A Square-sheet Structure of Paddlewheel Dirhodium Complexes in Mixed Oxidation States with Perrhenate Linkers

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A mixed oxidation-state (Rh_2^{4+} and Rh_2^{5+}) complex, $[\{Rh_2(acam)_4\}_2(\mu_4\text{-}ReO_4)]$ (**1**, Hacam = acetamide), was synthesized and characterized by X-ray structure analysis. A square-sheet structure is constructed from $Rh_2(acam)_4$ units and ReO_4^- ion linkers in which all dirhodium units are crystallographically equivalent. In the mixed oxidation-state compounds, the electrical conductivity of **1** ($8.9 \times 10^{-6}\,S\,cm^{-1}$) is higher than that of $[\{Rh_2(acam)_4\}_3(\mu_3\text{-}Cl)_2]\cdot 4H_2O$, but lower than that of $[\{Rh_2(acam)_4\}_2(\mu_4\text{-}I)]\cdot 6H_2O$.

Paddlewheel dinuclear complexes have rich redox chemistry and show various electronic configurations that are based on metal–metal bond orbitals.[1,2] They are useful modules for assembled structures, because the axial sites are available for coordination of linker ligands. Most of the structures with paddlewheel complexes consist of those with a unique oxidation state,[1] even though they are 2-D or 3-D structures.[3] In our recent study, we reported 1-D to 3-D assembled structures of paddlewheel complexes.[4–6] In particular, the 2-D honeycomb sheet structure of $[\{Rh_2(acam)_4\}_3(\mu_3\text{-}Cl)_2]\cdot 4H_2O$[5] and the 3-D diamondoid structure of $[\{Rh_2(acam)_4\}_2(\mu_4\text{-}I)]\cdot 6H_2O$[6] are mixed oxidation-state complexes that include cationic radicals (Rh_2^{5+}) and neutral complexes (Rh_2^{4+}) and show drastic changes in electrical conductivities depending on their hydrated water. We have attempted to make new mixed oxidation-state compounds with a novel structural type using anionic linkers that have m possible coordination sites and n negative charges, with $m > 2n$. Perrhenate ion is a potential linker: it is a univalent anion with four possible coordination sites. In the reported structures,[7] it bridges between two metal atoms using two oxygen atoms such as $[Ru_2(O_2CR)_4(\mu\text{-}ReO_4)]$ (R = CMe_3, CH_2CH_2OMe).[7e] In this paper, we report a new 2-D square-sheet compound constructed from acetamidate-bridged dirhodium complexes in mixed oxidation states and the quadruple coordinated perrhenate ion.

An aqueous solution containing equimolar amounts (2.0 mM) of $[Rh_2(acam)_4(H_2O)_2]\cdot 6H_2O$[8] and $[Rh_2(acam)_4(H_2O)_2]ClO_4$,[9] with NH_4ReO_4 (8.5 mM) was left for several days at 50 °C to gradually precipitate dark brown crystals of $[\{Rh_2(acam)_4\}_2(\mu_4\text{-}ReO_4)]$ (**1**).[10] From the more concentrated solution, brown plate crystals of $[Rh_2(acam)_4(H_2O)_2]ReO_4$[11] were obtained together with **1**.

Figure 1 shows the square-sheet structure of **1**.[12] The $Rh_2(acam)_4$ units are linked by ReO_4^- ions, in which Re atoms occupy $\bar{4}$ sites, with all O atoms coordinated to the axial sites of the dirhodium units. To our knowledge, this complex is the first example of perrhenate ion connecting to four metal complexes. Each Rh_2 unit has twofold symmetry, and all the Rh_2 units are crystallographically equivalent. The Rh_2 complexes hydrogen bond to the four neighboring complexes in the sheet (N1···O1′ 3.181(5) Å). The sheets extend parallel to the *ab* plane, and they are linked together by hydrogen bonds between NH and O (N2···O2″ 3.155(5) Å). The Rh–Rh distance of **1** (2.4047(6) Å) is shorter than that of the neutral complex (2.415(1) Å),[8] but longer than that in the cationic complexes (2.404(4) Å).[9,11,13] The Rh–O_{eq} (**1** 2.050(4) Å; neutral 2.073(6) Å; cation 2.034(6) Å) and Rh–N (**1** 1.995(4); neutral 2.008(11) Å; cation 1.976(5) Å) distances have a similar tendency. It is consistent with a 1:1 ratio of the neutral and cation complexes in **1**, of which HOMO and singly occupied MO are δ^* orbitals.[2]

