

## Structural Study on Metal-Molecule Hybrid Cluster Compounds

Nobuyuki NISHI, Kentaroh KOSUGI, Kazuhiko HINO, Junaid BUSHIRI, and  
Toshihiko YOKOYAMA

Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

### Introduction

Hybrid cluster compounds of transition metal atoms and molecules with  $\pi$  electrons are expected to reveal strong  $d$ - $\pi$  interaction due to proximate location of metal  $d$  orbitals and  $\pi$  orbitals of molecular groups both energetically and spatially. We first focus on  $\text{Co}^{2+}\text{C}_2^{2-}$  nano-clusters that can be ferromagnetic in contrast with antiferromagnetic electronic structure of  $\text{Co}^{2+}\text{O}^{2-}$ .  $\text{CoC}_2$  nanoparticles are synthesized from acetonitrile solution of  $\text{CoCl}_2$  with suspended  $\text{CaC}_2$  fine powder. The products obtained from the solution at 340 K is called Sample LT (low temperature product). The  $\text{CoC}_2$  nanoparticles are also available from the thermal or photochemical reaction of  $\text{Co}_4(\text{CO})_{12}$  with solvent  $\text{CH}_2\text{Cl}_2$ . Important is the pH of the solution. Since the catalytic reaction of one Co with two  $\text{CH}_2\text{Cl}_2$  produces one  $\text{CoC}_2$  and four HCl, the solution becomes very acidic at pH 1.0 ~ 1.5. The particles are embedded in amorphous carbon. This sample is called Sample ME (matrix embedded).

### Spectral measurement and analysis

**XANES** : The peak at 7723 eV seen for Sample LT coincides with that of hydrated  $\text{Co}^{2+}$  ion (as seen for  $\text{Co}(\text{NO}_3)_2(6\text{H}_2\text{O})$ ) suggesting that the Co is in a divalent cation state. The matrix embedded sample (Sample ME) also exhibits the peak at the same energy, while the width is expanded. This is in accord with the appearance of  $\text{C}_2^{2-}$  infrared absorption bands.

**XAFS** : The Fourier transform spectrum of XAFS signals of Sample ME exhibited a little difference from that of Sample LT, particularly in the region from 3.2~4.5 Å. As clearly seen from the appearance of water bands in IR spectra, the two samples contain coordinated water molecules. Therefore the peaks at 1.6Å (2.08Å after phase factor correction) are contributed from both Co-C and Co-O pairs. It is very difficult to analyze this peak. The peak at 2.8Å (3.18Å after phase factor correction) and other main peaks at much longer distances are attributed to Co-Co pairs. There is little contribution from the direct Co-Co bond at 2.05Å (2.5Å after phase factor correction). We have found, however, that the presence of oxygen gas in the solvent results in the appearance of the 2.05 Å peak. The de-oxygenation treatment in a globe box by Ar bubbling longer than 6 hours is necessary. On the basis of the assumption that the Co-C pairs hardly contribute to the peaks at distances longer than 3.5 Å, the Fourier transform spectra of Sample ME and Sample LT are analyzed with the models presented in Figure 1. Most of peaks are reproduced nicely, while the discrepancies in intensities between the calculated and observed spectra

become serious at longer distances. This is thought due to the structural disorder in nano-particles. The observed spectra shows drastic intensity decrease at longer distances.

$\text{CaC}_2$  is known to show four isomers[1] including the famous body centered tetragonal structure ( $\text{CaC}_2$  I:  $P4/mmm$ ) where the plane with  $-\text{Ca}-\text{C}=\text{C}-\text{Ca}-$  chains in parallel stacks also in parallel to plane by plane, while  $\text{MgC}_2$  shows perpendicular chain orientation in plane to plane ( $P4_2/mnm$ )[2]. The structure of Sample LT is similar to  $\text{CaC}_2$  I and that of Sample ME is close to that of  $\text{MgC}_2$ . The structures derived from the analyses for Sample LT and Sample ME are shown on the top and the bottom of Figure 1, respectively.

### Structural Relation to Magnetic Properties

Sample LT shows the blocking temperature at 4.6 K, while Sample ME behaves as an assembly of room temperature magnets with a blocking temperature higher than 300K. The very clear difference between the two structures is the anisotropy that determines the blocking barrier heights. Higher anisotropy as seen in the lower structure is certainly very much favorable for a higher blocking temperature.

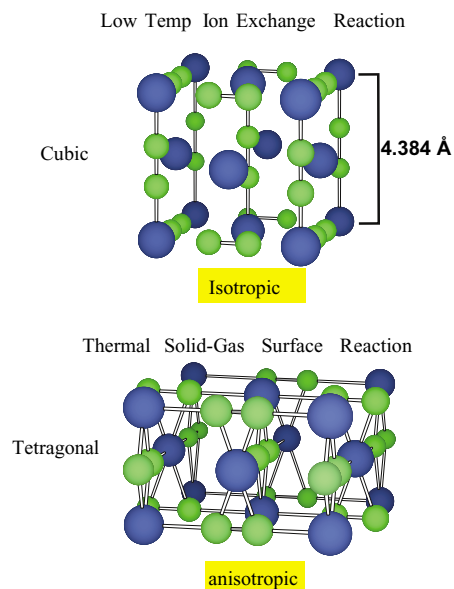


Figure 1. Structure Models of two  $\text{CoC}_2$  isomers obtained from XAFS analyses of Sample LT(top) and Sample ME(bottom).

\* nishi@ims.ac.jp

### References

- [1] M. Knapp and U. Ruschewitz, Chem. Eur. J. 7, 874 (2001).
- [2] P. Karen et al., J. Alloys and Compounds. Chem. 282, 8888 (1999).
- [3] N. Nishi et al., Chem. Phys. Lett. 369, 198 (2003)
- [4] N. Nishi et al., Bull. Soc. NanoSci. and Tec., 1, 73 (2003)