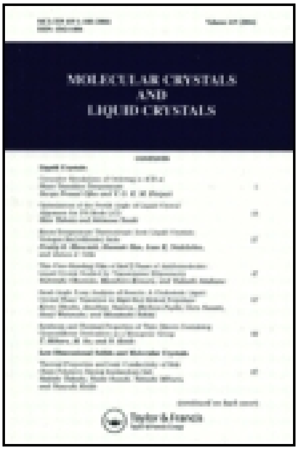

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A Triply Hydrogen-Bonding System Constructed by Self-Assembly of Biguanide Complex and Imide-Containing Compound

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A TRIPLY HYDROGEN-BONDING SYSTEM CONSTRUCTED BY SELF-ASSEMBLY OF BIGUANIDE COMPLEX AND IMIDE-CONTAINING COMPOUND

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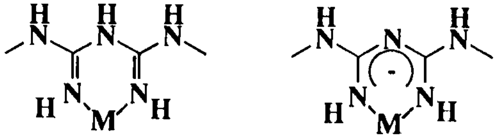
Abstract A triply hydrogen-bonding system has been constructed between bis(biphenylbiguanidado)nickel(II) ([Ni(bpbg)$_2$]) and phenobarbital (Phbar), which has been characterized by the IR and ^{1}H-NMR spectroscopies and the X-ray structure analysis.

INTRODUCTION

The BIGUANIDE compound is a strong chelating base which can form both neutral (biganide) and deprotonated (biguanidado) species (Scheme 1) by a pH control and has unique chemical properties that enable to stabilize high-valent metal ions[1] and to appeare aromatic character by the complexation with metal ions.[2,3] Since this type of ligand can also construct a hydrogen-bonding system, it is interested from a view-point of molecular recognition associated with biological activities and of crystal engineering of solid materials.[4-8] The complexation of metal ions into such a system can lead to an appearance of some interesting characters such as high electric conductivity, nonlinear optical property, and magnetism. Here, we describe a triply hydrogen-bonding complex system formed between [Ni(bpbg)$_2$] and Phbar.

Sheme 1.



biguanide-complex biguanidado-complex

EXPERIMENTAL

Materials.

N1, N5-biphenylbiguanide (bpbgH) hydrochloride was synthesized according to the previously reported method.[9] The [Ni(bpbg)$_2$] complex was prepared by the following procedure. To an ethanol solution (200 mL) containing bppgH·HCl (3.5 g, 12 mmol) was added $NiCl_2 \cdot 6H_2O$ (1.4 g, 6 mmol) in water (10 mL) at 60 °C. The resulting solution was adjusted to pH ca. 8.3 with an aqueous 28% NH_4OH to prepare the biguanidado complex. The pale-orange plate-like crystals (complex **1**) were obtained from $CHCl_3$. The sample (**2**) was also preparedby pressing the solid-state mixtures of [Ni(bpbg)$_2$] and Phbar in a 1:2 molar ratio.

Spectral measurements.

IR spectra were recorded on a JASCO A3 infrared spectrophotometer with a KBr disk method. ^{1}H-NMR spectral measurements were performed at 200 MHz on a Varian XL-200 spectrometer with TMS in $CDCl_3$ as an internal reference of the chemical shift.

X-ray structure determination.

Pale-orange plate-like single crystals (complex **1**) were obtained from a THF solution containing [Ni(bpbg)$_2$] and Phbar in a 1:1 molar ratio. The crystal with dimensions of 0.05 x 0.1 x 0.2 mm was used for collection of intensity data. Diffraction data were collected with an Enraf Nonius CAD4-EXPRESS four-circle diffractometer using graphite-monochromated Mo Kα radiation ($\bar{\lambda}$ = 0.71073 Å). Crystal data for **1**: $NiN_{10}C_{28}H_{28}$-$C_{12}H_{12}O_3N_2$, MW= 795.53, triclinic, space group $P\bar{1}$, a = 9.205(2), b = 13.433(3), c = 36.113(10) Å, α = 91.70(2), β = 90.74(2), γ = 92.43(2)°, V = 4458.9 Å^3, Z = 4.

RESULTS AND DISCUSSION

Figure 1 shows the solid state IR spectra of the complex **1** and the sample **2**, which were compared with those of [Ni(bpbg)$_2$], Phbar, and the sample (**3**) that is doubly stacked pellets of each disc of [Ni(bpbg)$_2$] and Phbar, as references. The N-H stretching vibration of the complex **1** was observed at 3250 cm^{-1}, which is in lower wavenumber region in comparison with those of [Ni(bpbg)$_2$] (3350 cm^{-1}) and Phbar (3475 cm^{-1}). The C=O stretching vibration of the complex **1** exhibited at 1660 cm^{-1}, which is also in lower wavenumber region in comparison with that of Phbar (1700 cm^{-1}). These facts indicate that [Ni(bpbg)$_2$] and Phbar form a hydrogen bonding system.

