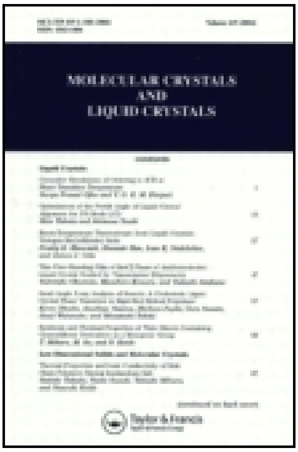

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Electronic State of A Hydrogen-Doped Copper Coordination Polymer: N , N ′-bis-(hydroxyethyl)dithiooxamidatocopper(II), (HOC 2 H 4) 2 dtoa Cu

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Electronic State of A Hydrogen-Doped Copper Coordination Polymer:*N*,*N*′-bis-(hydroxyethyl)dithiooxamidatocopper(II), $(HOC_2H_4)_2$*dtoa*Cu

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Hydrogen doping was electrochemically performed on the title coordination polymer, catena-*μ*-*N,N*′-bis-(hydroxyethyl)dithiooxamidatocopper(II), $(HOC_2H_4)_2$*dtoa*Cu. From X-ray photoelectron spectroscopy, the oxidation state of Cu(II) in $(HOC_2H_4)_2$*dtoa*Cu was revealed to be reduced to the Cu(I,II) mixed-valence state on hydrogen doping. While the spin susceptibility increases during initial hydrogen doping, it decreases and then shows no temperature dependence as the hydrogen doping proceeds. The temperature-independent behavior is supposed to be derived from Pauli paramagnetism.

Keywords: Coordination polymer; Hydrogen doping; Spin susceptibility; X-ray photoelectron spectroscopy.

INTRODUCTION

Recently, carrier doping into molecular materials has received a renaissance through its physical properties such as conductivity, magnetic property and dielectlic property. In particular, some of the alkali metal-doped fullerenes indicates superconductivity, in which the alkali metal acts as an electron donor to the fullerene. Taking into account the doping effect on the physical property, it is able to create novel functional materials such as switching device, capacitor and sensor by means of carrier doping.

The copper(II) complex, catena-μ-*N,N'*-bis-(hydroxyethyl)dithiooxamidatocopper(II), $(HOC_2H_4)_2$*dtoa*Cu (Figure 1), is an amorphous two-dimensional coordination polymer with Cu-dimeric units[1,2]. The electrical conductivity of $(HOC_2H_4)_2$*dtoa*Cu is increased by about nine orders of magnitude during hydrogen doping[3,4]. This polymer also indicates proton conduction[5-7]. Electron and proton conductive properties are derived from a dibasic-acid character of the ligand (Figure 2)[8] and a proton-coupled redox property. The electron-proton coupling like this plays an important role of energy metabolism in biological system. By the use of these properties induced by the hydrogen doping, a new type of functional material would be developed. In this work, X-ray photoelectron spectroscopy (XPS) and magnetic susceptibility measurements were carried out in order to reveal the electronic state of hydrogen-doped $(HOC_2H_4)_2$*dtoa*Cu.

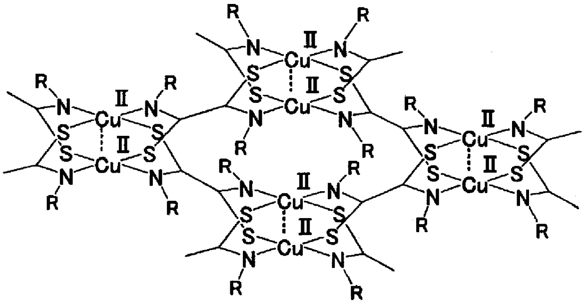

FIGURE 1 Two-dimensional coordination polymer (R = C_2H_4OH).

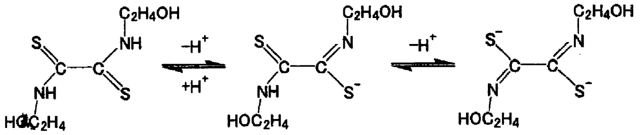

FIGURE 2 Dibasic-acid character of the ligand.

EXPERIMENTAL

Synthesis

The title coordination polymer was prepared by a simple stoichiometric mixing of ethanol solution of $(HOC_2H_4)_2$*dtoa* with aqueous solution of copper(II) sulfate[1,2]. The synthesized sol was washed with water and ethanol several times and separated from the supernatant fraction with the centrifuge. The qualities of obtained samples were checked by the elemental analysis and powder X-ray diffraction measurement.

Hydrogen doping

Hydrogen doping was performed by electrolysis of water with a conventional electrochemical cell. The 0.1 mol/l KCl solution was used as electrolyte. A Pt working electrode, a spiral of Pt-black wire as a counter electrode and a saturated calomel reference electrode were employed. The electrolyte was purged with Ar prior to use and blanket of Ar was maintained over the solution during the experiment. The applied potential to cathode was between –1.0 to –0.7 V. The colloidal $(HOC_2H_4)_2$-*dtoa*Cu dispersed into the electrolyte was exposed to generated hydrogen gas on the cathode's surface under stirring at room temperature. Hydrogen-doped samples were taken out of the cell at hourly intervals.

Measurement

X-ray photoelectron spectroscopy (XPS) measurement was performed using an Ulvac Phi 5600ci photoelectron spectrometer with a monochromated Al-Kα X-ray ($h\nu$=1487 eV) as an excitation light source at room temperature. Magnetic susceptibility measurements were performed with samples dried in an evacuated desiccator. The samples were wrapped with diamagnetic materials. The temperature dependences were measured in the temperature range 2 – 300 K on a Quantum Design MPMS-5 SQUID magnetometer. The total diamagnetic contributions were subtracted after the measurement.

