

## Thermal changes of structures and properties of pi-backdonating metal complexes (in 2010)

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### Introduction

Recently, (magnetic) cyanide-bridged bimetallic assemblies, which is typical systems of pi-backdonation, and the related precursor chiral, achiral or racemic Cu(II) complexes have been investigated by means of variable temperature XRD or XAS [1-4]. Additionally, we prepared  $[M_2O_7]$ -bridged ( $M = Cr, Mo, \text{ and } W$ ) bimetallic assemblies [5] for comparison of valences via bridging ligands indicating pi-backdonation ( $[A(CN)_n]^{m-}$ ) or non-pi-backdonation ( $[M_2O_7]^{-}$ ). Moreover, we have developed new preparations for bimetallic oxides  $[Cu_aM_bO_c]$  from these bimetallic assemblies of bridged complexes by burning. However, oxidation of metal ions must be expected and detailed measurements of valences should be carried out before and after preparations besides electronic states inner shell at low temperature. Herein, we have investigated valence states of Cu(II) ions as a standard some bimetallic assemblies and the resulting bimetallic oxides by means of soft X-ray spectroscopy.

### Experimental section

#### Preparations

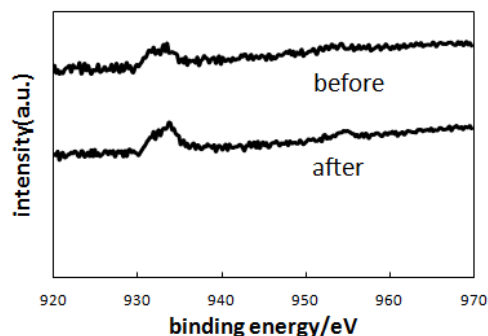
Bimetallic oxides have been prepared from the corresponding precursors of chiral or racemic bimetallic complexes as follows:  $[CuL'_2][CrO_4]$   $L' = (1R,2R)\text{-}N,N'$ -dimethyldiaminocyclohexane,  $[CuL'_2][Cr_2O_7]$ ,  $[CuL_2][CrO_4]$   $L = (1R,2R)\text{-diaminocyclohexane,}$   $[CuL_2][Cr_2O_7]$ ,  $[CuL_2][\text{reduced Mn12-SMM}]$ ,  $[CuL''_2][\text{reduced Mn12-SMM}]$   $L'' = N$ -ethylethylenediamine,  $[CuL_2][Mo_2O_7]$ ,  $[CuL''_2][Mo_2O_7]$ , and  $[CuL''_2][PtCl_4]$ . Characterization was carried out by means of IR spectra, magnetic measurements, and XRD.

The powder XRD patterns of the precursor complexes and resulting were also measured at KEK-PF BL-8B (2010G511; 8 keV,  $\lambda = 1.54 \text{ \AA}$ ) at 100 and 300 K.

#### Measurements

The  $Cu2p_{3/2}$  and  $Cu2p_{1/2}$  peaks of XAS (soft X-ray absorption spectra) for these samples were measured at KEK PF BL-19B (at a constant ring current) under variable temperature (room temperature – about 60 K). The spectra were corrected by the standard Au sample.

### Results and discussion



**Figure 1:** The XAS of  $Cu2p_{1/2}$  and  $Cu2p_{3/2}$  peaks for and  $[CuL_2][\text{reduced Mn12-SMM}]$  (before) and  $[Cu_aMn_bO_c]$  (after).

For example, we mention the results for chiral  $[CuL_2][\text{reduced Mn12-SMM}]$  and its oxide,  $[Cu_aMn_bO_c]$ . At room temperature, the precursor shows  $Cu2p_{1/2}$  and  $Cu2p_{3/2}$  peaks around 955 and 945 eV, respectively. The resulting oxides also shows  $Cu2p_{1/2}$  and  $Cu2p_{3/2}$  peaks around 955 and 945 eV, respectively. The results suggest that Cu(II) ion is not oxidized during preparation, while only Mn(III) or Mn(IV) ions may be oxidized up to higher valence states.

However, more stable ions such as Pt(II) in  $[CuL''_2][PtCl_4]$  or metal ions at the highest valence states, namely Cr(VI) in  $[CuL_2][Cr_2O_7]$ , could not be oxidized furthermore.

Of course, substitution of coordination atoms, for example  $[CuN_4O_2]$  environment for the precursor and  $[CuO_6]$  environment for the resulting oxides may be a factor of changing XAS peaks.

### References

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