

## A Diamondoid Network of Tetrakis(acetamidato)dirhodium in Mixed Oxidation States Linked by $\mu_4$ -Iodide Having a $10^5$ Enhancement of Its Electrical Conductivity by Water Molecules of Hydration

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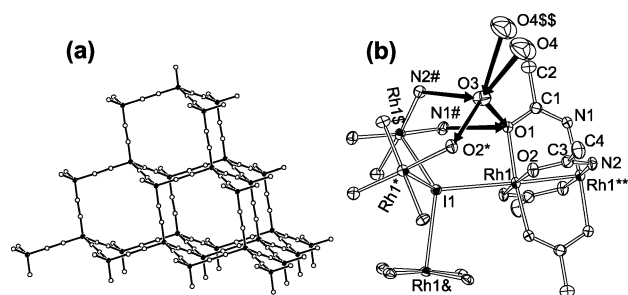
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Compounds with two or more centers of mixed valency in similar or identical surroundings<sup>1</sup> have been the subject of increased study.<sup>2</sup> One direction of recent effort is expanding the types of compounds to include those with metal–metal bonds,<sup>3</sup> which can potentially lead to enhanced redox processes and increased internal degrees of freedom such as charge polarization<sup>3a,b</sup> at the redox center. In our project to assemble paddlewheel-type dinuclear complexes with open-shell electronic structures,<sup>4–6</sup> we have reported a mixed oxidation state compound  $[\{\text{Rh}_2(\text{acam})_4\}_3(\mu_3\text{-Cl})_2]\cdot 4\text{H}_2\text{O}$  (Hacam = acetamide) with a honeycomb structure.<sup>6</sup> The frontier orbital of the  $[\text{Rh}_2(\text{acam})_4]^{0/+}$  center is the  $\delta_{\text{RhRh}}^*$  orbital,<sup>7</sup> which can have no or negligible overlap integrals with s and p orbitals on the axial linker,<sup>4b</sup> resulting in electronic isolation of the redox centers. Thus, mixed oxidation-state compounds of  $[\text{Rh}_2(\text{acam})_4]^{0/+}$  linked by halides are expected to be systems of multistability with respect to allocation of oxidation states. Small perturbations might lift the degenerate multistability, resulting in apparently large effects on some properties, such as electrical conductivity. In our study to exploit this expectation, we obtained a compound possessing a diamondoid network structure. The electrical conductivity of this diamondoid compound varies by  $10^5$  orders of magnitude during dehydration–rehydration cycles of the interstitial water molecules.

The standing of an aqueous solution containing  $[\text{Rh}_2(\text{acam})_4\cdot(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$ ,<sup>8</sup>  $[\text{Rh}_2(\text{acam})_4(\text{H}_2\text{O})_2]\text{ClO}_4$ ,<sup>9</sup> and sodium iodide for several days resulted in gradual precipitation of dark brown crystals of  $[\{\text{Rh}_2(\text{acam})_4\}_2\text{I}]\cdot 6\text{H}_2\text{O}$  (**1**).<sup>10</sup> The structure of this compound<sup>11</sup> is a diamondoid arrangement of the  $[\text{Rh}_2(\text{acam})_4]$  units linked by  $\mu_4$ -iodide as shown in Figure 1a. All of the  $\text{Rh}_2$  units are crystallographically equivalent, as are all of the iodide atoms. Four rhodium atoms are arranged around an iodide in a  $D_{2d}$  local geometry. Iodide in  $\mu_4$  geometries are known only in a limited number of transition metal complexes<sup>12</sup> and in  $n(\text{I})-\sigma^*(\text{BrC})$  charge-transfer compounds.<sup>13</sup> Figure 1b displays the arrangement of four  $\text{Rh}_2$  units and two types of hydration water molecules around an iodide atom. The arrows in Figure 1b display one of each of the crystallographically independent hydrogen bonds in the direction of hydrogen-atom donation. All of the N and O atoms of the acam ligands as well as the hydration water molecules are involved in a hydrogen-bond network. The crystal has two O4- and four O3- water molecules per unit of  $[\{\text{Rh}_2(\text{acam})_4\}_2\text{I}]$ . The O4 water molecules are disordered over two crystallographically equivalent sites with half occupancies (O4 and O4\$\$ in Figure 1b) and are involved in the hydrogen-bond network only in the hydrogen-atom donating mode to O3-water molecules.

