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A zigzag chain structure in *catena*-poly[[[tetra-μ-acetamidato-κ^4N:O;-κ^4O:N-dirhodium(II,III)]-μ-chloro] methanol solvate]

Masahiro Ebihara* and Yasuhiro Fuma

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan
Correspondence e-mail: ebihara@apchem.gifu-u.ac.jp

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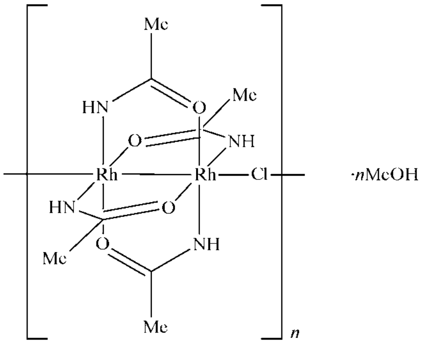
In $\{[Rh_2(C_2H_4NO)_4Cl]\cdot CH_3OH\}_n$, the cationic dirhodium complex and bridging chloro ligands form a one-dimensional zigzag chain, $[Rh_2(acam)_4(\mu\text{-}Cl)]$ (Hacam is acetamide). There is a large difference between the two Rh—Cl distances [2.6076 (14) and 2.5027 (14) Å]. Neighboring chains are connected by two N—H···O hydrogen bonds per link between the amidate ligands.

Comment

A halide-bridged one-dimensional chain is commonly observed in structures with metal–metal-bonded paddlewheel complexes, such as $K[Mo_2(O_2CH)_4Cl]$ (Robbins & Martin, 1984), $[Pt_2(S_2CR)_4I]$ (Bellitto *et al.*, 1983; Kitagawa *et al.*, 2001; Mitsumi *et al.*, 2002) and $[Ru_2(O_2CR)_4X]$ (X = Cl and Br; Angaridis, 2005). The chain in $K[Mo_2(O_2CH)_4Cl]$ is a zigzag one, that in $[Pt_2(S_2CR)_4I]$ is linear and $[Ru_2(O_2CR)_4X]$ contains both types. We have reported assemblies of acetamidate-bridged dirhodium paddlewheel complexes with halide linkers, *viz.* one-dimensional chain structures in $\{[Rh_2(acam)_4(\mu\text{-}X)]\cdot H_2O\}_n$ (Hacam is acetamide; X = Cl, Br and I; n = 0, 2, 3 and 7; Yang *et al.*, 2000, 2001), a two-dimensional honeycomb structure in $[\{Rh_2(acam)_4\}_3(\mu_3\text{-}Cl)_2]\cdot 4H_2O$ (Takazaki *et al.*, 2003) and a three-dimensional diamondoid structure in $[\{Rh_2(acam)_4\}_2(\mu_4\text{-}I)]\cdot 6H_2O$ (Fuma *et al.*, 2004). In the zigzag chain structure of $\{[Rh_2(acam)_4(\mu\text{-}X)]\cdot H_2O\}_n$, the Rh—Cl—Rh angle varies with the hydrogen bonding involving the water molecules. We have attempted to synthesize a chain structure with solvent molecules other than water. In this paper, we report the zigzag chain structure of $\{[Rh_2(acam)_4(\mu\text{-}Cl)]\cdot CH_3OH\}_n$, (I).

The structure of (I) is shown in Fig. 1. There are one independent $[Rh_2(acam)_4Cl]$ unit and one methanol molecule in the asymmetric unit. The bond distances in the $[Rh_2(acam)_4]$ skeleton are similar to those observed previously for the cationic $[Rh_2(acam)_4]$ unit (Yang *et al.*, 2000, 2001, 2006; Ebihara & Fuma, 2006; Baranovskii *et al.*, 1986). The $[Rh_2(acam)_4Cl]$ unit forms an infinite zigzag chain structure (Fig. 2) as in $[Rh_2(acam)_4(\mu\text{-}Cl)]$ and $[Rh_2(acam)_4(\mu\text{-}Cl)]\cdot 7H_2O$ (Yang *et al.*, 2000, 2001).



