A Honeycomb Network of a Paddlewheel-type Dirhodium Complex in Two Oxidation States and Pinning of the Oxidation States

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The reaction of a mixture of $[Rh_2(acam)_4(H_2O)_2]$ (Hacam = acetamide) and its radical cation salt with sodium chloride in an aqueous solution gave a mixed-valent 2-D honeycomb crystal of $[\{Rh_2(acam)_4\}_3(\mu_3\text{-}Cl)_2]_n{\cdot}4nH_2O$. The oxidation states of the dirhodium units are pinned at each of the crystal sites by hydrogen bonding with solvate-water molecules.

There is currently considerable interest in assembling paddlewheel-type dinuclear complexes into supramolecules and 1- to 3-D network compounds.[1] Dinuclear complexes of this type have rich redox chemistry[2] and span a wide variety of electronic structures controlled by ligands.[3] Thus resultant assembled compounds would give attractive electron-transfer, optical, magnetic and conducting properties. A few attempts have been successful to arrange this type of complexes into an extended 2-D network. These are crystals of $[Rh_2(CF_3CO_2)_4]$ and/or $[Ru_2(CF_3CO_2)_4]$ connected by organopolycyanides[4] or octasulfur.[5] The key has been proposed as the increased acidity of their dinuclear core induced by the electron-demanding CF_3CO_2 ligand.[5] We are trying to assemble dinuclear complexes in different oxidation states into a solid.[6] We report here the first example, to our best knowledge, of a crystal with a 2-D extended structure formed by combining a dinuclear complex in two oxidation states through self-assembling. The 2-D crystal consists of $[Rh_2(acam)_4]$ (Hacam = acetamide) in the neutral and the radical cation (namely, in the Rh_2^{4+} and the Rh_2^{5+}) states connected by a single-atom μ_3-ion, Cl^-.

Standing of an aqueous solution of a mixture of $[Rh_2(acam)_4(H_2O)_2]{\cdot}6H_2O$,[7] $[Rh_2(acam)_4(H_2O)_2]ClO_4$,[8] and NaCl resulted in slow precipitation of dark brown plates of $[\{Rh_2(acam)_4\}_3(\mu_3\text{-}Cl)_2]_n{\cdot}4nH_2O$ (**1**).[9] The tuning of the reaction conditions has been important. When the concentration of the dinuclear radical salt was too high, we obtained a chain product, $[Rh_2(acam)_4Cl]_n$.[10] Reaction mixtures with higher concentrations of NaCl gave **1** contaminated with unidentified dark brown solids.

The crystal of **1**[11] consists of layers of a honeycomb arrangement of $[Rh_2(acam)_4]$ units and μ_3-Cl^- ions (Figure 1). The honeycomb layer extends parallel to the *bc* plane. The layers stack along the *a* direction alternately with layers of solvate-water molecules. The walls of a honeycomb cell consist of three pairs of crystallographically independent dinuclear units and six crystallographically equivalent Cl^- ions at the corners. There exists a H-bond between an O atom and an NH group in a neighboring pair of the dinuclear units. Thus each of the cell rooms contains six NH···O H-bonds. The N···O distances are in the range of 2.995(5)–3.106(5) Å.