Interestingly, the IR spectral pattern of the sample **2** is very similar to that of the complex **1** but is quite different from that of the sample **3**; the N-H and C=O stretching vibrations of [Ni(bpbg)$_2$] and Phbar in the sample **2** showed lower wavenumber shifts as shown in that of complex **1**. This fact indicates that the high-press-formed mixture of [Ni(bpbg)$_2$] and Phbar with a 1:2 molar ratio in the solid-state also constructs the hydrogen-bonding system and that the ability for self-assembly by the hydrogen-bonding is very strong between [Ni(bpbg)$_2$] and Phbar.

The ^{1}H-NMR resonances of the N-H protons of [Ni(bpbg)$_2$] at 6.10 ppm in a CDCl$_3$ solution showed a gradual down-field shift and a line-broadening by the consecutive addition of Phbar (the left side of Figure 2). The proton resonance reached at 10.6 ppm in the addition of 2 eq. of Phbar to [Ni(bpbg)$_2$], but it was little affected by the addition of large excess of Phbar. On the other hand, the addition of [Ni(bpbg)$_2$] to Phbar resulted in the disapearance of the N-H proton resonance of Phbar (the right side of Figure 2). The N-H proton was not observed even in the presence of a trace amount of Phbar to [Ni(bpbg)$_2$]. These behaviors suggest the formation of hydrogen-bonding complex system, [Ni(bpbg)$_2$]-Phbar, accompanied by the proton transfer from Phbar to [Ni(bpbg)$_2$]. This evidence is due to the fact that the biguanidado moiety of [Ni(bpbg)$_2$] attracts protons to form biguanide moiety, and that the N-H proton of Phbar is protic to release

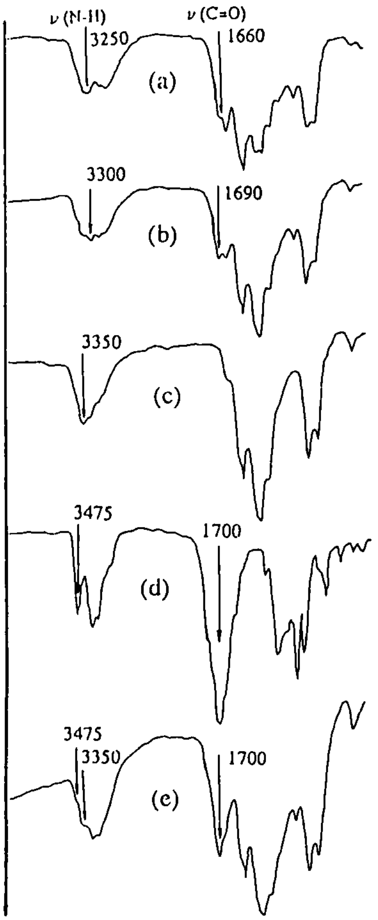


FIGURE 1 The solid-state IR spectra of the complex **1** (a), sample **2** (b), [Ni(bpbg)$_2$] (c), Phbar (d), and sample **3** (e).

the N-H proton. All of the ^{1}H-NMR spectral findings support the IR spectral result that the triply-hydrogen-bonds are formed between [Ni(bpbg)$_2$] and Phbar in a 1:2 molar ratio.

