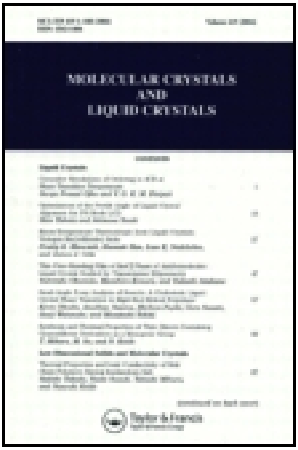

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Unique Self-Organization System Derived from Biguanidato and Biuretato Complexes Through Triple Hydrogen-Bonds

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Unique Self-Organization System Derived from Biguanidato and Biuretato Complexes Through Triple Hydrogen-Bonds

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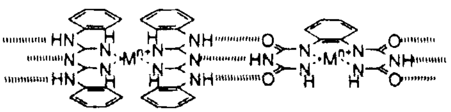
A unique triple hydrogen-bonding system has been constructed between the transition metal (Ni(II), Cu(II), Co(III)) complexes with bis(biphenylbiguanidato) and *ortho*-phenylenebis(biuretato) ligands, which have been characterized by IR and ^{1}H-NMR spectroscopies and thermogravimetric and X-ray structure analyses.

INTRODUCTION

The BIGUANIDE compound is a strong chelating base containing a DAD system (D and A denote proton donor and acceptor) for hydrogen-bond. We previously reported that reaction of bis(biphenylbiguanidato)nickel(II) complex, [Ni(bpbg)$_2$], with phenobarbital (Phbar) containing ADA system gave a self-organized system to form a triple hydrogen-bonding compound.[1] As more development of the study, we paid attention to a self-assembly formed between the transition metal complexes, which allow us to expect interesting physico-chemical functions such as nonlinear optical behavior, electric conductivity, and magnetism, due to the unique characteristics that result from combining organic and inorganic molecules.[2] Indeed, another DAD-ADA triple hydrogen-bonding system formed between the ethylenebis(biguanidato)-manganese(III) and bis(violurato)copper(II) complexes reported previously showed a unique electron transfer reaction from Mn and Cu through bridging OH group, accompanied by proton transfer between DAD-ADA system.[3] We newly designed and synthesized a triple hydrogen-bonding system between the transition metal (Ni(II), Cu(II), Co(III)) complexes with bis(biphenylbiguanidato), bpbg, and *ortho*-phenylene-bis(biuretato), $ph(bu)_2$, lignads (Chart 1), whose structures and physico-chemical properties were discussed.

CHART 1



$[M(bpbg)_2]^{(n-2)+}$ $[M\{ph(bu)_2\}]^{(4-n)-}$

EXPERIMENTAL

Materials

The bis(biphenylbiguanidato) complex, $[Ni(bpbg)_2]$ and $[Cu(bpbg)_2]$[1], and the *ortho*-phenylenebis(biuretato) complexes, $Na_2[Ni\{ph(bu)_2\}]$ $\cdot 4DMSO$[4] and $K[Co\{ph(bu)_2\}]$,[5] were prepared according to the literatures. In order to raise up their solubility for organic solvent, the counter cations of biuretato complexes were exchanged to teteraphenylphosphonium (PPh_4^+) or bis(triphenylphosphoranylidene)-ammonium (PPN^+). Reaction of $CHCl_3$ solution of $[Ni(bpbg)_2]$ and THF solution of $(PPh_4)_2[Ni\text{-}ph(bu)_2]$ in 1:1 molar ratio gave a pale orange precipitate (complex **1**).

The complexes $[Ni(bpbg)_2]\text{-}(PPh_4)[Co\{ph(bu)_2\}]$ (**2**) and $[Cu(bpbg)_2]\text{-}(PPh_4)[Co\{ph(bu)_2\}(phpy)_2]$ (**3**) (phpy = 4-phenylpyridine) were also prepared by the same method as complex **1**.

Measurements

IR spectra were recorded on a Jasco FT/IR-410 spectrometer, which were carried out with a KBr disk method. ^1H-NMR spectra were measured at 300 MHz on a Varian Gemini-2000 spectrometer in pyridine-d_5 with TMS as an internal standard. DSC measurements were performed with a Rigaku TAS 300 system equipped with a DSC 8230L. The heating rate of samples, which were packed in Al crucibles, was 5 Kmin^{-1}, and Al_2O_3 was used as a reference material. ESR spectra were obtained on a JEOL RE-1X spectrometer at 77K.

