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Anisotropy of functions and thermally structural changes for Cu(II) complexes (in 2010)

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Introduction

Recently, we have widely investigated metal-organic frameworks or transition metal complexes [1-4] by means of powder X-ray diffraction (XRD) in view of thermally-accessible structural changes of Jahn-Teller distortion (local distortion around coordination environment) and global strain of crystal lattice. Last year we have prepared several chiral or racemic bimetallic assemblies composed of Cu(II) complexes and Cr(VI), Mo(VI), or W(VI) complexes [5]. Furthermore, these types of bimetallic assemblies may be appropriate precursor for preparing bimetallic metal oxides because of highly homogeneous structures. Herein we have attempted to prepare bimetallic metal oxides from bimetallic assemblies of metal complexes by burning and measured their XRD patterns by changing temperature.

Experimental section

Preparation

For example, slow diffusion of aqueous solution of a precursor complex $[Cu(chxn)_2(H_2O)_2](NO_3)_2$ (chxn = (*1R, 2R*)-diaminocyclohexane) onto methanol solution of reduced Mn12-cluster (a typical single molecule magnet) as counter anions allowed to stand at 298 K for several days to gave rise to resulting precipitates. The bimetallic assemblies were burned to give rise to bimetallic metal oxides. The products were characterized by means of IR spectra, soft X-ray absorption spectra, magnetic measurements, and XRD.

X-ray Crystallography

Powder XRD patterns of the precursor complexes and resulting were measured at BL-8B (8 keV, λ = 1.54 Å) at 100 and 300 K.

Results and discussion

For example, we mention the results for chiral $[Cu(chxn)_2][Mn12]$ and its oxide. At 100 K, the precursor shows some intense peaks around 25 degrees, while the resulting oxide shows some predominant peaks around 35 degrees (Figure 1). Temperature dependence of shift of XRD peaks was commonly expected behavior. Because both XRD patterns differs completely, preparation of oxide can be confirmed. The corresponding IR spectra (organic ligands' moieties vs M-O bonds) also support the results. Interestingly, the precursor $[Cu(chxn)_2][Mn12]$ indicates paramagnetism merely besides characteristic behavior of single molecule magnets, while the resulting bimetallic oxide indicates ferromagnetism clearly. In this context, this is a good method for preparing bimetallic oxides as magnetic materials.

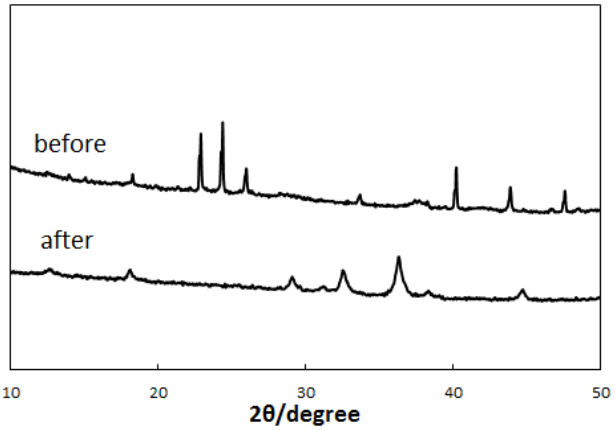

Figure 1: Temperature dependence of XRD patterns of a precursor, $[Cu(chxn)_2][Mn12]$ (before), and its oxides (after) at 100K.

Moreover, we have prepared other bimetallic oxides from the following precursors of chiral or racemic bimetallic complexes: $[CuL'_2][CrO_4]$ L' = (*1R,2R*)-*N,N'*-dimethyldiaminocyclohexane, $[CuL'_2][Cr_2O_7]$, $[CuL_2][CrO_4]$, $[CuL_2][Cr_2O_7]$, $[CuL''_2]$[reduced Mn12-SMM] L'' = *N*-ethylethylenediamine, $[CuL_2][Mo_2O_7]$, $[CuL''_2][Mo_2O_7]$, and $[CuL''_2][PtCl_4]$.

References

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