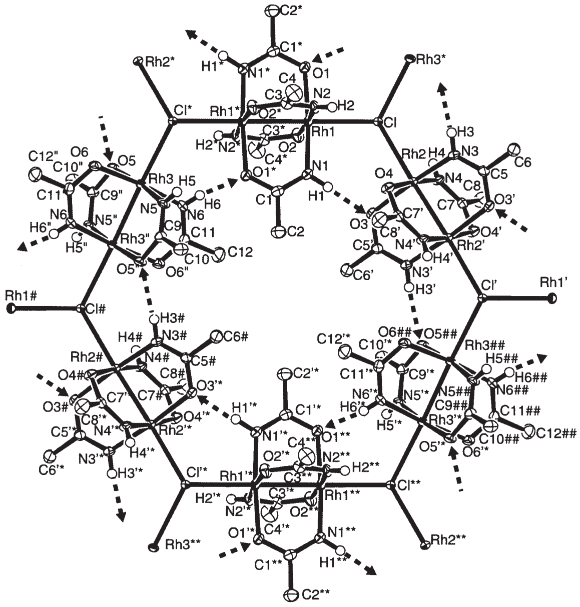

Figure 1. ORTEP view of the honeycomb structure in **1**. Water molecules and methyl-hydrogen atoms are omitted. The midpoints of the Rh–Rh bonds are crystallographic inversion centers. Broken-line arrows show H-bonds between dinuclear units in the H-donating direction. Symmetry operations: *: $-x,-y+1,-z$; ′: $-x,-y,-z+1$; ″: $-x,-y+2,-z$; ′*: $-x,-y+1,-z+1$; **: $x,y,z+1$; #: $x,y+1,z$; ##: $x,y-1,z+1$. Selected bond lengths and angles: Rh1–Rh1*, 2.4241(6); Rh2–Rh2′, 2.4218(6); Rh3–Rh3″, 2.4312(6); Rh1–Cl, 2.552(1); Rh2–Cl, 2.554(1); Rh3–Cl*, 2.610(1) Å; Rh1–Cl–Rh2, 117.74(4); Rh2–Cl–Rh3*, 120.04(4); Rh3*–Cl–Rh1, 114.46(4)°.

The crystal has two crystallographically independent water molecules (Figure 2). The arrows in this figure cover all of the H-bonds of the three dinuclear units at the Rh1, Rh2 and Rh3* sites with water molecules. The four acam O atoms of the Rh3*–Rh3*** unit form H-bonds with four water molecules; O5*···O7 = 2.805(5), O6*···O8 = 2.806(5) Å and their equivalents. These are the shortest H-bonds in this crystal. The dinuclear unit accepts H atoms from water molecules. The dinuclear unit at Rh2 has two H-donating H-bonds from its acam NH groups to water molecules (N4···O8 = 2.928(5) Å and its equivalent) and two H-accepting H-bonds to its acam O atoms from two water molecules (O4···O7 = 2.844(5) Å and its equivalent). The dinuclear unit at Rh1 has two H-bonds with water molecules only in a H-donating mode (N2–O7 = 3.107(5) Å and its equivalent).

The electrical conductivity of **1** (pellets, room temperature) was $2 \times 10^{-7}\,S\,cm^{-1}$. Its effective magnetic moment at 290 K was $\mu_{eff} = 2.08\beta$ when normalized to one mol of the Rh_2^{5+} unit. The temperature dependence of its corrected magnetic susceptibility fits a Curie-Weiss equation $[\chi_{mol} = N_A g^2 \beta^2 S(S+1)/\{3k(T-\theta)\}]$ with the parameters of $g = 2.09 \pm 0.01$, $S = 1/2$,

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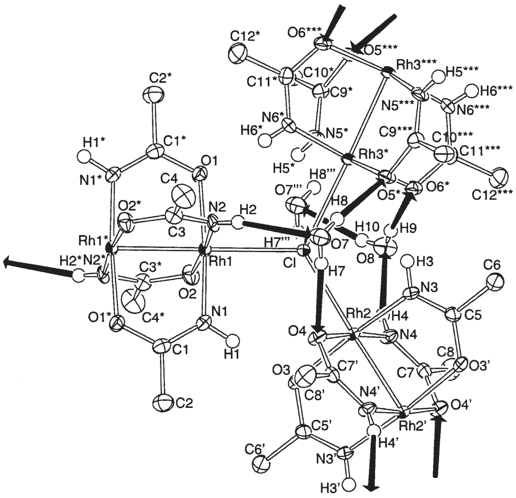

Figure 2. ORTEP view of solvate-water molecules and surroundings in **1** added with arrows showing H-bonds of water molecules in the H-donating direction. Methyl hydrogen atoms are omitted. Symmetry operations: $*$: $-x,-y+1,-z$; $'$: $-x,-y,-z+1$; $***$: $x,y-1,z$; $'''$: $x-1,y,z$.

and $\theta = 0.0 \pm 0.1$ K.

