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Preparation and proton transport property of *N, N'* – diethyldithiooxamidatocopper coordination polymer

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Abstract

A novel proton-conductive copper coordination polymer, $(H_5C_2)_2$*dtoa*Cu (R_2*dtoa*H_2 = dithiooxamide derivatives), was synthesized. From X-ray powder diffraction measurements, the crystal structure of $(H_5C_2)_2$*dtoa*Cu was found to be similar to that of a two-dimensional (2-D) coordination polymer $(HOH_4C_2)_2$*dtoa*Cu. This title coordination polymer was revealed to be a proton conductor by the relative humidity (RH) dependence of AC conductivity measurements. The proton conductivity (σ_p) was 4.2×10^{-6} S cm^{-1} under the RH of 100 % and the ionic transport number was more than 0.99. The σ_p of $(HOH_4C_2)_2$*dtoa*Cu was two orders of magnitude higher than that of $(H_5C_2)_2$*dtoa*Cu, which would be derived from the existence of -OH groups in the alkyl substituent R.

Keywords: transport measurements, ion conductivity, conjugated conducting polymers, fuel cells

1. Introduction

Over the last 10 years inorganic-organic hybrid materials have received increasing attention as the functional materials, *i.e.* electronic conductors, ionic conductors, superconductors, molecule-based magnets, single-molecule magnets, ferromagnetic metals, *etc.* [1 - 5]. These materials have the possibility of creating and developing new research fields. One of the most urgent subjects in the field of inorganic-organic hybrid materials is to create a novel proton conductor, from the viewpoint of developing new energy and energy conservation technologies [6 - 10].

As a new proton-conductive system, we have investigated a series of the inorganic-organic hybrid polymers, R_2*dtoa*Cu (R_2*dtoa*H_2 = dithiooxamide derivatives, R = –H, $–C_2H_4OH$, $–C_3H_6OH$, *etc.*) [11 - 20]. *N, N'*–bis(2–hydroxyethyl)dithiooxamidatocopper(II), $(HOH_4C_2)_2$*dtoa*Cu, is a proton-conductive 2-D coordination polymer with Cu-dimeric units and bridging ligands (Fig. 1) [13 - 17]. Such a metal-dimer system with multi-redox property has a large potentiality for the creation of new-functional and high-performance materials in metal-complex solids [21-23]. The $(HOH_4C_2)_2$*dtoa*Cu shows a high proton conductivity of 3.1×10^{-4} S cm^{-1} under the relative humidity (RH) of 100 % and 300 K. The proton conductivity depends on the quantity

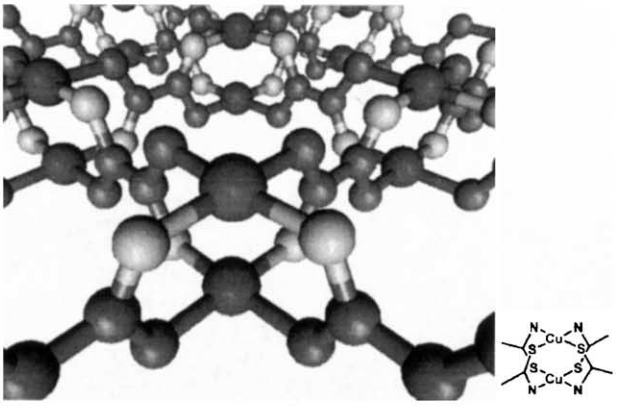

Fig. 1. Crystal structure of $(HOH_4C_2)_2$*dtoa*Cu. Repeating unit of the polymer is shown on the right side. (Substituent group at N atom is omitted for the sake of clarity).

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of water molecules included in the polymer [15, 16, 18, 19].

As an extension of this system, we have investigated a new derivative, $(H_5C_2)_2$*dtoa*Cu (*N, N'*–diethyldithiooxamidato-copper), to evaluate the contribution of -OH group to the proton conduction.

2. Experimental

The ligand, *N, N'*–diethyldithiooxamide $(H_5C_2)_2$*dtoa*H_2 was prepared by a reaction of dithiooxamide (MERCK Ltd.) with ethylamine [24]. The $(H_5C_2)_2$*dtoa*H_2 was identified by ^{1}H NMR, EI-MS, and IR spectroscopy. m.p. 53–54 °C. ^{1}H-NMR (270 MHz, DMSO-d_6) δ 10.49 (2H, s), 3.62 (4H, q, J = 7.25 Hz), 1.16 (6H, t, J = 7.25 Hz). EI-MS m / z 176 (100 %). IR (KBr, cm^{-1}) 3168, 2977, 2934, 1534, 1038, 926, 834, 714.

The title coordination polymer was prepared by a simple mixing of ethanol solution of *N, N'*–diethyldithiooxamide and aqueous solution of $CuSO_4 \cdot 5H_2O$ (WAKO Pure Chemical Industries, Ltd.). The precipitate was washed with water and ethanol several times and separated from the supernatant fraction with the centrifuge. The synthesis of *N, N'*–bis(2–hydroxyethyl)dithiooxamidatocopper coordination polymer, $(HOH_4C_2)_2$*dtoa*Cu, has been reported [13].