X-ray diffraction data for complex **3** were collected with a Rigaku R-AXIS-4 imaging plate diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). The structure was solved by the heavy-atom method and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Crystal data: monoclinic, space group $P2_1/n$, a = 12.696(9), b = 46.338(10), c = 19.091(4) Å, β = 99.31(4)°, V = 11084(7) $Å^3$, and Z = 4.

RESULTS AND DISCUSSION

Figure 1 illustrates the solid state IR spectra of $[Ni(bpbg)_2]$, $(PPh_4)_2[Ni\{ph(bu)_2\}]$, and the complex **1**. The N-H stretching vibration of complex 1, 3354 cm^{-1}, was observed at apparent lower wavenumber region in comparison with those of $[Ni(bpbg)_2]$ (3415 cm^{-1}) and $(PPh_4)_2[Ni\{ph(bu)_2\}]$ (3451 cm^{-1}). The C=O stretching vibration of complex **1**, 1588 cm^{-1}, was also detected in a lower wavenumber region compared with that of $(PPh_4)_2[Ni\{ph(bu)_2\}]$ (1596 cm^{-1}). Combining with the elemental analysis, these findings indicate that the complex **1** forms a 1:1 adduct linked by hydrogen-bonds between $[Ni(bpbg)_2]$ and $(PPh_4)_2[Ni\{ph(bu)_2\}]$.

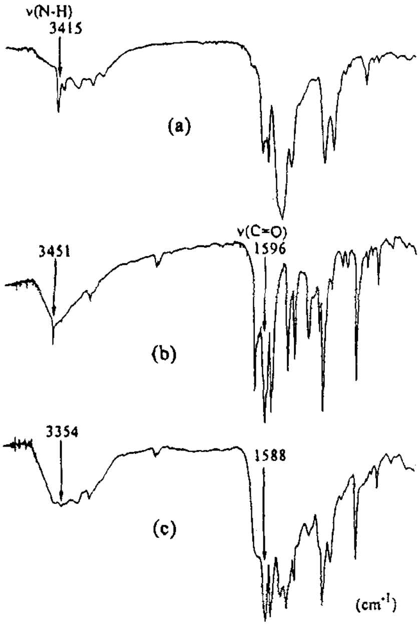


FIGURE 1 Solid state IR spectra of $[Ni(bpbg)_2]$ (a), $(PPh_4)_2[Ni\{ph(bu)_2\}]$ (b) and complex **1** (c).

In order to examine the formation of hydrogen-bonds between them in solution, ^{1}H-NMR chemical shifts of the N-H protons involving triple hydrogen-bonds were followed by titration method. The N-H protons of [Ni(bpbg)$_2$] and (PPN)$_2$[Ni{ph(bu)$_2$}] observed at 9.07 and 7.01 ppm in pyridine-d_5 showed drastic down-field shift to10.08 and 8.43 ppm, respectively, by formation of 1:1 complex. The 1:1 adduct (complex **2**) of [Ni(bpbg)$_2$] and (PPh$_4$)[Co{ph(bu)$_2$}] (7.15 ppm) also exhibited distinct down-field shift to 9.66 and 8.89 ppm, respectively. These down-field shifts were also accompanied by line-broadening of the N-H proton signals. These facts strongly support the formation of triple hydrogen-bonding networks in solution.

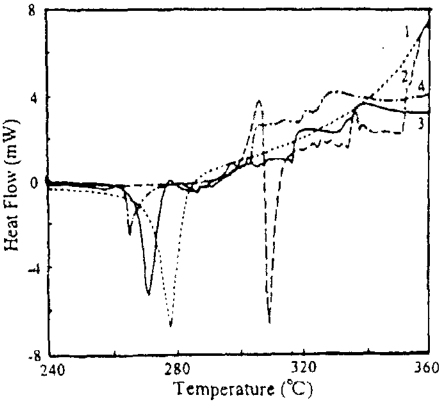


FIGURE 2 DSC curves of [Ni(bpbg)$_2$] (1), (PPh$_4$)$_2$[Ni{ph(bu)$_2$}] (2), complex 1 (3) and the 1:1 mixture of the starting materials (4).