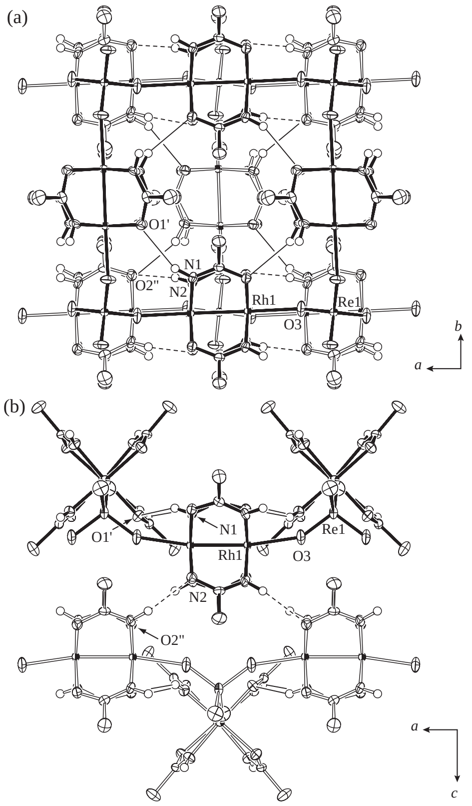

Figure 1. (a) Top view and (b) side view of two adjacent layers in $[\{Rh_2(acam)_4\}_2(\mu_4\text{-}ReO_4)]$ (**1**). Thermal ellipsoids are shown at 50% probability. Methyl hydrogen atoms are omitted for clarity. The layers are distinguished by the bond types. Intralayer hydrogen bonds were drawn as solid thin lines, and interlayer ones as dashed thin lines. Symmetry operations ′: $5/4 - y$, $1/4 + x$, $1/4 - z$; ″: $1/2 + x$, y, $1/2 - z$.

The diffuse reflectance spectrum of **1** (Figure S1, see SI)[14] did not show any clear-cut extraneous band assignable to an intervalence charge-transfer (IVCT) transition. It indicates that the crystallographically equivalent Rh_2 units in **1** are given by time- and space-average of the Rh_2^{4+} and Rh_2^{5+} units, the same as the diamondoid complex of $[\{Rh_2(acam)_4\}_2(\mu_4\text{-}I)]\cdot 6H_2O$.[6]

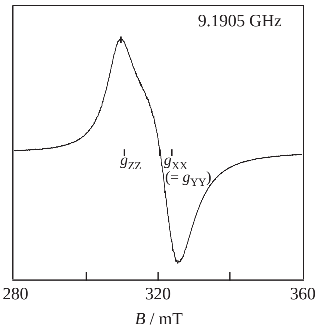

Figure 2. The X-band ESR spectrum of crystalline powder of **1** at 77 K.

The effective magnetic moment of **1** at 295 K was 1.78β per formula unit of $\{Rh_2(acam)_4\}_2ReO_4$, and the temperature dependence of its magnetic susceptibility fits a Curie–Weiss law with $S = 1/2$, $g = 1.90 \pm 0.01$, and $\theta = 0.0 \pm 0.3$ K (Figure S2, see SI).[14] This result is consistent with one $Rh_2{}^{5+}$ unit, that has one odd electron per $\{Rh_2(acam)_4\}_2ReO_4$, and suggests that the magnetic interaction between the Rh_2 units is vanishingly small.