(I)

In the reported zigzag chain structures of $[M_2L_4X]$ [M = Ru and Rh, L = O_2CR and HN(O)CR, and X = Cl, Br and I; Bennett *et al.*, 1969; Togano *et al.*, 1980; Kimura *et al.*, 1982; Chakravarty & Cotton, 1985; Chakravarty *et al.*, 1985; Das & Chakravarty, 1991; Abe *et al.*, 1992; Barral *et al.*, 1998, 1999, 2000, 2004; Cukiernik *et al.*, 1998; Yang *et al.*, 2000, 2001], the dimetal unit usually lies on an inversion center or on a twofold axis. For example, in the chain structure of $[Rh_2(acam)_4(\mu\text{-}Cl)]$ (Yang *et al.*, 2001), which crystallizes in $C2/c$, the dirhodium unit lies on an inversion center and the Cl atom lies on a twofold axis. In the structure of $[Ru_2(O_2CC_6H_4OMe)_4Cl]$ (Das & Chakravarty, 1991), there are three independent diruthenium units, of which two lie on inversion centers and one occupies a general position. In the structure of (I), the chain is propagated along the c axis with each unit of the complex connected to adjacent units generated by the c-glide plane at $y = \frac{1}{4}$. Compound (I) is the first example of a zigzag chain

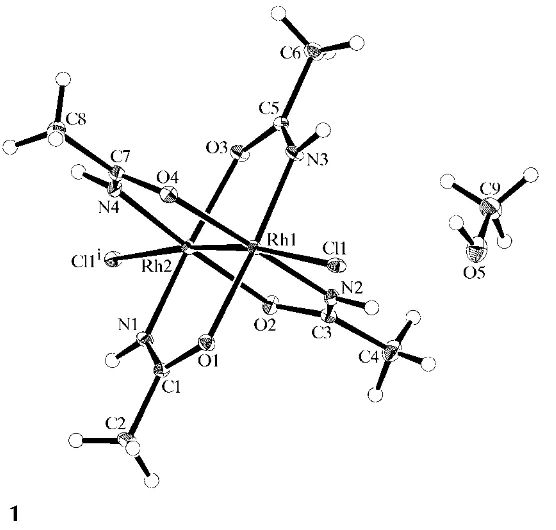


Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) x, $-y + \frac{1}{2}$, $-\frac{1}{2} + z$.]

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constructed from one independent paddlewheel complex that does not have any symmetry.

The Rh—Cl—Rh angles in [Rh$_2$(acam)$_4$(μ-Cl)] and [Rh$_2$(acam)$_4$(μ-Cl)]·7H$_2$O are 115.48 (10) and 153.50 (6)°, respectively. Since the corresponding angle in (I) is 114.59 (5)°, the chain structure in (I) more closely resembles that in [Rh$_2$(acam)$_4$(μ-Cl)]. Hydrogen bonds from the NH groups of the acam ligands to the O atoms of the next complexes along the chain [N1···O4^{i} and N3···O2^{ii}; symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; Table 2] also support the chain structure, as was observed in [Rh$_2$(acam)$_4$(μ-Cl)] (Yang *et al.*, 2001). The methanol molecule lies beside the chain, accepting a hydrogen bond from an N atom of an acam ligand (N2) and donating a hydrogen bond to an O atom of a neighboring complex (O2^{ii}).

The Rh—Rh—Cl angles in (I) (Table 1) are slightly more bent than that in [Rh$_2$(acam)$_4$(μ-Cl)] [174.52 (4)°]. The Rh1—Cl1 and Rh2—Cl1^{i} distances (Table 1) are both different from the corresponding value in [Rh$_2$(acam)$_4$(μ-Cl)] [2.581 (1) Å]. The difference between these Rh—Cl distances is very large (*ca* 0.1 Å). In the previously reported chain structures, the largest differences (*ca* 0.04 Å) between *M*—Cl bonds were observed in [Ru$_2${HN(O)CC$_6$H$_4$*R*}$_4$(μ-Cl)] [*R* = H (Chakravarty & Cotton, 1985) and *R* = Cl (Chakravarty *et al.*, 1985)]. The long–short pattern of the *M*—Cl bonds in the Cl—*MM*—Cl—*MM*—Cl unit is long–long–short–short for [Ru$_2${HN(O)CC$_6$H$_4$*R*}$_4$(μ-Cl)], since two independent diruthenium units lie on inversion centers, but long–short–long–short for (I).

The chains are mutually parallel and are connected to each other by a pair of hydrogen bonds [N4···O3^{iii} and N4^{iii}···O3; symmetry code: (iii) $-x+1, -y+1, -z+1$]. These interchain hydrogen bonds were not observed in other chain structures with amidate-bridged paddlewheel complexes (Chakravarty & Cotton, 1985; Chakravarty *et al.*, 1985; Yang *et al.*, 2000, 2001).

