok.turel@fkt.uni-lj.si

Received 8 September 2006

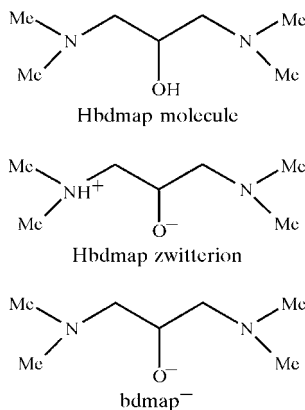
Accepted 4 October 2006

Online 31 October 2006

In the structure of the title compound, $\{[\text{Rh}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{C}_7\text{H}_{18}\text{N}_2\text{O})]\cdot 0.5\text{C}_4\text{H}_8\text{O}\}_n$ or $\{[\text{Rh}_2(\text{O}_2\text{CMe})_4(\text{Hbdmap})]\cdot 0.5\text{C}_4\text{H}_8\text{O}\}_n$, where Hbdmap is 1,3-bis(dimethylamino)propan-2-ol, each Hbdmap ligand is coordinated to two $[\text{Rh}_2(\text{O}_2\text{CMe})_4]$ units by two N atoms, resulting in a polymeric chain structure. The observed coordination mode of the Hbdmap molecule is unprecedented.

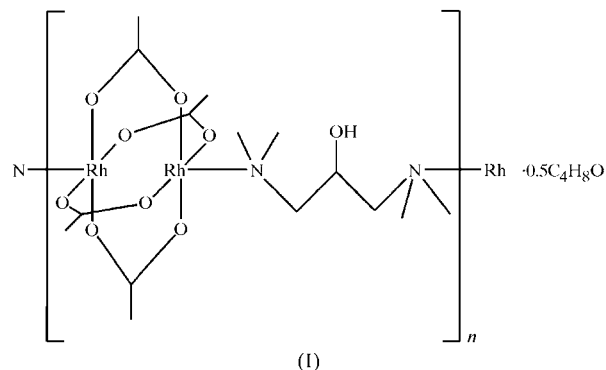
Comment

Much interest has been devoted to the dirhodium(II) carboxylates since 1960 with respect to their structure, reactivity and electronic properties. X-ray diffraction studies have revealed dimeric 'lantern' or 'paddlewheel' structures,



which also possess a metal-metal bond. The interest in dirhodium(II) carboxylates has been maintained in recent years especially as a result of their potential practical applications as antitumor agents and as catalysts in organic synthesis. The ability of dirhodium(II) carboxylates to form $[\text{Rh}_2(\text{O}_2\text{CR})_4L_n]$ ($n = 1$ or 2) complexes with the ligands (L) in

axial positions is well established (Boyar & Robinson, 1983; Cotton *et al.*, 1999). The largest class of such compounds are diadducts with discrete structure. Additionally, polymeric



structures comprising axial ligands with two binding sites are known (Cotton *et al.*, 1999, and references therein; Kim *et al.*, 2001). It is known that dirhodium(II) carboxylates interact with DNA, this possibly being the reason for their cytotoxic effect. Moreover, it is proposed that they can interact, through vacant axial positions, with adenine (at N7) but not with N9-substituted guanine and N1-substituted cytosine, this selectivity being due to intramolecular interligand interactions associated with the octahedral coordination environment about the Rh atom (Aoki & Yamazaki, 1984; Aoki & Salam, 2001, 2002). It is also reported that they can react, through

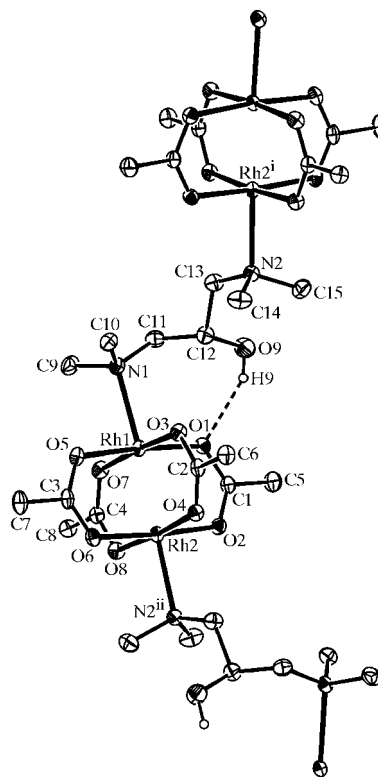


Figure 1

A view of the title compound, showing the atom-numbering scheme. Non-hydroxy H atoms and tetrahydrofuran solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. The dashed line indicates the intramolecular hydrogen bond. [Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.]