The X-band ESR of crystalline powder of **1** showed a broad single line ($g_{iso} = 2.072$) at room temperature. At 77 K, **1** shows an axially symmetric g-tensor ($g_{//} = 2.119$, $g_{\perp} = 2.048$), as shown in Figure 2. This 77 K spectrum different from that observed for a frozen aqueous solution of $[Rh_2(acam)_4(H_2O)_2]ClO_4$ ($g_{//} = 1.935$, $g_{\perp} = 2.115$) is due to the rapid electron transfer between the $Rh_2{}^{4+}$ and $Rh_2{}^{5+}$ units. When the principal axes of X, Y, and Z are chosen as the crystallographic a, b, and c axes, respectively, the local z axis of the Rh_2 units direct toward the X or Y axis. The local x axis also directed toward the X or Y axis, and the local y axis are parallel to the Z axis. If the electron-transfer rate between the $Rh_2{}^{4+}$ and $Rh_2{}^{5+}$ units is fast enough, the g-anisotropic resonance must be averaged as $g_{XX} = g_{YY} = (g_z + g_x)/2 = (g_{//} + g_{\perp})/2$, and $g_{ZZ} = g_y = g_{\perp}$, of which $g_{//}$ and $g_{\perp}$ are g values of $Rh_2(acam)_4{}^+$. The calculated values of $g_{ZZ} = 2.115$ and $g_{XX} = g_{YY} = 2.025$ using the g-tensor of $[Rh_2(acam)_4(H_2O)_2]ClO_4$ are in good agreement with the observed $g_{//}$ and $g_{\perp}$ of **1**.

The electrical conductivity of **1** (room temperature, pellets) was 8.9×10^{-6} S cm^{-1}. This value is higher than the 2×10^{-7} S cm^{-1} of $[\{Rh_2(acam)_4\}_3(\mu_3\text{-}Cl)_2]\cdot 4H_2O$[5] but lower than the 1.4×10^{-3} S cm^{-1} of $[\{Rh_2(acam)_4\}_2(\mu_4\text{-}I)]\cdot 6H_2O$.[6] In the former structure, the $Rh_2{}^{4+}$ and $Rh_2{}^{5+}$ units are distinguishable and are pinned by the water of crystallization, whereas in the latter complex, all the Rh_2 units are equivalent. The electrical conductivity depends on the facility of the odd electron to hop between the Rh_2 sites. The barrier in **1** is lower than that in $[\{Rh_2(acam)_4\}_3(\mu_3\text{-}Cl)_2]\cdot 4H_2O$ because all Rh_2 units are equivalent in **1**. The difference between **1** and $[\{Rh_2(acam)_4\}_2(\mu_4\text{-}I)]\cdot 6H_2O$ may be due to the longer interunit Rh···Rh separation in the former (5.80 Å) than that in the latter (4.60 Å)[6] and/or the different anisotropies of the conductivity in the 2-D and 3-D network structures.

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References and Notes

1 *Multiple Bonds Between Metal Atoms*, 3rd ed., ed. by F. A. Cotton, C. A. Murillo, R. A. Walton, Springer Science and Business Media Inc, New York, **2005**.

2 a) T. Kawamura, H. Katayama, H. Nishikawa, T. Yamabe, *J. Am. Chem. Soc.* **1989**, *111*, 8156. b) T. Kawamura, M. Maeda, M. Miyamoto, H. Usami, K. Imaeda, M. Ebihara, *J. Am. Chem. Soc.* **1998**, *120*, 8136.

3 a) F. A. Cotton, Y. Kim, *J. Am. Chem. Soc.* **1993**, *115*, 8511. b) F. A. Cotton, E. V. Dikarev, M. A. Petrukhina, *Angew. Chem., Int. Ed.* **2001**, *40*, 1521. c) H. Miyasaka, C. S. Campos-Fernández, R. Clérac, K. R. Dunbar, *Angew. Chem.* **2000**, *39*, 3831. d) H. Miyasaka, T. Izawa, N. Takahashi, M. Yamashita, K. R. Dunbar, *J. Am. Chem. Soc.* **2006**, *128*, 11358. e) D. Yoshioka, M. Mikuriya, M. Handa, *Chem. Lett.* **2002**, 1044. f) T. E. Vos, Y. Liao, W. W. Shum, J.-H. Her, P. W. Stephens, W. M. Reiff, J. S. Miller, *J. Am. Chem. Soc.* **2004**, *126*, 11630. g) S. Furukawa, M. Ohba, S. Kitagawa, *Chem. Commun.* **2005**, 865.

