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Coordination structure analysis of a vapochromic complex [$CoCl_2$(bppp)]

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Introduction

In order to construct a soft and flexible supramolecular structure using a simple mononuclear metal complex and its weak intermolecular interactions, a complex [$Co^{II}Cl_2$(bppp)] (**1**) , in which bppp was a tridentate ligand, 2,6-bis(5-phenyl-3-pyrazolyl)-pyridine, was synthesized (Fig. 1). **1** was designed to have amphiphilic character, which comes from the hydrophobic planar molecular plane of bppp and the hydrophilic parts of the pyrazole moieties in bppp and the Cl- ligands. They were expected to exert supramolecular interactions of π-π interaction and hydrogen bonding on surrounding molecules. Our previous single crystal X-ray diffraction study confirmed that in crystals obtained from recrystallization of **1** using polar solvents **1** and the solvent molecules formed supramolecular type assemblies by the expected interactions. Moreover, powder of the crystals showed vapochromic behaviour. For example, green powder of [$CoCl_2$(bppp)]·CH_3OH·CH_3CN(**2**) changed its colour to pink on exposure to acetone vapour. IR spectrum of **2** exposed to acetone vapour (**3**) showed that acetone was included in **3**. Powder X-ray diffraction study also confirmed change of the crystal structure in the process from **2** to **3**. Namely, the assembly of **1** showed structural softness and flexibility even in the solid state. This flexibility of the crystal structure is considered to come from the weak interactions designed in the molecular structure of **1**. However, the colour change suggests a flexibility of the coordination structure of **1** besides the above structural flexibility. To clarify this point, we attempted to investigate the coordination structure of the Co^{II} centre using EXAFS spectroscopy.

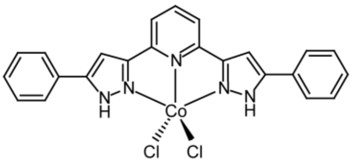

Fig. 1 [$Co^{II}Cl_2$(bppp)] (**1**)

Results and discussion

Co K-edge XAFS spectra of **2** and **3** were measured in the transmission mode at BL-27B station of PF-KEK. FT functions $|FT(k^3\chi(k))|$ observed are shown in Fig.2(a) and (b). A clear difference between the two spectra can be recognized. In the case of **3**, a new peak appeared at ca. 2.5 Å. This finding strongly suggests that the inclusion of acetone molecules brought influence on the coordination structure of the Co^{II} centre.

Curve fitting for **2** was performed based on the molecular structure of **1**, considering only single scattering paths(Fig.2(a)). Three N atoms of bppp and two Cl ligands, which are directly coordinating to Co, and non-coordinating four C atoms of bppp were taken account of. The resultant best fit curve matched with the first peak around 2Å. The second peak around 3 Å was also confirmed to come from the non-coordinating C atoms. This analysis suggests that the new peak around 2.5Å in **3** reflects a structural change in the region between the coordinating and the non-coordinating atoms.

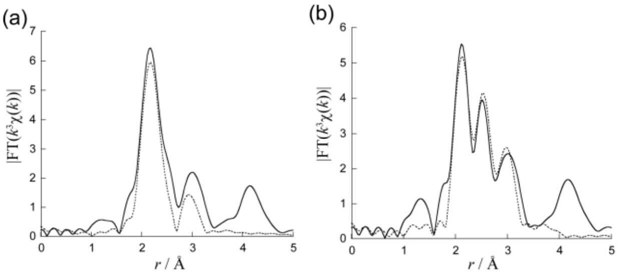

Fig.2 FT functions $|FT(k^3\chi(k))|$ observed (solid line) and fitting results (dotted line) for 2 (a) and 3(b).

Fitting for **3** was carried out based on two models. Model 1 is a [$CoCl_2$(bppp)] model, in which bppp was fixed and the Co-Cl length was treated as a variable parameter of the fitting. Model 2 is a hexa-coordinated complex [$CoCl_2$(acetone)(bppp)], in which an acetone molecule coordinates to Co with the O atom. After the fitting based on Model 1, the Co-Cl length was elongated to from 2.3 to ca. 2.5 Å and the resultant curve well reproduced the experimental function (Fig.2(b)). In Model 2, the Co-O length was fixed to 2.5 Å. The results obtained on Model 2 were very similar to those of Model 1 and their difference was subtle. This is because the contribution from the O atom, whose scattering power is weak compared to that of a Cl atom, is not actually reflected in the resultant curve. Therefore, it was difficult to know whether the acetone molecule coordinates to Co or not. However, the Co-Cl bond lengthened similarly to the case of Model 1. The elongation of the Co-Cl bond is necessary for reproducing the experimental results of **3**.

In conclusion, a change of the coordination structure of **1** was confirmed. The trapped acetone gives some structural distortion including the elongation of the Co-Cl length and this distortion is considered to be the main reason for the color change.

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