A New Strategy toward Construction of Organic-Inorganic Hybridized Molecules. An Infinite One-Dimensional Chain Structure Assembled with Hydrogen- and Coordinate-Bonds

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Two novel organic-inorganic hybridized molecules assembled with hydrogen- and coordinate-bonds, $[Rh_2(O_2CMe)_4(daapy)_2]$ (daapy = 2,6-diacetylaminopyridine) and $\{[Rh_2(O_2CMe)_4][Ni(bpbg)_2]\}_n$ (bpbg = biphenylbiguanide), have been prepared, which have been characterized by UV-vis, IR, and ^1H NMR spectroscopic and thermogravimetric (TG) and X-ray diffraction methods.

New proposal of the construction principle of organic-inorganic hybridized compounds allows us to expect unique electronic properties such as nonlinear optical behavior, electric conductivity, and magnetism.[1] The synthesis of molecular assembly using a coordinate bond is an intensive current interest in chemistry.[2] Besides the covalent bonds, the control of hydrogen bond, which is also an efficient organizing force in the design of solid-state materials,[3] is one of strategies to achieve the formation of molecular assemblies because of its high directionality and appropriate strength. Recently, we[4] and others[5] have reported some hydrogen-bond-assembled metal complexes. Introduction of the hydrogen bond as an assembling tool into the metal complexes may offer a means for precise structural control and new materials with interesting characters by synergistic contribution of hydrogen- and coordinate-bonds. As the complex system that will enable this strategy to come true, we selected two systems, $Rh_2(O_2CMe)_4$-daapy (daapy = 2,6-diacetylaminopyridine) and $Rh_2(O_2CMe)_4$-$Ni(bpbg)_2$ (bpbg = biphenylbiguanide). Here, we report the two structures of dirhodium acetate complexes assembled with hydrogen- and coordinate-bonds, which have been characterized by UV-vis, IR, and ^1H NMR spectroscopic and thermogravimetric (TG) and X-ray diffraction methods.

(i) $[Rh_2(O_2CMe)_4(daapy)_2]$: Addition of 2 equiv. of daapy to $Rh_2(O_2CMe)_4$ (**1**)[6] in an acetone solution gave a blue solution. Standing the solution for a few days gave a single crystal suitable for X-ray analysis.[7] The crystal structure is shown in Figure 1(a). The complex has the crystallographic inversion center at the center of the $[Rh_2(O_2CMe)_4]$ core. The Rh-Rh separation is 2.4035(9) Å, which lies in the usual range (2.396 - 2.415 Å).[8] As was expected, daapy are linked to $Rh_2(O_2CMe)_4$ from both the apical sites through coordinate- and hydrogen-bonds; Rh-N(2) = 2.390(5) Å, N(1)···O(5) = 2.89, N(1)···O(6) = 3.10, N(3)···O(3) = 2.91, and N(3)···O(4) = 2.89 Å. Although the Rh(II)-N(2) bond is clearly lengthened in comparison with that of **1**·$(pyridine)_2$ (2.227(5) Å)[8a] reported previously, it is slightly shorter than that for the complex with acrizine (2.413(3) Å) at the axial positions, **1**·$(acridine)_2$,[8b] which is considered to have been elongated by repulsion between the benzene rings of acridine and the coordinated acetate oxygens. The Rh-N bond length found here may result from a competition of the hydrogen bond and steric repulsion between the carboxylate oxygens and amino groups. The daapy molecules coordinated to the Rh(II) atom with the Rh-N(2)-C(5) and Rh'-Rh-N(2) angles of 162.3(2)° and 178.3(2)°, respectively. The Rh(II) atom is slightly displaced 0.08 Å out of the carboxylate planes toward the axial nitrogen atom. The daapy plane approximately bisects the acetate groups; it forms dihedral angles of 47.6 and 46.3° with the O(3)-O(5)-O(3')-O(5') and O(4)-O(6)-O(4')-O(6') planes.

This effective hydrogen bonding interaction is also supported by the fact that these complexes show higher decomposition temperature as measured by TG. The decrease of mass for **1**·$(daapy)_2$ originated in release of daapy molecules was observed at 230-300 °C, which is significantly high as compared with that for **1**·$(pyridine)_2$ (200-240 °C) with axial ligands having no hydrogen bonding groups in contrast to daapy. It may indicate that **1**·$(daapy)_2$ is thermally stabilized by hydrogen bonds, which is too stable for the longer Rh-N bond.

