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Structural Study on Metal-Molecule Hybrid Cluster Compounds

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Introduction

Anisotropic nanocrystals of high spin hybrid cluster compounds of transition metal atoms and molecules can exhibit interesting physical natures, especially magnetism. The monomers of transition metal acetylide compounds, MC_2 (M= Sc, V, Cr, Mn, Fe, Co) that have unpaired 3d electrons were investigated by Li et al. [1] Although crystalline structures of closed shell acetylide compounds, CaC_2 and MgC_2, were revealed to be tetragonal by x-ray diffraction, those of MC_2 have not been reported. We synthesized CoC_2 by the high pressure reaction of $Co_4(CO)_{12}$ with CH_2Cl_2 and investigate its crystalline structure experimentally.

CoC_2 nano particles

The X-ray absorption near-edge structure (XANES) spectrum shows cobalt cations in this sample are Co^{2+}. Two bands observed at 1490 and 1415 cm^{-1} in the FT-IR spectra correspond to the C-C stretching modes of C_2^{2-} in CaC_2 (1488 and 1417 cm^{-1}). Transmission electron microscope (TEM) images show cobalt-rich particles that have ordered structures are embedded in matrices. The average diameter of these particles is 12 nm. The energy loss spectroscopy (EELS) spectra are measured by irradiating electron beam to the particle and the matrix, respectively. No oxygen band is seen in the spectra. In the EELS spectrum of the particles, the Co-L2,3 bands at 781 and 796 eV, and the C-K band at 292 eV are observed. The C-K band with a distinct π^* peak at 285 eV is similar to that of graphite. This similarity indicates that almost all carbon atoms form π-bondings in the particle. The particles are the nano crystalline of CoC_2 hybrid clusters. The C-K band with a dominated σ^* peak is the only observable band in the matrix spectrum. The FT-IR spectrum shows O-H strech vibrations assigned to coordinate water molecules. Thermal analysis of the products indicated that the CoC_2 is prone to adsorb water molecules. These results suggest the presence of $[CoC_2 \cdot 2(H_2O)]$.

Crystal structure of CoC_2

The crystalline structure of the CoC_2 nano particle was investigated by the extended X-ray absorption fine structure (EXAFS). The Fourier transform pattern of the observed EXAFS signal is shown in Fig. 1. The calculated patterns for $[Co(H_2O)_6]^{2+}$ complex and a tetragonal crystalline model ($P4_2/mnm$) of CoC_2 are also desplayed in Fig. 1. The experimental pattern is in good agreement with the superposition of the calculated patterns. The tetragonal crystalline model is shown is Fig. 2. The *a* and *c* axes are 3.85 Å and 3.36Å, respectively. All C_2^{2-} are perpendicular to the *c* axis and the C-C bond length is 1.25 Å. The closest Co-C_2 pair is the T-shaped cluster in which C_2 is located on the *c* axis direction of Co. This suggests that the d-π interaction is strong in this crystal structure. This can be consistent with the density functional calculation (DFT) for CoC_2 monomer by Arbuznikov and Hendrickx in which the T-shaped isomer is found to be most stable. [2]

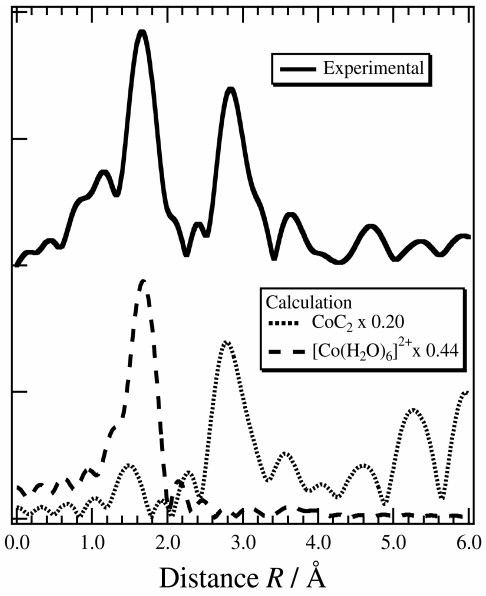

Fig. 1. Experimental and Calculated Fourier Transforms

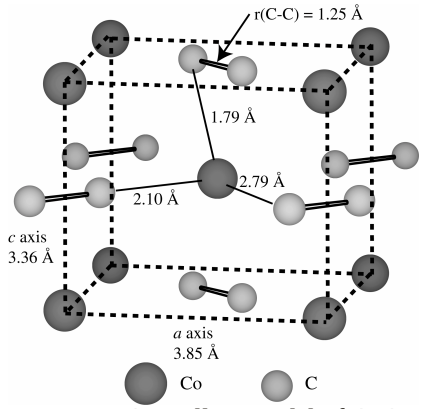

Fig. 2. Crystalline model of CoC_2

References

[1] X. Li and L. S. Wang, J. Chem. Phys., **111**, 8389, (1999).
[2] A. V. Arbuznikov and M. Hendrickx, Chem. Phys. Lett., **320**, 575, (2000).
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