The quality of the obtained sample was checked by elemental analysis, thermogravimetric (TG) analysis, powder X-ray diffraction (XRD), and infrared (IR) spectra. Elemental analysis result (Found: C, 28.4; H, 4.13; N, 11.1) showed the formula of $(H_5C_2)_2$*dtoa*Cu·0.7H_2O. Anal. Calc for $(H_5C_2)_2$*dtoa*Cu·0.7H_2O : C, 28.8; H, 4.59; N, 11.2. The concentration of water molecules as crystal water was in good agreement with the result of the TG analysis. The XRD measurements were performed with synchrotron radiation at KEK-PF (BL-1B). IR spectra were recorded on a Thermo Nicolet NEXUS 670 FT-IR spectrometer in the wavenumber range of 400 – 4000 cm^{-1}. For DC and AC conductivity measurements, the powdered sample was processed into pellets of 0.31 mm thickness and 2.5 mm ϕ under pressure (~ 1 GPa) and vacuous condition. The impedance measurements were carried out by two-probe method using gold paste (Tokuriki Chemical Research, SILBEST No. 8560) and gold wires of 50 μm ϕ (Tanaka Denshi Kogyo K. K.) with a Solartron SI1260 Impedance / Gain-Phase Analyzer and 1296 Dielectric Interface in the frequency range of 10^2 – 10^7 Hz at 296 K. The magnitude of the impedance at 1 kHz is limited to less than 2×10^9 Ω because of the leakage current. The RH was controlled in the range of 47 – 100 % by using water and saturated solution of salts, generating an atmosphere of a defined RH [25].

3. Results and discussions

3.1 XRD and IR spectra

As shown in Fig. 2, the title compound exhibits an XRD pattern with broad peaks due to the water-insoluble and amorphous-like coordination polymer. The XRD pattern of $(H_5C_2)_2$*dtoa*Cu was very similar to that of $(HOH_4C_2)_2$*dtoa*Cu. The crystal structure of the coordination polymer $(HOH_4C_2)_2$*dtoa*Cu was revealed to be a 2-D coordination polymer with Cu-dimeric units and bridging ligands as shown in Fig. 1, from the XRD and extended X-ray absorption fine structure (EXAFS) analyses [14]. Due to the similarity between the X-ray diffraction patterns, the crystal structure of the title compound is considered to be analogous to that of $(HOH_4C_2)_2$*dtoa*Cu.

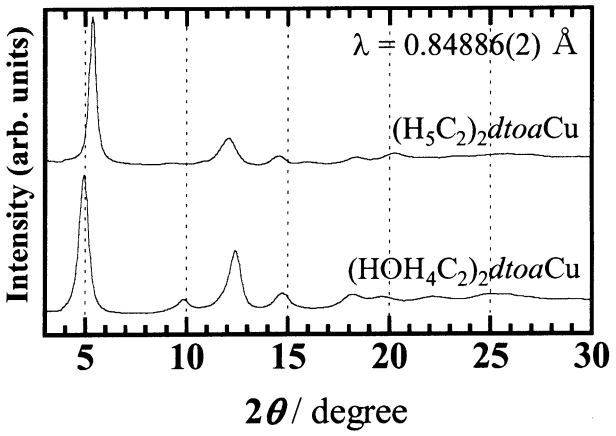

Fig. 2. XRD patterns for $(H_5C_2)_2$*dtoa*Cu and $(HOH_4C_2)_2$*dtoa*Cu.

Fig. 3 shows IR spectra for the ligand $(H_5C_2)_2$*dtoa*H_2 and the coordination polymer $(H_5C_2)_2$*dtoa*Cu. The absorptions of N-H stretching mode at 3170 cm^{-1} and N-H

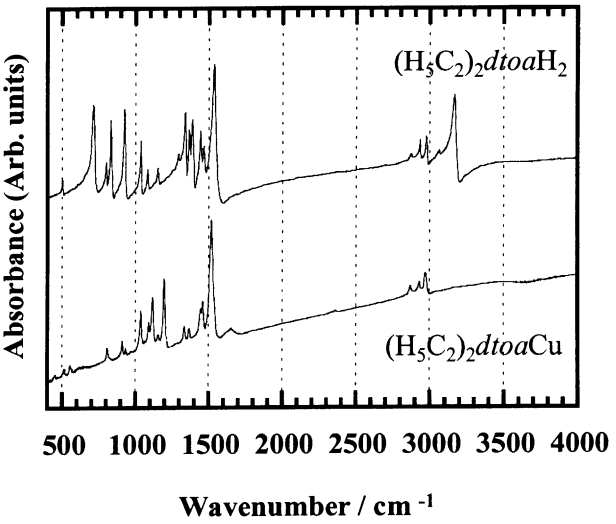

Fig. 3. IR spectra for $(H_5C_2)_2$*dtoa*H_2 and $(H_5C_2)_2$*dtoa*Cu.