The formation of hydrogen bonds for **1**·$(daapy)_2$ in solution was also detected by ^1H NMR and UV-vis spectra. The N-H proton signal for daapy observed at 7.59 ppm in $CDCl_3$, as examined by ^1H NMR measurement, exhibited a larger downfield shift (9.20 ppm) by its binding to **1**, indicating that the amide protons of daapy form strong hydrogen-bonds with the acetate oxygens of **1**. The UV-vis spectrum of **1**·$(daapy)_2$ in the d-d region in acetone exhibited a peak that is assignable to $\pi^*_{RhRh} \rightarrow \sigma^*_{RhRh}$ transition[8d,9] at 584 nm, which is in a shorter wavelength region compared with those of **1** in acetone solution (603 nm) and of tetrakis(pivalato)dirhodium(II) in $CHCl_3$ (622 nm). This blue shift is too small for coordination of pyridine-type ligand; that of **1**·(4-*tert*-butylpyridine)$_2$ in $CHCl_3$ are observed at 519 nm. These facts suggest that the σ-donation of daapy for the σ^*_{RhRh} orbital has been weakened in comparison with pyridine and 4-*tert*-butylpyridine because of the steric repulsion between the amino and acetate groups.

(ii) $\{[Rh_2(O_2CMe)_4][Ni(bpbg)_2]\}_n$: On the basis of the above strategy, the construction of an organic-inorganic hybridized compound has been attempted for a combination of $[Rh_2(O_2CMe)_4]$ and $[Ni(bpbg)_2]$. Addition of an equimolar amount of $[Ni(bpbg)_2]$ into a DMF solution containing $[Rh_2(O_2CMe)_4]$ (**1**)[6] gave purple precipitate almost immediately. Fortunately, we succeeded in obtaining a single crystal suitable for X-ray diffraction analysis.[10] The crystal structure, as shown in Figure 1(b), revealed the formation of 1:1 complex of **1**·$[Ni(bpbg)_2]$. The complex has the crystallographic inversion centers on the nickel atom and at the center of the $[Rh_2(O_2CMe)_4]$ core. The Rh-Rh separation is 2.411(2) Å, which is almost the same as that of **1**·$(daapy)_2$ (2.4035(9) Å). Interestingly, the $[Ni(bpbg)_2]$ has been linked to $[Rh_2(O_2CMe)_4]$ through coordinate- and hydrogen-bonds to form an infinite one-dimensional chain structure; Rh-N(3) = 2.319(9) Å, N(1)···O(3) = 2.85, N(1)···O(4) = 3.04, N(5)···O(1) = 3.08, and N(5)···O(2) = 2.86 Å. The tightly-bound NH···O hydrogen bonds have also been confirmed by solid state IR spectra; the N-