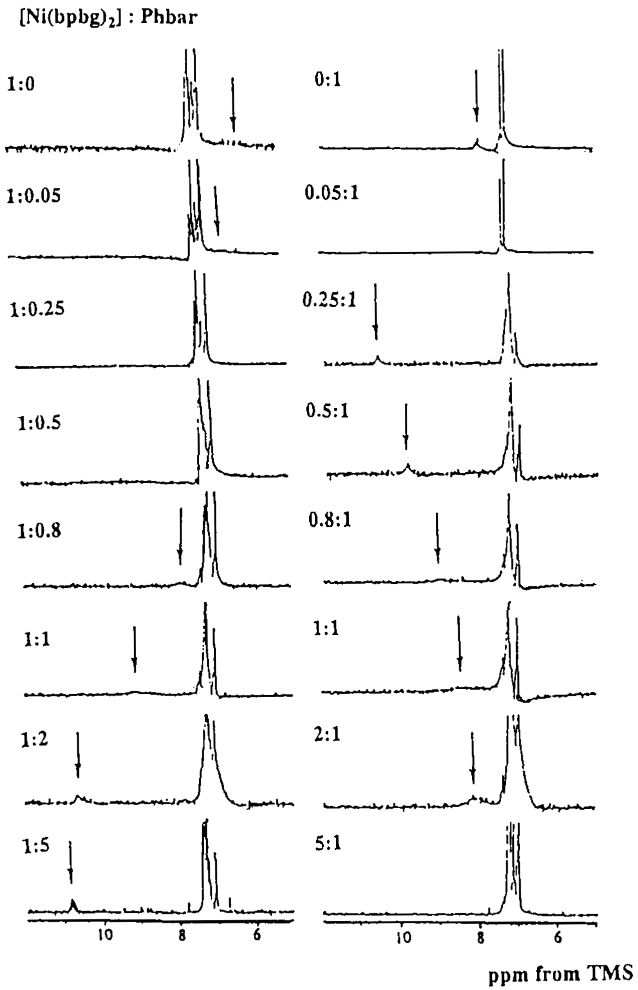
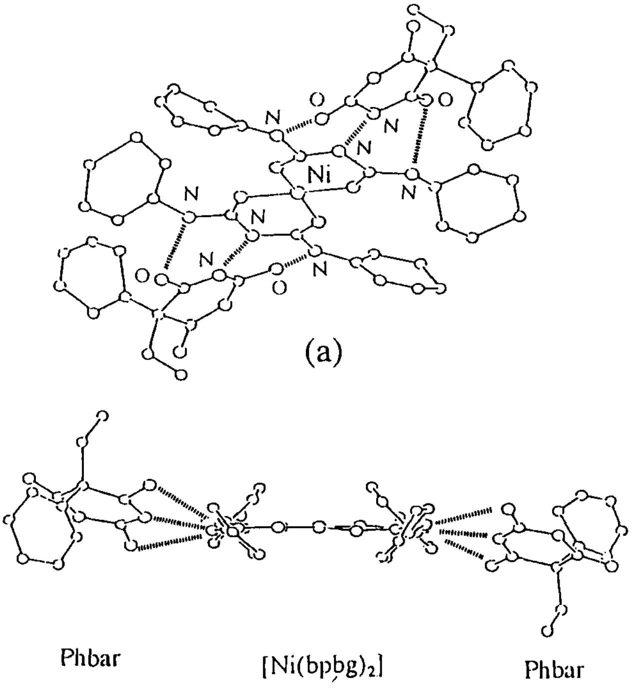


FIGURE 2 The ^{1}H-NMR spectra of [Ni(bpbg)$_2$]-Phbar systems with various constituents in $CDCl_3$.

The crystal structure of the complex **1** (Figure 3) revealed that [Ni(bpbg)$_2$] and Phbar form a triply hydrogen-bonded network in a 1:2 ratio, which is very similar to the hydrogen-bonded network found in the melamine-barbiturate complex.[10] This structural result demonstrates that the triply hydrogen-bonding system, as also speculated from the results by the IR and ^{1}H-NMR spectroscopies, is really constructed between metal-biguanide complex and imide-containing compound. The hydrogen bond distances found here, ca. 2.9 Å, are in the range of typical hydrogen-bond distances reported hitherto (2.4 - 3.0 Å),[11] although the Phbar ring plane is twisted from the [Ni(bpbg)$_2$] chelate ring plane. This may be due to the subtle difference between the CO-NH-CO covalent angles for Phbar and the NH-CNC-NH covalent angles for [Ni(bpbg)$_2$]. Such a twisting conformation has also been observed in the melamine-barbiturate complex. Hence, it is concluded that this type of complexes is favorable for the construction of triply hydrogen-bonding system.



(a)

(b)

FIGURE 3 Perspective drawing of the [Ni(bpbg)$_2$]-(Phbar)$_2$ complex (**1**) showing the hydrogen-bonding network between [Ni(bpbg)$_2$] and Phbar (a) and side-view showing the twisted structure (b).

CONCLUSION

The triply hydrogen-bonding complex system formed by self-assembly of [Ni(bpbg)$_2$] and Phbar in aprotic solvent was spectroscopically and structurally characterized. The solid state IR spectra assignable to the C=O and N-H stretching vibrations which contribute to the hydrogen-bonding interactions were observed at a lower wavenumber region in comparison with those for the respective starting compounds. This complex formation was also evidenced in the IR spectrum of the system obtained by pressing the solid-state mixtures of [Ni(bpbg)$_2$] and Phbar in a 1:2 molar ratio, indicating that this hydrogen-bonding complex is formed in the solid-state reaction. The ^{1}H-NMR resonances of the N-H protons for [Ni(bpbg)$_2$] and Phbar in a CDCl$_3$ solution showed drastic down-field shifts and line-broadening by the complex formation. These facts suggest that [Ni(bpbg)$_2$] and Phbar form a tight hydrogen-bonding complex between the two constituents. The X-ray structure of the complex **1** confirmed that [Ni(bpbg)$_2$] and Phbar form triply hydrogen-bonded networks in a ratio of 1:2.

This triply hydrogen-bonded complex established here has significant implications for the control of molecular assembly using supramolecular interactions in crystal engineering chemistry and biochemistry.

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