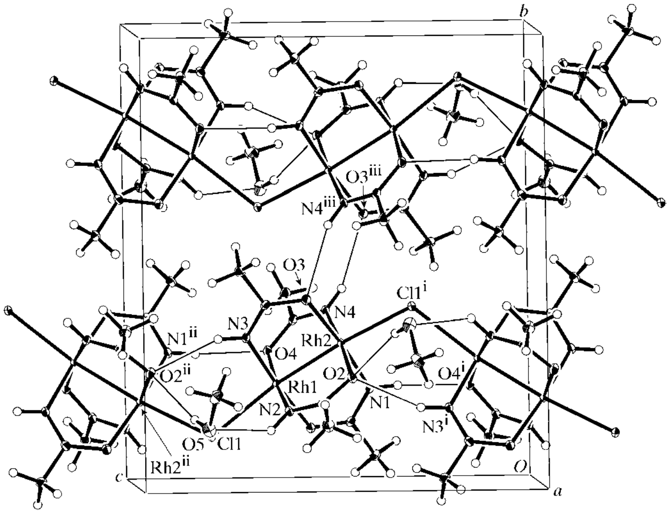

Figure 2
The crystal structure of (I). Hydrogen bonds are drawn as thin lines. [Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $-x+1, -y+1, -z+1$.]

Experimental

[Rh$_2$(acam)$_4$(H$_2$O)$_2$]ClO$_4$ was prepared according to the method described by Baranovskii *et al.* (1986). Into a methanol solution of [Rh$_2$(acam)$_4$(H$_2$O)$_2$]ClO$_4$ (3.1 mmol l^{-1}), a methanol solution of CoCl$_2$·6H$_2$O (0.21 mol l^{-1}) was diffused slowly. After several days, brown crystals of (I) were obtained.

Crystal data

[Rh$_2$(C$_2$H$_4$NO)$_4$Cl]·CH$_4$O
M_r = 505.56
Monoclinic, $P2_1/c$
a = 8.601 (4) Å
b = 14.254 (7) Å
c = 12.664 (7) Å
β = 98.854 (5)°
V = 1534.1 (13) Å^3
Z = 4
D_x = 2.189 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 2.35 mm^{-1}
T = 173 (2) K
Prism, brown
0.30 × 0.10 × 0.10 mm

Data collection

Rigaku/MSC Mercury CCD diffractometer
ω scans
Absorption correction: integration (*NUMABS*; Higashi, 1999)
$T_{\min}$ = 0.624, $T_{\max}$ = 0.755
12335 measured reflections
3496 independent reflections
3246 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.034
$\theta_{\max}$ = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.071
S = 1.17
3496 reflections
198 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2 + 3.6476P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.95 e Å^{-3}
$\Delta\rho_{\min}$ = −0.80 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Rh1—Rh2	2.4247 (11)	Rh2—Cl1^{i}	2.5027 (14)
Rh1—Cl1	2.6076 (14)	Rh2—O2	2.057 (3)
Rh1—O1	2.026 (3)	Rh2—O3	2.051 (3)
Rh1—O4	2.052 (3)	Rh2—N1	1.978 (3)
Rh1—N2	1.975 (3)	Rh2—N4	1.968 (3)
Rh1—N3	1.979 (3)		
Rh2—Rh1—Cl1	170.82 (2)	Rh2^{ii}—Cl1—Rh1	114.59 (5)
Rh1—Rh2—Cl1^{i}	173.94 (2)		
O1—Rh1—Rh2—N1	1.08 (12)	N3—Rh1—Rh2—O3	3.73 (12)
N2—Rh1—Rh2—O2	3.40 (12)	O4—Rh1—Rh2—N4	5.04 (12)

Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O4^{i}	0.88	2.30	3.180 (4)	175
N2—H2···O5	0.88	2.28	2.976 (5)	136
N3—H3···O2^{ii}	0.88	2.43	3.251 (5)	155
N4—H4···O3^{iii}	0.88	2.45	3.277 (4)	158
O5—H17···O2^{ii}	0.86 (6)	2.25 (6)	3.045 (4)	155 (5)

Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $-x+1, -y+1, -z+1$.

The positional parameters of the H atom attached to atom O5 were refined, with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O). All other H atoms were placed in idealized positions and treated as riding atoms, with C—H distances of 0.98 Å, N—H distances of 0.88 Å, and $U_{\rm iso}$(H) values of 1.5$U_{\rm eq}$(C) or 1.2$U_{\rm eq}$(N).

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3040). Services for accessing these data are described at the back of the journal.

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