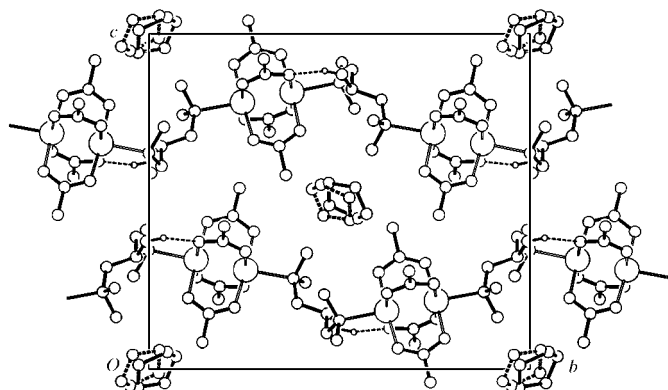


Figure 2
The disordered tetrahydrofuran molecules and polymeric chains in the structure of (I), viewed along the *a* axis.

equatorial positions, with guanine and adenine by displacing carboxylate ligands (Chifotides & Dunbar, 2005).

1,3-Bis(dimethylamino)propan-2-ol (Hbdmap) has two amine groups and one hydroxy group which can be readily deprotonated. Several complexes with deprotonated bdmap⁻ or zwitterionic Hbdmap (see first scheme above) as a ligand for metal ions have been isolated and structurally characterized. By far the highest in number of complexes with this ligand are copper(II) complexes (Wang *et al.*, 1992, 1993; Wang, 1996; El Fallah *et al.*, 2004), but complexes with Zr (Fleeting *et al.*, 1999), B (Huskens *et al.*, 1998), Ga (Sun *et al.*, 1999), Si (Lo *et al.*, 2004), Bi (Breeze *et al.*, 1996), Y (Guillon *et al.*, 2000), Zn (Demsar *et al.*, 2002) and Li (Henderson *et al.*, 1995) are also known. Additionally, several heterometallic complexes that contain two different metal ions in the structure are known. The reason for extensive work in the field may also be due to the possible interesting magnetic properties of the products or isolation of precursors for preparation of superconductors (Wang, 1998; Wang *et al.*, 1994, 1995). However, no structure was found where the Hbdmap molecule is bonded as a ligand to a dimetal carboxylate core.

The molecular structure of the title compound, (I) (Figs. 1 and 2, and Table 1), consists of a zigzag chain of dirhodium(II)-tetraacetate bridged by the Hbdmap molecule as a ligand. The chains run along the *b* axis with van der Waals interactions between the chains. The disordered tetrahydrofuran (THF) molecules occupy the vacancies in the structure. It is interesting to note that in the reaction of dicopper(II) acetate with Hbdmap, a tetranuclear complex, [Cu₄(OAc)₆(bdmap)₂(H₂O)₆]_n, was isolated (Wang *et al.*, 1992). Obviously, after coordination of anionic bdmap⁻ in this reaction, the dicopper-dicarboxylate core was converted to a polynuclear structure, where bdmap⁻ acts as a tridentate ligand. In our reaction between dirhodium(II) acetate and Hbdmap, the isolated product is structurally completely different. The basic dirhodium-dicarboxylate core remains intact, with an Rh...Rh distance of 2.4085 (5) Å, but Hbdmap is coordinated only in axial positions, through its terminal N atoms, to form a polymeric structure. A unique role of the Hbdmap hydroxy group was observed in this structure, *viz.* it is not involved in

coordination but participates in intramolecular O—H...O hydrogen bonding with an O atom from the dirhodium-dicarboxylate core (Table 2 and Fig. 1). The coordination of the Hbdmap molecule in the title compound represents, to the best of our knowledge, a new coordination mode of this ligand.