Since all of the  $[\text{Rh}_2(\text{acam})_4]$  units are crystallographically equivalent, this compound may seem to fit into the Robin–Day class IIIB category (complete delocalization).<sup>1</sup> However, the  $\delta_{\text{RhRh}}^*$  SOMO of  $[\text{Rh}_2(\text{acam})_4]^+$  is difficult to mix extensively with the  $\delta_{\text{RhRh}}^*$  orbitals on the neighboring  $\text{Rh}_2$  units when mediated by iodide lone-pair orbitals (through-bond mixing). The shortest

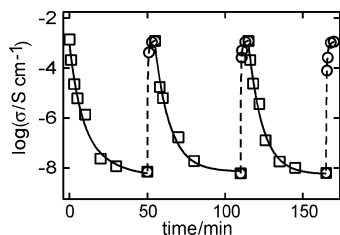


**Figure 1.** ORTEP views of  $[\{\text{Rh}_2(\text{acam})_4\}_2\text{I}]\cdot 6\text{H}_2\text{O}$  (**1**·6H<sub>2</sub>O). (a) Diamondoid geometry. Only Rh (blank thermal ellipsoids) and I (hatched ellipsoids) atoms are shown for clarity. (b) Arrangement of  $[\text{Rh}_2(\text{acam})_4]$  units and water molecules around an iodide atom. Thermal ellipsoids are shown at 30% probability. Rh1–Rh1\*, 2.4385(7); Rh1–I1, 2.9750(4) Å. Rh1–I1–Rh1\* = Rh1&–I1–Rh1\$ = 127.39(1)°; the other Rh–I1–Rh angles are 101.324(6)°. Hydrogen-bond distances: N1# → O1, 2.992(5); O3 → O1, 2.872(5); O3 → O2\*, 2.800(5); O4 → O3, 2.82(1); O4\$\$ → O3, 2.77(1) Å.

interunit  $\text{Rh}\cdots\text{Rh}$  separation is 4.60 Å, and the direct interaction between the  $\delta_{\text{RhRh}}^*$  MOs on the neighboring units (through-space mixing) must be small. Therefore, we cannot rule out the possibility that this complex belongs to the Robin–Day class II category.<sup>1</sup>

Thermal analyses of **1**·6H<sub>2</sub>O revealed that upon heating, hydration water molecules are lost in a stepwise manner at least through **1**·H<sub>2</sub>O, and finally to anhydrous compound **1** (Figures S1 and S2a; Figures S1–S6 are given in Supporting Information). When anhydrous compound **1** was left in moisture-saturated argon at room temperature, it recovered hydration water molecules to give **1**·6H<sub>2</sub>O in ca. 24 h (Figure S2b). The dehydration–rehydration process can be cycled with recovery of X-ray diffraction powder patterns characteristic of the hydrated and dehydrated compounds (Figure S3). This is indicative of retention of the diamondoid skeleton during these cycles. Diamondoid networks have been predicted to have high stability because the attractive forces extend isotropically in three dimensions.<sup>14</sup>

The magnetic susceptibility of **1**·6H<sub>2</sub>O obeys the Curie–Weiss law with  $S = 1/2$ ,  $g = 1.99$ , and  $\theta = -3.9$  K (antiferromagnetic) per formula unit of  $[\{\text{Rh}_2(\text{acam})_4\}_2\text{I}]\cdot 6\text{H}_2\text{O}$  (Figure S4). Each pair of  $\text{Rh}_2$  units in the current compound has one odd electron. These results are puzzling; although all the  $[\text{Rh}_2(\text{acam})_4]$  units in **1**·6H<sub>2</sub>O are crystallographically equivalent, the magnetic study showed that one-half of the units are in the  $\text{Rh}_2^{5+}$  state with one odd electron and the other half in the diamagnetic  $\text{Rh}_2^{4+}$  state. The electronic transition bands in the diffuse reflectance spectrum of **1**·6H<sub>2</sub>O (Figure S5) were similar to either of those in an absorption spectrum of an aqueous solution of  $\text{Na}_2[\{\text{Rh}_2(\text{acam})_4\}_2\text{I}_2]$  or those in the diffuse reflectance spectrum of the  $[\{\text{Rh}_2(\text{acam})_4\}_n\text{I}]_n$  chain compound<sup>4b</sup> and did not show any clear-cut extraneous band assignable to an intervalence charge-transfer (IVCT) transition. This result is consistent with the preceding proposal that the interaction



**Figure 2.** Oscillation in electrical conductivity of a pellet of  $1 \cdot 6\text{H}_2\text{O}$  arising from cycles of dehydration under vacuum at room temperature (squares and solid lines) and rehydration in a moisture-saturated argon flow at room temperature (circles and broken lines).

between  $\text{Rh}_2^{4+}$  and  $\text{Rh}_2^{5+}$  units is small, otherwise a strong IVCT band would be expected in the long wavelength region of the spectrum of the current compound.<sup>1</sup>

A dynamic valence-fluctuation model is consistent with these observations. Since the SOMO/HOMO ( $\delta_{\text{RhRh}}^* - \delta_{\text{RhRh}}^*$ ) interaction between neighboring  $\text{Rh}_2$  units is expected to be small (small values of  $\beta$  in the Hückel Molecular Orbital (HMO) terminology) and the units are crystallographically equivalent and thus have the same effective electronegativities (same values of  $\alpha$  in the HMO terminology), geometrical fluctuation or antisymmetric vibration (of Rh–I bonds, shrinking of acam ligands, or fluctuation of hydrogen-bond network, for example) may inhomogeneously modulate the effective electronegativities of the  $\text{Rh}_2$  units (a small shift of  $\alpha$ , but exceeding the small value of  $\beta$ ), inducing the valence fluctuation of the units. Note that the X-ray diffraction analysis gives only a time- and space-averaged structure.