The composition of the crystal shows that it contains $Rh_2{}^{4+}$ and $Rh_2{}^{5+}$ units in the mole ratio of 1:2 or uniformly oxidized $Rh_2{}^{(14/3)+}$ units. The Rh–O and Rh–N bond distances are good criteria to assign the oxidation states of this class of complexes where the highest occupied molecular orbital (HOMO) is the $\delta_{RhRh}{}^*$ orbital delocalized onto the bridging ligands in π-antibonding phase.[12] The Rh–O bond distances around the Rh3 and its equivalent atoms are 0.032(3)–0.069(3) Å longer than the corresponding distances around the Rh1 and Rh2 atoms and their equivalents. The Rh–N distances around Rh3 and its equivalents also have a trend to be longer than those around Rh1 and Rh2 and their equivalents. These observations show that the neutral state is pinned at the Rh3 sites, and the cationic radical state at the Rh1 and Rh2 sites. Consistent with this assignment, the Rh3–Cl distance of 2.610(1) Å is 0.057(2) Å longer than the Rh–Cl distances around the Rh1 and Rh2 atoms.

We propose that the pinning of the oxidation states of the dinuclear units arises from their H-bonds with water molecules and that two cooperative mechanisms work for the pinning. Firstly (electrostatic pinning), in the H-bonds with water molecules, the dinuclear unit at the Rh3 site accepts four H atoms. The units at the Rh2 and Rh1 sites are H-bonded in a H-accepting mode from only two and no water molecules, respectively. The unit at Rh3 is thus located in the most positive electric field supplied by the positively polarized H atoms of water molecules. This stabilizes the neutral state at this site rather than the cationic one. Secondly (geometric pinning), the water molecules pull acam ligands away from the Rh3 and its equivalent atoms by their shortest H-bonds. The number of H-bonds with water molecules is a largest for the unit at this site among the three types of the dinuclear units. These features stabilize the neutral state at this site, because the neutral unit has longer Rh–N and Rh–O bonds than the cationic one because of electron-configuration reasons.[12]

The observed low electrical conductivity of **1** reflects the pinning of the oxidation states. The small Weiss parameter shows that the $Rh_2{}^{5+}$ units in **1** are magnetically isolated each other. In an idealized geometry the $\delta_{RhRh}{}^*$ singly occupied molecular orbital (SOMO) of the $Rh_2{}^{5+}$ unit is symmetry-forbidden to mix with the 3s and 3p valence orbitals of the Cl^- connectors[10b] and is rather localized on each of the units. We suppose that the localized nature of the SOMO/HOMO of the present units is an origin for the pinning of the oxidation states under the influence of H-bonds.

The oxidation states of the dirhodium units are pinned by their H-bonds with solvate-water molecules. The proposed mechanism for the pinning of the oxidation states may lead to an expectation that if the solvate-water molecules are removed or fluctuated, then hopping of the oxidation states would result in. Studies to manipulate solvate-water molecules are under progress.

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References and Notes

1 a) D. Yoshioka, M. Mikuriya, and M. Handa, *Chem. Lett.*, **2002**, 1044. b) Y. Liao, W. M Shum, and J. S. Miller, *J. Am. Chem. Soc.*, **124**, 9336 (2002). c) J. K. Bera, C. S. Campos-Fernández, C. Rodolphe, and K. R. Dunbar, *Chem. Commun.*, **2002**, 2536. d) B. E. Bursten, M. H. Chisholm, R. J. H. Clark, S. Firth, C. M. Hadad, A. M. MacIntosh, P. J. Wilson, P. M. Woodward, and J. M. Zaleski, *J. Am. Chem. Soc.*, **124**, 3050 (2002). e) J. K. Bera, P. Angaridis, F. A. Cotton, M. A. Petrukhina, P. E. Fanwick, and R. A. Walton, *J. Am. Chem. Soc.*, **123**, 1515 (2002). f) S. Lo Schiavo, S. Serroni, F. Puntoriero, G. Tresoldi, and P. Piraino, *Eur. J. Inorg. Chem.*, **2002**, 79, and references cited therein.