RESULTS AND DISCUSSION

XPS measurements

XPS measurements were made on $(HOC_2H_4)_2$*dtoa*Cu to examine the oxidation state of Cu during hydrogen doping. Figure 3 shows the XPS spectra of Cu $2p_{3/2}$ region for $(HOC_2H_4)_2$*dtoa*Cu. In the spectrum of the hydrogen-undoped sample, a peak centered at 934.2 eV was observed, which is a typical binding energy of Cu(II). As the hydrogen doping proceeds, a new shoulder peak centered at 932.2 eV appears, which is derived from a signal of Cu(I). The hydrogen doped coordination polymer, therefore, is considered to reduce the Cu(II) into the Cu(I,II) mixed-valence state. The broad peak centered at 943-945 eV is a satellite peak derived from Cu(II).

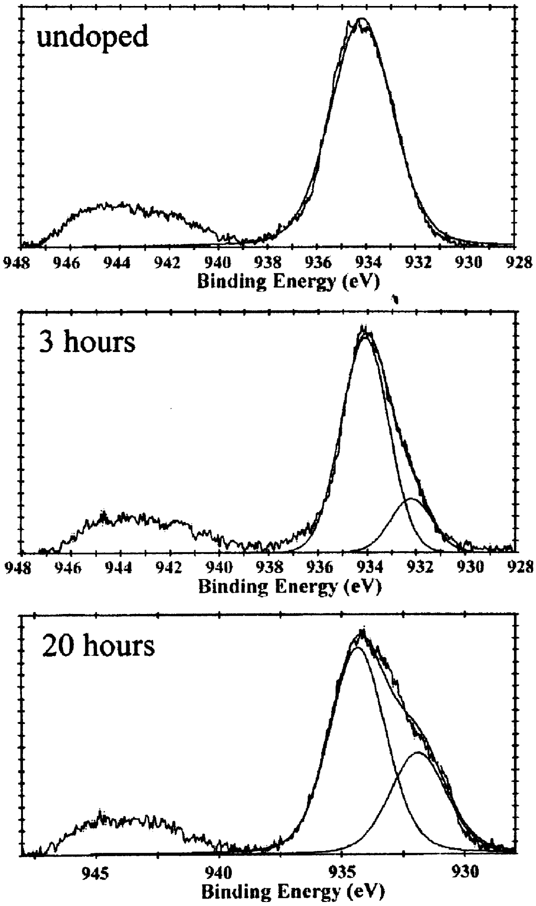

FIGURE 3 Hydrogen-doping time dependence of XPS spectra.

Magnetic susceptibility measurements

In order to confirm the reduction of Cu(II) into the Cu(I,II) mixed-valence state by hydrogen doping, the temperature dependences of molar spin susceptibilities per dimer unit of the coordination polymer were measured, as shown in Figure 4. From the theoretical consideration of spin susceptibility of hydrogen-undoped sample[9], the observed antiferromagnetic susceptibility, in which the estimated *J* value is -594 K, is considered to be due to the intradimer superexchange interaction between Cu(II) ions *via* ligands. The spin susceptibility for the three-hours hydrogen-doped sample increases compared to the undoped one in the whole temperature region. This can be explained as follows. As the Cu(II) ions proceed to be reduced to Cu(I), the cancelled spins by a large negative *J* become revived on losing the opposite spin. The spin susceptibility for the twenty-hours hydrogen-doped sample decreases from that for the three-hours one, which indicates no temperature dependence. This temperature-independent behaviour is supposed to be derived from Pauli paramagnetism.

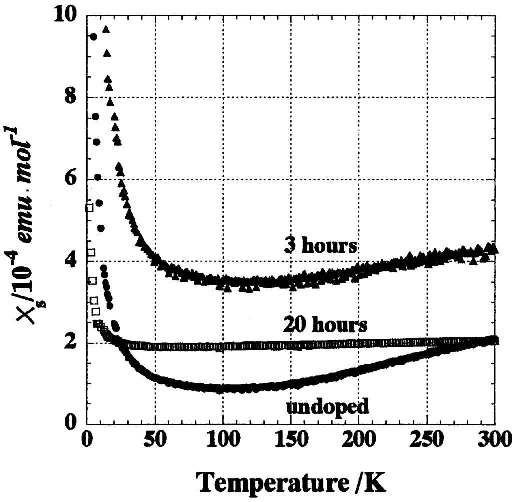

FIGURE 4 Temperature dependences of spin susceptibility of $(HOC_2H_4)_2$*dtoa*Cu, (hydrogen doping time ●:undoped, ▲:3 hours, □:20 hours).

CONCLUSION

The hydrogen doping was electrochemically performed on $(HOC_2H_4)_2$-*dtoa*Cu. The oxidation state of Cu(II) in $(HOC_2H_4)_2$*dtoa*Cu was revealed from XPS measurement to be reduced to the Cu(I,II) mixed-valence state on hydrogen doping. While the spin susceptibility increases during initial hydrogen doping, it decreases and then showed no temperature dependence as the hydrogen doping proceeds. The temperature-independent behavior is supposed to be derived from Pauli paramagnetism. In this coordination polymer, it is possible to control physical properties continuously by hydrogen doping, which is achieved by the proton- coupled redox property of this system.

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