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Mixed Valency in Hydrogen-Bonded Dimers of Half-Lantern Dirhodium Complexes

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1 Introduction

Mixed-valence complexes have received much attention in coordination chemistry over the last four decades. Recently, a few examples of mixed valency in hydrogen-bonded dimer complexes have been reported. In 2007 Tadokoro and co-workers reported a hydrogen-bonded dimerized complex $[Re^{III}Cl_2(PBu_3)_2(Hbim)]_2$ (H_2bim = biimidazole) that showed two successive one-electron oxidation and two successive one-electron reduction processes. They explained that the first oxidation step generated the asymmetrically protonated mixed-valence species $[Re^{IV}Cl_2(PBu_3)_2(bim)]$-$[Re^{III}Cl_2(PBu_3)_2(H_2bim)]^+$. Synchronized motion of proton and electron stabilized this type of mixed-valence compound. We have synthesized half-lantern-type dirhodium complexes with two biimidazole ligands $[Rh_2(O_2CR)_2(H_2bim)_2(L)_2]^{2+}$ (R = Bu ($[\mathbf{1}(L)_2]^{2+}$), Pr ($[\mathbf{2}(L)_2]^{2+}$)) and their deprotonated dimerized species $[Rh_2(O_2CR)_2(Hbim)_2(L)_2]_2$ (R = Bu ($[\mathbf{1}'(PPh_3)_2]_2$), Pr ($[\mathbf{2}'(PPh_3)_2]_2$)). The latter complexes formed hydrogen-bonded dimers with four complementary NH···N hydrogen bonds.

2 Experiment

$[\mathbf{1}Cl_2]$ and $[\mathbf{2}Cl_2]$ was obtained by the reaction of H_2bim with $Rh_2(O_2CR)_4]$ (R = Pr and Bu), respectively, in 1,2-dichloroethane and consecutive treatment with HCl/MeOH. $[\mathbf{1}](PF_6)_2$ was afforded in a similar method to that for $[\mathbf{1}Cl_2]$ using HPF_6 instead of HCl. $[\mathbf{1}](PF_6)_2$ reacted with PPh_3 to afford $[\mathbf{1}(PPh_3)_2](PF_6)_2$. Proton abstruction from $[\mathbf{1}(PPh_3)_2](PF_6)_2$ and $[\mathbf{2}(PPh_3)_2](PF_6)_2$ by KOH/MeOH solution gave hydrogen bonded dimers of $[\mathbf{1}'(PPh_3)_2]$ and $[\mathbf{2}'(PPh_3)_2]$, respectively. The crystals of $[\mathbf{1}Cl_2]$, $[\mathbf{2}Cl_2]$, $[\mathbf{1}(PPh_3)_2]Cl_2$, $[\mathbf{1}'(PPh_3)_2]$ and $[\mathbf{2}'(PPh_3)_2]$ were obtained and their X-ray structures were determined. The X-ray data collection of $[\mathbf{2}'(PPh_3)_2]$ was carried out in KEK.

3 Results and Discussion

The structure of $[\mathbf{1}'(PPh_3)_2]_2$ shown in Figure 1 is a hydrogen-bonded dimer of the half-lantern complex. The NH of each biimidazolate ($Hbim^-$) ligand donates a hydrogen to the N of $Hbim^-$ on the neighboring complex and then four hydrogen bonds connect two dirhodium complexes. The structure of $[\mathbf{2}'(PPh_3)_2]_2$ is very similar to $[\mathbf{1}'(PPh_3)_2]_2$. Dihedral angles between two $Hbim^-$ ligands on each dirhodium unit are ca 16°. These angles hindered coplanar self-complementary hydrogen bonds between the biimidazolate ligands on the different dirhodium units. To form hydrogen bonds between the noncoplanar biimidazolate ligands, the Rh2–Rh2′ axis in $[\mathbf{1}'(PPh_3)_2]_2$ was rotated 25.7° from the eclipsed position with the Rh1–Rh1′ around the two-fold axis, and the dihedral angle between the biimidazolate ligands is 34.90(13)°.

The CV of $[\mathbf{1}](PF_6)_2$ in CH_3CN did not show any clear redox process between –2.1 V and 1.9 V. However, $[\mathbf{1}(PPh_3)_2](PF_6)_2$ and $[\mathbf{1}'(PPh_3)_2]_2$ in CH_2Cl_2 showed some oxidation processes The biimidazole complex monomer $[\mathbf{1}(PPh_3)_2](PF_6)_2$ exhibits one reversible ($E_{1/2}$ = 0.208 V) and two irreversible oxidation waves (E_{pa} = 0.484 V and 0.697 V). The first reversible oxidation wave can be assigned to oxidation of the dirhodium core Rh_2^{4+}/Rh_2^{5+} and the second one to Rh_2^{5+}/Rh_2^{6+}. On the other hand, the biimidazolate complex dimer $[\mathbf{1}'(PPh_3)_2]_2$ shows two sets of two successive reversible oxidation waves and one irreversible oxidation wave. This indicated that relatively stable mixed-valence state existed for $[\mathbf{1}'(PPh_3)_2]_2$.

The ESR spectra of the oxidized $[\mathbf{1}'(PPh_3)_2]_2^+$ and optimized structure of the model complex cations suggested that stability of the mixed valence state is due to proton coupled electron motion. We have proposed the complex cation that consist of the oxidized and completely deprotonated $[Rh_2(O_2CR)_2(bim)_2(PPh_3)_2]^-$ hydrogen bonded with the dication of $[Rh_2(O_2CR)_2(H_2bim)_2(PPh_3)_2]^{2+}$.

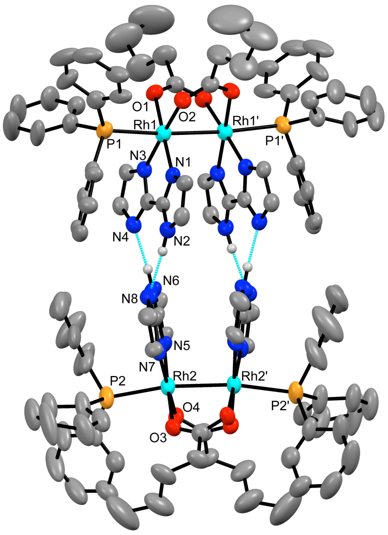

Fig. 1: The structure of $[\mathbf{1}'(PPh_3)_2]_2$

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References

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