Halide-Bridged Zigzag Chain of Tetrakis(acetamidato)dirhodium Cationic Radical Assisted by Hydrogen Bond

Zhiyong Yang, Tomoharu Fujinami, Masahiro Ebihara, Kiyohiko Nakajima,[†] Hiroshi Kitagawa,[††] and Takashi Kawamura*
Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193
[†]*Department of Chemistry, Aichi University of Education, Kariya, Aichi 448-8542*
[††]*Department of Chemistry, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8571*
[††]*Department of Materials Science, Japan Advanced Institute of Science & Technology*
Asahidai 1-1, Tatsunokuchi, Ishikawa 923-1292

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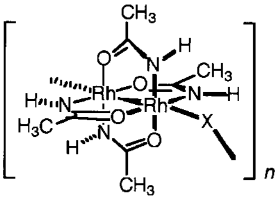
The reaction of a Rh_2^{5+} cationic radical salt, 2,2-*cis*-$[Rh_2(acam)_4(H_2O)_2]ClO_4$ (Hacam = acetamide), with sodium halides in aqueous solution gave crystals of $[Rh_2(acam)_4Cl]_n \cdot 7nH_2O$ and $[Rh_2(acam)_4Br]_n$, both of which consist of zigzag chain of $(–Rh–Rh–X–)_n$, which is supported by hydrogen bond between amidato–NH and amidato–O atoms for the chain of the bromide and between O atoms of amidato bridges through interstitial water molecules for the chloride chain.

Interaction between metal–metal bonds across ligand or directly is interesting from view points of material science, and some recent efforts have been reported for construction of low-dimensional arrangements of paddlewheel-type rhodium(II) dinuclear complexes.[1,2] Compounds with interactions between metal–metal bonds would be interesting especially when they have open-shell electronic structure.[3] Baranovskii and his co-workers examined oxidation of 2,2-*cis*-$[Rh_2(acam)_4]$ (**1**) with halogens. Based on elemental analyses and IR spectra, they reported isolation of $Rh_2(acam)_4Br \cdot Br_2$,[4] $Rh_2(acam)_4Br$,[4] $Rh_2(acam)_4Br \cdot 0.5H_2O$,[5] $Rh_2(acam)_4I$,[4] $Rh_2(acam)_4I \cdot H_2O$[5] and $Rh_2(acam)_4Cl$.[5] Initially a chain structure with bridging bromides at axial sites was proposed as a possibility for $Rh_2(acam)_4Br \cdot 0.5H_2O$.[4] However, a discrete structure with non-equivalent rhodium atoms and a bromide coordinated to only one of them was suggested as the most probable structure on the basis of its X-ray photoelectron study.[5] Since chain structures with bridging halide cannot be ruled out for this type of complexes, we prepared chloride and bromide salts of the cationic radical of **1**[6] and examined their structures by using X-ray diffraction method. Both of the halides have zigzag chain structures bridged by halide ions (Scheme 1) and assisted by hydrogen bond. These chain structures are the first example for the paddlewheel-type Rh_2^{5+} complexes to our best knowledge, although $(–M–M–Cl–)_n$ infinite zigzag chain structure has been known for chlorides of Ru_2^{5+} carboxylates and amidates.[7]

Scheme 1.



Upon reaction of 2,2-*cis*-$[Rh_2(acam)_4(H_2O)_2]ClO_4$ (**2**)[4] (100 mg, 0.17 mmol) with NaBr (50 mg, 0.48 mmol) in water (20 mL) at 40 °C, dark brown crystals precipitated out slowly in 48 h (yield 96%). The elemental analysis of the precipitate shows that it has the composition of $[Rh_2(acam)_4Br]_n$ (**3**).[8] The same material precipitated out when **2** reacted with NaBr in the mole-ratio range of 1 : 3 to 1 : 0.5, which shows that the precipitate with the present composition is a stable solid phase formed from **1**$^+$ and Br^- in water.

The crystal[9] consists of infinite zigzag chains of $(–Rh–Rh–Br–)_n$ (Figure 1) which are arranged mutually parallel. The Rh–Rh bond length is 2.4302(5) Å which is longer than those of a neutral compound, $[Rh_2(acam)_4(H_2O)_2] \cdot 3H_2O$ (**4**), (2.415(1) Å)[10] and the cationic radical, **2**, (2.399(1) Å).[4] Most probably this is due to enhanced σ-donation of the axial bromides into σ_{RhRh}^* orbital in comparison to the axial water ligands of the latter two complexes. The centers of the Rh–Rh bonds are located at crystallographic inversion centers, and the bromide ions are present on two-fold axes. All the Rh atoms are equivalent as are the bromide ions. A neighboring pair of $[Rh_2(acam)_4]^+$ units bridged by a bromide ion is supported doubly by hydrogen bonds. The hydrogen bond is formed between an N–H moiety of an acam ligand of a Rh_2^{5+} unit and an O atom of an acam ligand of the other unit. The N···O hydrogen-bond distance is 3.138(4) Å. No hydrogen-bond was found between the chains.