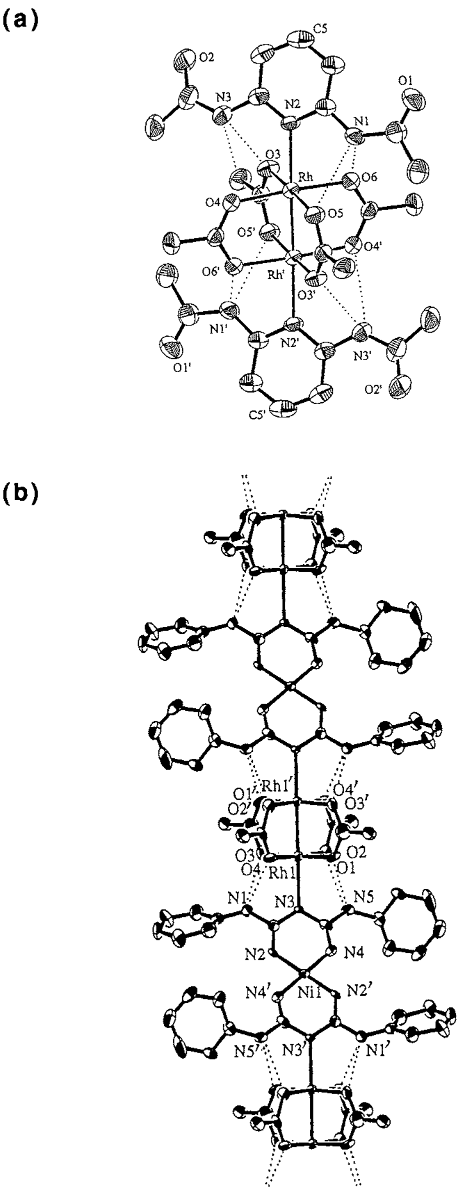

Figure 1. ORTEP drawings of **1**·(daapy)$_2$ (a) and {**1**·[Ni(bpbg)$_2$]}$_n$ (b) with atom labels. The primed and non-primed atoms are related by a crystallographic center of symmetry.

H stretching vibration of the [Ni(bpbg)$_2$] complex observed at 3408 cm^{-1} shifted to 3342 cm^{-1} with sharpening of absorption band by the complexation. Such an organic-inorganic hybridized compound composed of dimeric Rh(II) lantern-type complex and [Ni(bpbg)$_2$] that are assembled with both double-hydrogen- and coordinate-bonds is to the best of our knowledge the first example.[8b] The slightly longer Rh(II)-N(3) bond may be explained in the same way as **1**·(daapy)$_2$. The [Ni(bpbg)$_2$], in which the Ni(II) atom is coordinated with the four nitrogen atoms in a square-planar geometry, binds to the Rh(II) atom with the Rh-N(3)-Ni and Rh'-Rh-N(3) angles of 148.9(7)° and 176.3(5)°, respectively. The Rh(II) atom is slightly displaced 0.06 Å out of the carboxylate planes toward the axial nitrogen atom. The [Ni(bpbg)$_2$] plane approximately bisects the acetate groups; it forms dihedral angles of 36.5 and 54.5° with the O(1)-O(3)-O(1')-O(3') and O(2)-O(4)-O(2')-O(4') planes of the bridging acetates.

The UV-vis spectrum of {**1**·[Ni(bpbg)$_2$]}$_n$ in a dilute acetone solution exhibited a $\pi^*_{\mathrm{RhRh}} \rightarrow \sigma^*_{\mathrm{RhRh}}$ transition[8d,9] at 571 nm, which is in a slightly shorter wavelength region compared with that of **1**·(daapy)$_2$ in acetone (584 nm). It indicates that the strength of the coordinate- and hydrogen-bonds in {**1**·[Ni(bpbg)$_2$]}$_n$ may be somewhat stronger than that in **1**·(daapy)$_2$.

The above findings indicate that the hydrogen bonding interaction is strongly formed in both solution and solid states, and that such a combination of coordinate- and hydrogen-bonds is useful as an assembling tool in the construction of organic-inorganic hybridized compounds such as a molecular-wire.

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7 Crystal data for **1**·(daapy)$_2$: C$_{26}$H$_{34}$N$_6$O$_{12}$Rh$_2$, *F. W.* = 828.40, monoclinic, space group $P2_1/c$, a = 9.873(2), b = 10.999(7), c = 15.100(6) Å, β = 104.83(2)°, V = 1585(1) Å^3, Z = 2, D_C = 1.526 gcm^{-3}, μ(Mo Kα) = 10.97 cm^{-1}, F(000) = 732.0, T = 298 K, 2621 reflections measured (2θ$_{\max}$ = 52°), 2006 ($I > 3\sigma(I)$) used in the refinement, R = 0.050, R_w = 0.078.

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10 Crystal data for **1**·[Ni(bpbg)$_2$]: C$_{39}$H$_{47}$N$_{11}$NiO$_9$Rh$_2$, *F. W.* = 1078.37, triclinic, space group $P\bar{1}$, a = 11.959(8), b = 13.091(3), c = 8.706(4) Å, α = 91.84(3), β = 105.24(4), γ = 64.52(3)°, V = 1181(1) Å^3, Z = 1, D_C = 1.516 g cm^{-3}, μ(Mo Kα) = 11.51 cm^{-1}, F(000) = 548.0, T = 298 K, 2910 reflections measured (2θ$_{\max}$ = 52°), 1300 ($I > 3\sigma(I)$) used in the refinement, R = 0.049, R_w = 0.043.