4 a) Z. Yang, T. Fujinami, M. Ebihara, K. Nakajima, H. Kitagawa, T. Kawamura, *Chem. Lett.* **2000**, 1006. b) Z. Yang, M. Ebihara, T. Kawamura, T. Okubo, T. Mitani, *Inorg. Chim. Acta* **2001**, *321*, 97. c) Z. Yang, M. Ebihara, T. Kawamura, *Inorg. Chim. Acta* **2006**, *359*, 2465. d) T. Sugiura, K. Ota, M. Ebihara, T. Kawamura, *C. R. Chim.* **2005**, *8*, 1760.

5 Y. Takazaki, Z. Yang, M. Ebihara, K. Inoue, T. Kawamura, *Chem. Lett.* **2003**, *32*, 120.

6 Y. Fuma, M. Ebihara, S. Kutsumizu, T. Kawamura, *J. Am. Chem. Soc.* **2004**, *126*, 12238.

7 a) C. Calvo, N. C. Jayadevan, C. J. L. Lock, *Can. J. Chem.* **1969**, *47*, 4213. b) R. Petrova, O. Angelova, J. Macícek, *Acta Crystallogr., Sect. C* **1996**, *52*, 1935. c) C. V. K. Sharma, S. T. Griffin, R. D. Rogers, *Chem. Commun.* **1998**, 215. d) J. Luo, B. Alexander, T. R. Wagner, P. A. Maggard, *Inorg. Chem.* **2004**, *43*, 5537. e) G. Arribas, M. C. Barral, R. González-Prieto, R. Jiménez-Aparicio, J. L. Priego, M. R. Torres, F. A. Urbanos, *Inorg. Chem.* **2005**, *44*, 5770.

8 M. Q. Ahsan, I. Bernal, J. L. Bear, *Inorg. Chem.* **1986**, *25*, 260.

9 I. B. Baranovskii, M. A. Golubnichaya, L. M. Dikareva, A. V. Rotov, R. N. Shchelokov, M. A. Porai-Koshits, *Russ. J. Inorg. Chem.* **1986**, *31*, 1652.

10 **1**: When $[Rh_2(acam)_4(H_2O)_2]\cdot 6H_2O$ (176 mg, 0.30 mmol), $[Rh_2(acam)_4(H_2O)_2]ClO_4$ (173 mg, 0.30 mmol), and NH_4ReO_4 (343 mg, 1.28 mmol) were dissolved in 150 mL of water and left at 50 °C for several days, **1** was obtained as dark brown crystals (yield: 105 mg, 31%). Anal. Calcd for $C_{16}H_{32}N_8O_{12}ReRh_4$: C, 17.06; H, 2.86; N, 9.95%. Found: C, 16.80; H, 2.78; N, 9.57%.

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12 Crystal data for **1**: $C_{16}H_{32}N_8O_{12}ReRh_4$, MW 1126.34, tetragonal, space group $I4_1/a$ (No. 88), $a = 9.6445(5)$, $c = 29.651(2)$ Å, $V = 2758.0(3)$ Å^3, $Z = 4$, $D_{calcd} = 2.713$ g cm^{-3}, $2\theta < 55.0°$, $\mu = 67.89$ cm^{-1}, 11250 reflections collected, 1580 unique ($R_{int} = 0.036$), the data was collected on a Rigaku AFC7R Mercury CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The structure was solved using direct methods SIR97, and least-squares refinement was carried out using SHELXL97. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms in the riding model on their carrier atoms. $R_1 = 0.030$ for $I > 2\sigma(I)$, $R_w = 0.049$ for all data, GOF = 1.31. (CCDC-621965).

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14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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