Chemistry

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Gelator of a supramolecular gel formed with Co(II) bppp complex

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Introduction

Supramolecular gels formed with a metal complex gelator are common now. In such type of gels, the metal complex gelators are usually coordinated by ligands having large and flexible functional groups. Contrary to such ordinary cases, the ligand of our metal complex gelator has a very compact and rigid structure as shown in Fig. 1. The ligand, which is abbreviated to bppp, and $CoCl_2 \cdot 6H_2O$ formed a mono-type complex $[CoCl_2(bppp)] \cdot 2H_2O$ (Fig. 2) in methanol. When water was gradually added to a methanol solution of $[CoCl_2(bppp)] \cdot 2H_2O$, the solution turned to gel. On the other hand, a bis-type complex $[Co(bppp)_2](NO_3)_2$ (Fig. 3) was obtained from a methanol solution of bppp and $Co(NO_3)_2 \cdot 6H_2O$. Although several conditions were tried, gelation from $[Co(bppp)_2](NO_3)_2$ was never achieved. Therefore, the gelator of the gel was considered to be $[CoCl_2(bppp)]$ at the first stage. However, the color of $[CoCl_2(bppp)]$ is blue-green but those of the gel and $[Co(bppp)_2]^{2+}$ are close to yellow. A question about the true gelator arose. In order to determine the true gelator, EXAFS, which is a suitable method to obtain the structural information around a metal centre in a solution state, was carried out.

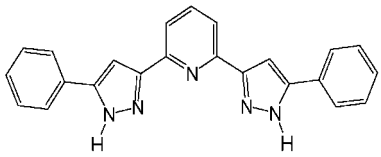

Fig.1 2,6-bis(5-phenil-3-pyrazolyl)pyridine(bppp)

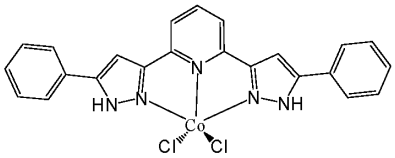

Fig.2 $[CoCl_2(bppp)]$

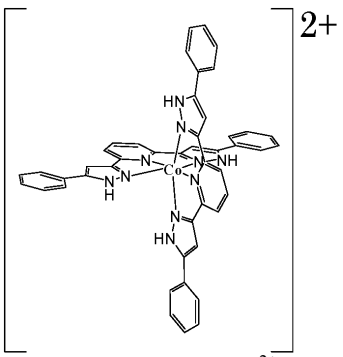

Fig.3 $[Co(bppp)_2]^{2+}$

Experimental

The gel, which was formed by adding $[CoCl_2(bppp)] \cdot 2H_2O$ into a methanol/water(1:2) solution, was packed in a small vinyl bag. The bag was set at an angle of 45º against the incident beam of BL-27B station of PF-KEK. The measurement of Co K-edge EXAFS spectrum was carried out in the fluorescence mode at room temperature.

Results

FT functions $|FT(k^3\chi(k))|$ observed and simulated are shown in Fig. 4. The simulated line is the result of refinement based on the molecular structure of $[Co(bppp)_2]^{2+}$obtained from our single crystal X-ray structure analysis. The coincidence between the observed and calculated ones is good and the refined parameters were within a reasonable range. The refinement based on the structure of $[CoCl_2(bppp)]$ was also performed. However, the calculation was failed because the Debye-Waller factors for the atoms in the first nearest shell were converged in negative values. This gives a clear result. The gelator is $[Co(bppp)_2]^{2+}$. Considering the problem of the color, this conclusion is reasonable. $[Co(bppp)_2]^{2+}$ is considered to be generated from complexation equilibrium between $[CoCl_2(bppp)]$ and $[Co(bppp)_2]^{2+}$. However, the observation that no gel was obtained from $[Co(bppp)_2](NO_3)_2$ suggests that another factor is necessary for the gel formation. Our recent study performed from another direction indicated the factor to be the presence of Cl^- ion. The work for elucidating the mechanism of this gelation is in progress.

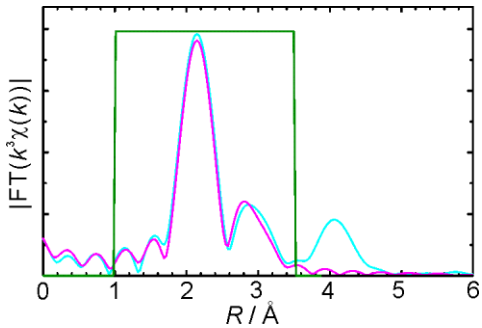

Fig.4 Observed(blue) and simulated(red) $|FT(k^3\chi(k))|$ functions. The refinement was carried out including the atoms within the second nearest shell of $[Co(bppp)_2]^{2+}$. The green line indicates the window.

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