The electrical conductivity of  $1 \cdot 6\text{H}_2\text{O}$  (room temperature, pellets) was  $1.4 \times 10^{-3} \text{ S cm}^{-1}$ . The conductivity decreased to  $7.0 \times 10^{-9} \text{ S cm}^{-1}$  upon dehydration of the compound. The dehydration to the formal composition of  $1 \cdot 1.9\text{H}_2\text{O}$  resulted in a decrease of the conductivity on the order of  $10^{-8} \text{ S cm}^{-1}$ . The conductivity oscillated over a range of  $10^5$  during the dehydration–rehydration cycles, as shown in Figure 2.

The X-band ESR of the powder of  $1 \cdot 6\text{H}_2\text{O}$  is an isotropic single line ( $g_{\text{iso}} = 2.06$ ) at temperatures between 77 and 300 K. Contrary to this, the powder of the compound obtained by partial dehydration to the formal composition of  $1 \cdot 1.9\text{H}_2\text{O}$  (corresponding to the conductivity on the order of  $10^{-8} \text{ S cm}^{-1}$ ) gave an anisotropic spectrum arising from an axially symmetric  $g$ -tensor ( $g_{\text{parallel}} = 1.99$ ,  $g_{\text{perpendicular}} = 2.08$ ) at lower temperatures (77–150 K) (Figure S6). These  $g$  principal values are characteristic of  $\text{Rh}_2^{5+}$  species with a  $\delta_{\text{RhRh}}^* \text{ SOMO}$ .<sup>4b</sup> The odd electron staying in a local site for a long enough time ( $\tau \gg \{h/(|g_{\text{perpendicular}} - g_{\text{parallel}}| \mu_B B)\} \approx 2 \times 10^{-9} \text{ s}$ ) should give an anisotropic resonance characteristic to the site. If the lifetime of the hopping of the odd electron (i.e., rapid valence fluctuation) over the  $\text{Rh}_2$  sites is short enough ( $\tau \ll \{h/(|g_{\text{perpendicular}} - g_{\text{parallel}}| \mu_B B)\} \approx 2 \times 10^{-9} \text{ s}$ ), then the  $g$ -anisotropic resonance must be globally averaged into an isotropic resonance at  $g_{\text{iso}} = (1/3)(g_{\text{parallel}} + 2g_{\text{perpendicular}})$ . This expectation is consistent with the observed ESR of the current compounds. Thus, the isotropic ESR and the moderate conductivity of the hydrated compound show that the odd electrons are hopping over the  $\text{Rh}_2$  units without experiencing much of a barrier, whereas those in the partially dehydrated

compound are localized in some of the  $\text{Rh}_2$  sites, resulting in the anisotropic ESR and the small conductivity.

The honeycomb compound  $[\{\text{Rh}_2(\text{acam})_4\}_3(\mu_3\text{-Cl})_2] \cdot 4\text{H}_2\text{O}$  in our previous communication consisted of  $[\text{Rh}_2(\text{acam})_4]$  and  $[\text{Rh}_2(\text{acam})_4]^+$  units with different geometries, and its conductivity was low,  $2 \times 10^{-7} \text{ S cm}^{-1}$ .<sup>6</sup> Therefore, we suppose that the partial dehydration of the current diamondoid compound induced geometrical nonequivalence among the  $\text{Rh}_2$  units, triggered by deformation of the hydrogen-bond network, resulting in the small electrical conductivities and the anisotropic ESR.

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**Supporting Information Available:** Preparation and Figures S1–S6 describing physicochemical data (PDF) and the crystallographic data for  $1 \cdot 6\text{H}_2\text{O}$  (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) Crystal data for  $1 \cdot 6\text{H}_2\text{O}$ :  $\text{C}_{16}\text{H}_{44}\text{In}_8\text{O}_{14}\text{Rh}_4$ ,  $M = 1111.10$ , brown block,  $T = 23^\circ \text{C}$ , tetragonal,  $I4_1/a$  (no. 88),  $a = 15.099(1)$ ,  $c = 14.607(1)$  Å,  $V = 3330.1(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $2\theta < 55.0^\circ$ ,  $\mu = 29.4 \text{ cm}^{-1}$ , 13 879 reflections collected, 1902 unique ( $R_{\text{int}} = 0.077$ ),  $R_1 = 0.028$  (for  $I > 2\sigma(I)$ ),  $R_w = 0.055$  (for all data), GOF = 0.59.
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