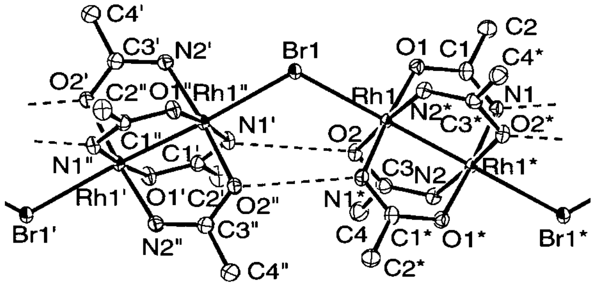


Figure 1. ORTEP drawing of the chain structure of $[Rh_2(HNCOCH_3)_4Br]_n$ (**3**) with thermal ellipsoids (50% probability). Broken line represents hydrogen bond. Selected bond distances (Å) and bond angles (degree): Rh1-Rh1* 2.4302(5), Rh1-Br1 2.6838(3), Rh1-O1 2.031(2), Rh1-O2 2.037(2), Rh1*-N1 1.982(3), Rh1*-N2 1.980(3), N1'···O2 3.138(4), Rh1*-Rh1-Br1 174.54(2), Rh1-Br1-Rh1" 113.81(2).

A chloride-bridged polymeric crystalline compound, $[Rh_2(acam)_4Cl]_n \cdot 7nH_2O$ (**5**), was obtained in 85% yield by reacting **2** with NaCl in aqueous solution at room temperature. This compound loses solvate water molecules quickly upon exposure to air at room temperature. The 1 : 1 constituent ratio of the Rh_2 unit and Cl ion was confirmed by the elemental analysis of the compound freed from the solvate molecules.[11] The X-ray diffraction data of a freshly prepared crystal of **5** was collected at –80 ˚C at which the crystal was stable.[12]

Crystal **5** also consists of infinite zigzag chains of $(\text{–Rh–Rh–Cl–})_n$ (Figure 2). The chains are arranged mutually parallel in the crystal. There are two types of Rh_2^{5+} units, which differ 0.0015(8) Å in their Rh–Rh bond lengths each other. These two types of units are connected alternately by chloride ligands at axial sites. All the water molecules in the crystal of **5** are involved in extensive hydrogen-bond network: N···O(water) hydrogen-bond lengths are in the range of 2.931(6)–3.038(6) Å, and O(water)···O(water or acam) in the range of 2.591(9)–2.855(6) Å. Most notable hydrogen bonds are those of O5 and O6 in Figure 2. Each of these two H_2O molecules bridges as a hydrogen donor between two acam–O atoms of a neighboring pair of Rh_2^{5+} units in a chain. The intra-chain acam–O···O(water) hydrogen-bond distances are in the range of 2.752(5) – 2.855(6) Å.

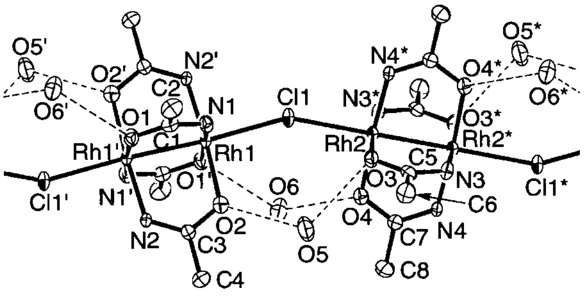


Figure 2. ORTEP drawing of the chain structure of $[Rh_2(HNCOCH_3)_4Cl]_n$-$\cdot 7nH_2O$ (**5**) with thermal ellipsoids (50% probability). Broken line represents hydrogen bond. Selected bond distances (Å) and bond angles (degree): Rh1-Rh1' 2.4171(4), Rh2-Rh2* 2.4156(4), Rh1-Cl1 2.564(1), Rh2-Cl1 2.554(1), Rh1-O1' 2.031(3), Rh1-O2 2.021(3), Rh2-O3 2.036(3), Rh2-O4 2.026(3), Rh1-N1 1.977(4), Rh1-N2' 1.997(4), Rh2-N3* 1.979(4), Rh2-N4* 1.989(4), O2···O5 2.752(5), O3···O5 2.855(6), O6···O1' 2.814(4), O4···O6 2.841(5), Rh1'-Rh1-Cl1 176.75(3), Rh2*-Rh2-Cl1 178.16(3), Rh1-Cl1-Rh2 153.41(6).

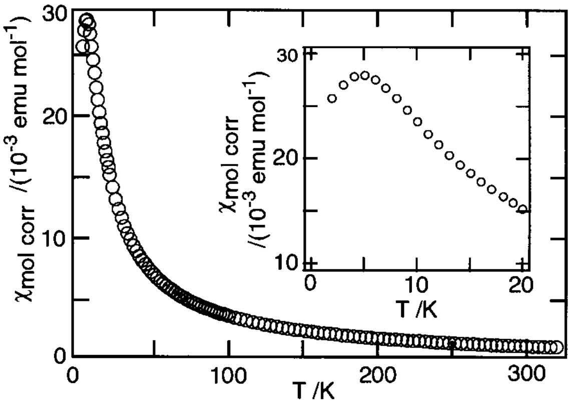


Figure 3. (a) Temperature dependence of molar magnetic susceptibility of $[Rh_2(HNCOCH_3)_4Br]_n$ (**3**). (b) Inset: An expansion of the dependence for a low-temperature region.

