Tetraethylammonium tetra-μ-benzamidato-κ⁴N:O;κ⁴O:N-dichlorodirhodate(II,III)(Rh—Rh) dichloromethane disolvate

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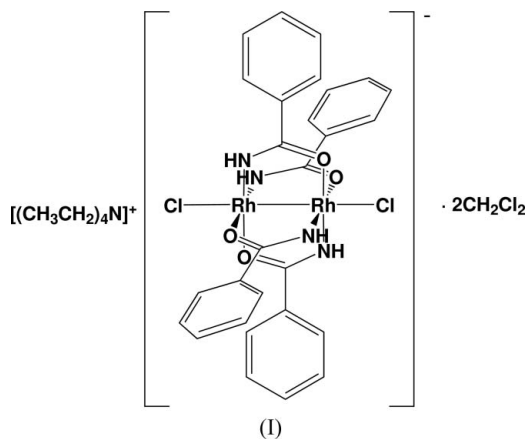Correspondence e-mail: ebihara@apchem.gifu-u.ac.jp

The title compound, $(C_8H_{20}N)[Rh_2(C_7H_6NO)_4Cl_2]\cdot 2CH_2Cl_2$, has the acetamidate-bridged-Rh_2 anion on an inversion centre. The tetraethylammonium cation is disordered on another inversion centre. The Rh—Rh bond distance is 2.4265 (13) Å; the metal atom shows octahedral coordination. The chloro ligands both occupy axial stes.

Comment

Paddlewheel dinuclear complexes are good modules for constructing assembled structures since they have linearly arranged axial sites. Halide ions are the most common linker ligands for cationic paddlewheel dinuclear complexes in the construction of chain structures, such as $[Ru_2(O_2CR)_4(\mu\text{-}Cl)]$ (Aquino, 1998, 2004). For dirhodium complexes, we have reported chain structures constructed from the acetamidate-bridged cationic complex and halide ions, $[Rh_2(acam)_4(\mu\text{-}X)]\cdot nH_2O$ (Hacam = acetamide; X = Cl, Br, I; n = 0, 2, 3, 7; Yang *et al.*, 2000, 2001). Discrete paddlewheel dirhodium complexes with chloro ligands may be important modules for the construction of assembled structures with metal cations, but so far examples have only been reported for the oxidation state Rh_2^{4+} (Miskowski *et al.*, 1984, 1987; Zhou *et al.*, 1991; Galdecka *et al.*, 1999). In this paper, we report the title dirhodium(II,III) complex with chloro ligands at both axial sites, $[(C_2H_5)_4N][Ru_2(bzam)_4Cl_2]\cdot 2CH_2Cl_2$, (I) (Hbzam = benzamide).

(I)

The structure of (I) is shown in Fig. 1. The dirhodium complex lies on an inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The tetraethylammonium ion lies on another inversion centre at $(0, \frac{1}{2}, 0)$. The Rh—Rh distance of 2.4265 (13) Å in (I) is similar to that in $[Rh_2(bzam)_4(py)_2]$ [2.437 (1) Å; Chakravarty *et al.*, 1985]. This small difference in the Rh—Rh distance between the

Rh_2^{4+} and Rh_2^{5+} complexes is consistent with the δ^* odd-electron orbital of amidate-bridged dirhodium complexes (Kawamura *et al.*, 1989, 1998). The Rh—Rh distance is also similar to those of the chloro-bridged chain structures of the Rh_2^{5+} complexes [$Rh_2(acam)_4Cl$] [2.428 (1) Å; Yang *et al.*, 2001] and [$Rh_2(acam)_4Cl$]·7H$_2$O [2.4172 (7) Å; Yang *et al.*, 2000].

The Rh—Cl distance of 2.5168 (16) Å is shorter than those observed in the chain complexes [$Rh_2(acam)_4Cl$] [2.581 (1) Å] and [$Rh_2(acam)_4Cl$]·7H$_2$O [2.564 (1) Å]. It is also shorter than that in the Rh_2^{4+} complexes [$C(NH_2)_3$]$_2$[$Rh_2(O_2CCH_3)_4Cl_2$] [2.5853 (6) Å; Miskowski *et al.*, 1987], Li$_2$[$Rh_2(O_2CCH_3)_4Cl_2$]·8H$_2$O [2.601 (1) Å; Miskowski *et al.*, 1984] and Na$_2$[$Rh_2(O_2CCH_3)_4Cl_2$]·4H$_2$O [2.564 (1) Å; Galdecka *et al.*, 1999].