Experimental

The reaction was carried out under a nitrogen atmosphere using standard Schlenk line techniques. In a Schlenk flask, Rh₂(O₂CCH₃)₄ (52.4 mg) was suspended in THF (4.0 ml) and Hbdmap (17.0 mg) was added. The green suspension was stirred for 24 h. The resulting pink solution was filtered to remove traces of undissolved Rh₂(O₂CCH₃)₄. Pink crystals formed during slow evaporation of the solvent *in vacuo*.

Crystal data

[Rh ₂ (C ₂ H ₃ O ₂) ₄ (C ₇ H ₁₈ N ₂ O)]·0.5C ₄ H ₈ O	<i>V</i> = 2430.79 (9) Å ³
<i>M_r</i> = 624.28	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	<i>D_x</i> = 1.706 Mg m ⁻³
<i>a</i> = 8.4443 (2) Å	Mo <i>K</i> α radiation
<i>b</i> = 18.0873 (4) Å	<i>μ</i> = 1.41 mm ⁻¹
<i>c</i> = 15.9154 (3) Å	<i>T</i> = 150 (2) K
<i>β</i> = 90.3330 (9)°	Block, pink
	0.10 × 0.05 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer	10601 measured reflections
<i>ω</i> scans	5542 independent reflections
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)	4012 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T_{min}</i> = 0.872, <i>T_{max}</i> = 0.933	<i>R_{int}</i> = 0.037
	<i>θ_{max}</i> = 27.5°

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0172 <i>P</i>) ² + 4.6899 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.038	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>wR</i> (<i>F</i> ²) = 0.078	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.05	Δρ _{max} = 0.70 e Å ⁻³
5542 reflections	Δρ _{min} = -0.56 e Å ⁻³
307 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Rh1—O1	2.060 (3)	Rh2—O8	2.036 (2)
Rh1—O3	2.045 (2)	Rh2—N2 ⁱⁱ	2.307 (3)
Rh1—O5	2.028 (3)	N1—C9	1.475 (5)
Rh1—O7	2.030 (3)	N1—C10	1.475 (5)
Rh1—N1	2.321 (3)	N1—C11	1.483 (5)
Rh1—Rh2	2.4085 (5)	N2—C13	1.464 (5)
Rh2—O2	2.040 (3)	N2—C14	1.482 (5)
Rh2—O4	2.046 (2)	N2—C15	1.472 (5)
Rh2—O6	2.043 (3)	O9—C12	1.431 (5)
O5—Rh1—O7	89.46 (11)	N1—Rh1—Rh2	176.66 (8)
O5—Rh1—O3	89.81 (10)	O2—Rh2—O6	175.57 (11)
O5—Rh1—N1	88.40 (11)	O6—Rh2—O4	90.72 (10)
O7—Rh1—N1	91.67 (11)	O2—Rh2—Rh1	88.39 (8)

Symmetry code: (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

Table 2

Hydrogen-bond 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>
O9—H9...O1	0.84	2.16	2.884 (4)	145

All H atoms were positioned geometrically, fixing the C–H bond lengths at 0.98, 0.99 and 1.00 Å for CH₃, CH₂ and CH groups, respectively, and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$ [or $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms]. The H atom attached to the O atom was constrained to ride on the parent atom with an O–H distance of 0.84 Å and a $U_{\text{iso}}(\text{H})$ value of $1.5U_{\text{eq}}(\text{O})$. The THF solvent molecule is disordered over two sets of positions, which are related by a center of symmetry. The occupancy factor for each of atoms O10, C20, C30, C40 and C50 from the THF solvent molecule was set at 0.5 in the refinement.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported by the Japan Society for the Promotion of Science, and the Ministry of Higher Education, Science and Technology, Republic of Slovenia, through the scientific and technical collaboration between Japan and Slovenia, and also by project P1-0175.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3054). Services for accessing these data are described at the back of the journal.

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