A frozen aqueous solution of $[Rh_2(acam)_4Br_2]^-$ (**6**), generated by mixing a dilute solution of **2** with a concentrated solution of NaBr, gave an axially symmetric ESR spectrum with g_{parallel} = 1.93 and $g_{\text{perpendicular}}$ = 2.12. This shows that the singly occupied molecular orbital (SOMO) of **6** is $\delta_{\text{RhRh}}*$.[13] The Rh–N and Rh–O bond lengths of **3** and **5** are shorter (0.025(10)–0.043(8) Å) than those of **4** and similar to those of **2**. These geometric characteristics are consistent with that the SOMO of the Rh_2^{5+} unit in **3** and **5** is also the $\delta_{\text{RhRh}}*$ orbital.[14]

Both of the electrical conductivities of powdered crystals of **3** and **5** were less than 2×10^{-7} S cm^{-1} (room temperature, pellets; the sample of **5** had lost some of its hydrate molecules during the measurement). The magnetic susceptibility of **3** measured at 1 T is shown in Figure 3. The molar magnetic susceptibility was corrected for the diamagnetic term calculated from the observed diamagnetic susceptibility of **1** and Pascal's constants. The Curie–Weiss plots of the corrected susceptibility in the temperature range of 20 – 60 K gave parameters of μ_{eff} = 1.78 μ_B and θ = –6 K for $\chi_{\text{mol corr}} = (N_A\ \mu_{\text{eff}}^2)/\{3k(T - \theta)\}$. Compound **3** is paramagnetic with weak antiferromagnetic interaction between neighboring Rh_2^{5+} units. The non-linear arrangement of $Rh_2^{5+}\text{–}Br^-\text{–}Rh_2^{5+}$ in **3** formally allows the $\delta_{\text{RhRh}}*$ SOMOs of the neighboring dirhodium units to interact each other through lone-pair orbitals of the bridging bromide. We suppose these orbital interactions would be one of origins for the weak antiferromagnetic interaction.

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References and Notes

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6 The neutral complex, **1**, was prepared by following the method of Doyle and his coworkers: M. P. Doyle, V. Bagheri, T. J. Wandless, N. K. Harn, D. A. Brinker, C. T. Eagle, and K.-L. Loh, *J. Am. Chem. Soc.*, **112**, 1906 (1990).
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8 $[Rh_2(acam)_4Br]_n$ (**3**): Anal. Found: C, 18.39; H, 3.06; N, 10.75; Br, 15.34%. Calcd for $C_8H_{16}N_4O_4BrRh_2$: C, 18.55; H, 3.11; N, 10.82; Br, 15.43%.
9 a) Crystal data for $[Rh_2(acam)_4Br]_n$ (**3**): MW= 517.95, dark brown prism, crystal dimensions 0.14 × 0.11 × 0.07 mm, monoclinic, space group *C*2/*c* (#15), a = 14.6120(9), b = 7.3932(9), c = 13.1315(7) Å, β = 102.324(5)°, V = 1385.9(2) Å^3, T = –80 °C, Z = 4, μ(Mo Kα) = 52.83 cm^{-1}, Mo Kα λ = 0.71069 Å. 1411 Unique reflections [$I > 2.00\ \sigma(I)$]. Structure solved by direct methods (SHELXS 86).[9b] Refinement converged at R = 0.023, R_w = 0.055, and *GOF* = 1.22. The identification of N and O atoms in the acam ligands was based on their thermal parameters, R, R_w, and *GOF*. b) G. M. Sheldrick, SHELXS 86, Program for crystal structure determination, Göettingen University, Germany (1986).
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11 $[Rh_2(acam)_4Cl]_n \cdot 7nH_2O$ (**5**): Anal. after drying at 110 °C under vacuum for 24 h and as $[Rh_2(acam)_4Cl]$. Found: C, 20.03; H, 3.27; N, 11.74; Cl, 7.41%. Calcd for $C_8H_{16}N_4O_4ClRh_2$: C, 20.29; H, 3.41; N, 11.83; Cl, 7.49%.
12 Crystal data for $[Rh_2(acam)_4Cl]_n \cdot 7nH_2O$ (**5**): MW= 599.61, dark brown prism, crystal dimensions 0.20 × 0.10 × 0.08 mm, monoclinic, space group $P2_1/c$ (#14), a = 8.441(1), b = 17.014(1), c = 14.692(2) Å, β = 95.72(1)°, V = 2099.5(4) Å^3, T = –80 °C, Z = 4, μ(Mo Kα) = 17.50 cm^{-1}, Mo Kα λ = 0.71069 Å. 3438 Unique reflections [$I > 2.00\ \sigma(I)$]. Structure solved by direct methods (SHELXS 86).[9b] Refinement converged at R = 0.035, R_w = 0.075, and *GOF* = 1.31. The identification of N and O atoms in the acam ligands was based on their thermal parameters, R, R_w, and *GOF*.
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