Experimental

[$Rh_2(bzam)_4(py)_2$] (py = pyridine) was prepared using the literature method of Chakravarty *et al.* (1985). To a CH$_2$Cl$_2$ solution of [$Rh_2(bzam)_4(py)_2$] (0.090 g, 0.11 mmol), AgPF$_6$ (0.234 g, 0.93 mmol) in toluene (10 ml) was added. The resulting black precipitate was removed by filtration and the remaining solution was evaporated to dryness to afford the crude product, [$Rh_2(bzam)_4(py)_2$]PF$_6$. This crude product was washed with H$_2$O and toluene and dissolved in CH$_2$Cl$_2$. [$(C_2H_5)_4N$]Cl in CH$_2$Cl$_2$ was slowly diffused into a CH$_2$Cl$_2$ solution of [$Rh_2(bzam)_4(py)_4$]PF$_6$ to obtain crystals of (I).

Crystal data

($C_8H_{20}N$)[$Rh_2(C_7H_6NO)_4Cl_2$]·2CH$_2$Cl$_2$	$\gamma = 83.479$ (18)°
$M_r = 1057.33$	$V = 1107.1$ (10) Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 9.649$ (5) Å	$D_x = 1.586$ Mg m^{-3}
$b = 10.506$ (6) Å	Mo $K\alpha$ radiation
$c = 12.202$ (6) Å	$\mu = 1.15$ mm^{-1}
$\alpha = 76.571$ (16)°	$T = 173$ (2) K
$\beta = 66.996$ (13)°	Prism, brown
	$0.10 \times 0.10 \times 0.10$ mm

Data collection

Rigaku/MSC Mercury CCD area-detector diffractometer	5028 independent reflections
ω scans	4109 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{int} = 0.032$
9060 measured reflections	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 2.8887P]$
$R[F^2 > 2\sigma(F^2)] = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.07$	$\Delta\rho_{max} = 0.72$ e Å^{-3}
5028 reflections	$\Delta\rho_{min} = -0.80$ e Å^{-3}
270 parameters	
H-atom parameters constrained	

Table 1
Selected bond lengths (Å).

Rh1—Rh1^i	2.4266 (13)	Rh1—O2^i	2.043 (3)
Rh1—Cl1	2.5167 (16)	Rh1—N1	1.975 (3)
Rh1—O1^i	2.038 (3)	Rh1—N2	1.970 (3)

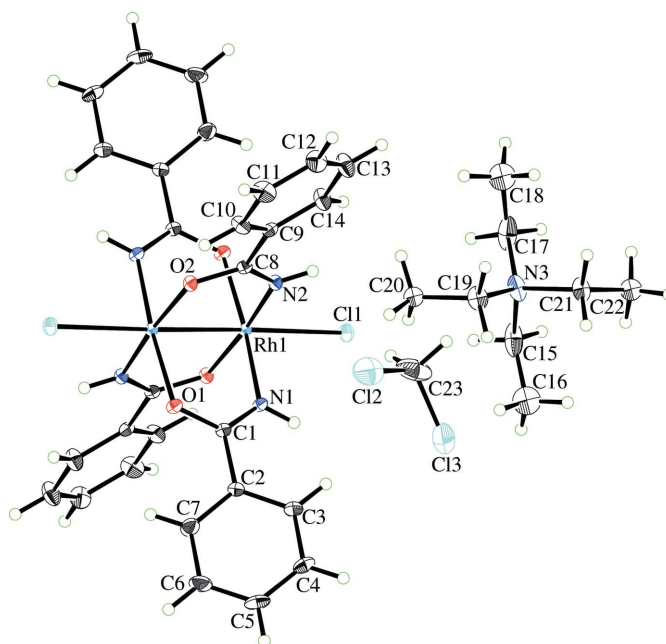Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabelled atoms are related to labelled atoms by $1 - x, 1 - y, 1 - z$.

The N—C and C—C distances in the tetraethylammonium ion were restrained (SADI, 0.005) and methyl C atoms were refined with isotropic displacement parameters. All H atoms were placed in idealized positions and treated as riding atoms, with C—H distances in the range 0.95–0.99 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$, and with N—H = 0.88 Å and $U_{iso}(H) = 1.2U_{eq}(N)$. The occupancy factors of all C atoms (C15–C22) in the disordered tetra-ethylammonium ion were set at 0.5.

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *TEXSAN*.

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