Thermal analyses, TG and DSC, were performed for [Ni(bpbg)$_2$], (PPh$_4$)$_2$[Ni{ph(bu)$_2$}], complex **1**, and the 1:1 mixture of their starting materials in the temperature range of 50-400 ℃ in order to estimate the strength of the hydrogen-bond. For the complex **1**, the gradual decrease of the mass assignable to releasing of CHCl$_3$ molecules were detected in the range of 50-150 ℃, indicating that the CHCl$_3$ molecules are tightly maintained in the crystal. Their DSC curves in the range of 240-360 ℃ are shown in Figure 2. The decomposition temperature of complex **1** is clearly different from those of not only the starting materials but also the 1:1 mixture. The decomposition energies for complex **1** and the 1:1 mixture were estimated to be 91.5 and 27.0 kJ/mol, respectively, from the endothermic process areas, whose difference, 64.5 kJ/mol, is about three times of the value calculated for the NH···N hydrogen-bonds for melamine, ~25 kJ/mol. This energy may be reasonable value when considering formation of the triple hydrogen-bonds for the complex **1**.

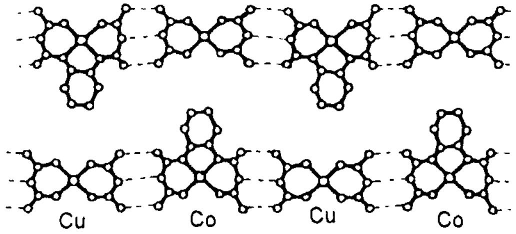


FIGURE 3 ORTEP drawing of the [Cu(bpbg)$_2$]-(PPh$_4$)[Co{ph(bu)$_2$}(phpy)$_2$] system showing a infinite tape structure linked by triple hydrogen-bonds. (Only the skeltons around the metal atoms are represented for clarity.

Fortunately, the single crystals of complex **3** suitable for X-ray analysis were obtained from the reaction solution of [Cu(bpbg)$_2$], (PPh$_4$)[Co{ph-(bu)$_2$}(phpy)$_2$] and phpy in CHCl$_3$. The crystal structure, as shown in Figure 3, revealed one-dimensional infinite tape structure that were linked with alternate DAD-ADA type triple hydrogen-bonds between [Cu(bpbg)$_2$] and (PPh$_4$)[Co{ph(bu)$_2$}(phpy)$_2$], in which the complementary hydrogen-bonds seen in the case of only the biuretato complex were not observed.[6] The intermolecular N(H)···N distances found here, ca. 2.9 Å, are in the range of typical hydrogen-bond distances.[7] The chelate ring planes of the complexes slightly twisted each other. Such a twisting conformation has also been detected in the [Ni(bpbg)$_2$]-Phbar complex[1] and (NBu$^n_4$)[Rh(or)(cod)]-dapy (or = orotato, dapy = 2, 6-diaminopyridine) reported previously,[8] which are due to the subtle difference between the C(O)-N(H)-C(O) and N(H)-N-N(H) distances around the central N-H···N hydrogen-bond.

ESR spectrum of the complex **3** may support the crystal structure described above: Frozen solution ESR measurement of complex **3** in CHCl$_3$ afforded a spectrum typical of square-planar geometry ($g_{\perp}$ = 2.06, $g_{\parallel}$ = 2.17, $A_{\parallel}$ = 191 G) with a clear hyperfine splitting showing the strong coordination of four nitrogen atoms, although that of [Cu(bpbg)$_2$] showed an isotropic spectral pattern at g = 2.08.

CONCLUSION

The DAD-ADA type triple hydrogen-bonding system formed by self-assembly of the transition metal (Ni(II), Cu(II), Co(III)) complexes with bis(biphenylbiguanidado) and *ortho*-phenylenebis(biuretato) ligands were constructed in aprotic solvent, which were spectroscopically, structurally and thermodynamically characterized. The system accidentally derived from [Cu(bpbg)$_2$] and (PPh$_4$)[Co{ph(bu)$_2$}(phpy)$_2$] revealed an infinite one-dimensional triple hydrogen-bonding networks, which was first confirmed by X-ray diffraction analysis. The systems reported here are organic-inorganic hybrids formed between transition metal complexes through triple hydrogen-bonds, which may make us expect appearance of unique physico-chemical functions.

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