2 F. A. Cotton and R. A. Walton, "Multiple Bonds between Metal Atoms," 2nd ed., Oxford University Press, Oxford (1993).

3 T. Kawamura, H. Katayama, H. Nishikawa, and T. Yamabe, *J. Am. Chem. Soc.*, **111**, 8156 (1989).

4 a) F. A. Cotton and K. Youngmee, *J. Am. Chem. Soc.*, **115**, 8511 (1993). b) H. Miyasaka, C. S. Campos-Fernandez, R. Clerac, and K. R. Dunbar, *Angew. Chem., Int. Ed. Engl.*, **39**, 3831 (2000).

5 F. A. Cotton, E. V. Dikarev, and M. A. Petrukhina, *Angew. Chem., Int. Ed. Engl.*, **40**, 1521 (2001).

6 T. Kawamura, H. Kachi, H. Fujii, C. Kachi-Terajima, Y. Kawamura, N. Kanematsu, M. Ebihara, K. Sugimoto, T. Kuroda-Sowa, and M. Munakata, *Bull. Chem. Soc. Jpn.*, **73**, 657 (2000).

7 M. Q. Ahsan, I. Bernal, and J. L. Bear, *Inorg. Chem.*, **25**, 260 (1986).

8 I. B. Baranovskii, M. A. Golubnichaya, L. M. Dikareva, A. V. Rotov, R. N. Scelokov, and M. A. Porai-Koshits, *Zh. Neorg. Khim.*, **31**, 2876 (1986).

9 **1**: When NaCl (70 mg, 1.2 mmol), $[Rh_2(acam)_4(H_2O)_2]\cdot 6H_2O$ (58 mg, 0.10 mmol) and $[Rh_2(acam)_4(H_2O)_2]ClO_4$ (115 mg, 0.20 mmol) were dissolved together in 60 ml of water and left at 50 °C for several days, **1** (32 mg, 0.022 mmol, 22%) precipitated as dark brown plates. Anal. Calcd for $C_{24}H_{56}Cl_2N_{12}O_{16}Rh_6$: C, 19.78; H, 3.87; N, 11.54. Found: C, 19.67; H, 3.86; N, 11.27.

10 a) Z. Yang, T. Fujinami, M. Ebihara, K. Nakajima, H. Kitagawa, and T. Kawamura, *Chem. Lett.*, **2000**, 1006. b) Z. Yang, M. Ebihara, T. Kawamura, T. Okubo, and T. Mitani, *Inorg. Chim. Acta*, **321**, 97 (2001).

11 Crystallographic data for **1** ($C_{24}H_{56}Cl_2N_{12}O_{16}Rh_6$): $M_r = 1457.12$, triclinic, space group $P\bar{1}$ (#2), $a = 8.215(3)$, $b = 12.729(4)$, $c = 13.169(4)$ Å, $\alpha = 59.823(8)$, $\beta = 79.22(1)$, $\gamma = 88.19(1)^\circ$, $V = 1166.2(7)$ Å^3, $Z = 1$, $T = -80\,^\circ C$. $2\theta_{max} = 54.96^\circ$. Rigaku AFC7R Mercury CCD system, Mo Kα radiation ($\lambda = 0.71070$ Å). 9784 reflections measured, corrected for Lorentz, polarization and absorption effects, solution by direct methods (SHELXS-86). Refinement of F^2, all non-H atoms anisotropically, all NH and H_2O H atoms isotropically, and isotropic thermal parameters of all methyl H atoms at the most-likely calculated positions, $R1$ (on F) = 0.046, $wR2$ (on F^2) = 0.073 for 330 parameters and 5291 independent reflections. Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 192014. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

12 T. Kawamura, M. Maeda, M. Miyamoto, H. Usami, K. Imaeda, and M. Ebihara, *J. Am. Chem. Soc.*, **120**, 8136 (1998).