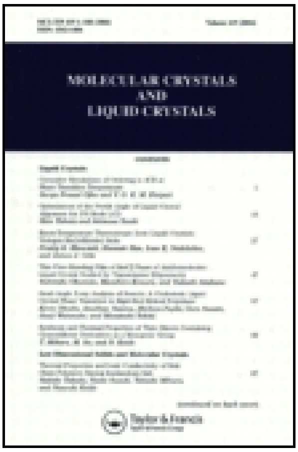

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Electronic State of a Halogen-Bridged Mixed-Valence Binuclear Complex, Ni 2 (dta) 4 I

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Electronic State of a Halogen-Bridged Mixed-Valence Binuclear Complex, $Ni_2(dta)_4I$

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The electronic state of a halogen-bridged mixed-valence binuclear nickel complex, $Ni_2(dta)_4I$ ($dta = CH_3CS_2^-$), has been investigated by optical and magnetic measurements. The X-ray photoelectron spectrum of Ni $2p_{3/2}$ region is reasonably fitted with two components. Under the time scale of X-ray photoelectron spectroscopy (10^{-16} s), the charges of nickel ions in $Ni_2(dta)_4I$ were detected as Ni^{2+} and Ni^{3+}. The strong absorption band was observed at 0.65 eV, which is attributable to an interdimer ($d_{\sigma*} \rightarrow d_{\sigma*}$) transition. This band was clearly split below 100 K, implying a charge ordering in the one-dimensional -Ni-Ni-I- chains, such as $\cdots Ni^{2+}\text{-}Ni^{3+}\text{–}I\text{–}Ni^{3+}\text{-}Ni^{2+}\cdots I\cdots Ni^{2.5+}\text{-}Ni^{2.5+}\cdots I\cdots$. This distortion is also suggested by the spin concentration ~1/3, the splitting of υ(Ni-Ni) mode, and the activation of υ(Ni-I) mode in Raman spectra at low temperature.

Keywords: 1-D chain compound; Mixed-Valence; MX chain; MMX chain; Interdimer transition; Raman spectra

INTRODUCTION

Halogen-bridged(X) one-dimensional(1-D) transition-metal(M) complexes, the so-called MX chains show unique physical properties relating to a 1-D electronic system[1-3]. One of the most important features of MX-chain materials is that their electronic states can be controlled by varying their constituents of the metal ions, the bridging halogen ions, the ligands, the counter ions and also by the external field of light or pressure.

Recently, attention has been directed to MMX chains in which 1-D –M-M–X–M-M–X– chains are formed[4-10]. According to our recent works[11-14], the $Pt_2(dta)_4I$ (dta = $CH_3CS_2^-$) was found to exhibit metallic conduction around room temperature, which is the first observation of a metallic halogen-bridged 1-D transition-metal complex. Such a 1-D mixed-valence polynuclear unit-assembled conductor is expected to a spin-charge-lattice coupled system. In addition, novel electronic phases were found, such as $-X\cdots M^{2+}\text{-}M^{3+}-X\cdots M^{2+}\text{-}M^{3+}-X\cdots$ (charge-polarization state) and $\cdots X\cdots M^{2+}\text{-}M^{3+}-X-M^{3+}\text{-}M^{2+}\cdots X\cdots$ (alternate charge-polarization state). On the other hand in the Ni analogue, the physical properties have not been enough investigated except a few reports[6-10]. A strong on-site Coulomb repulsion (U) is expected to interact between the Ni spins (S = 1/2), different from the Pt system.

From these interests, the electronic state of $Ni_2(dta)_4I$ was investigated by X-ray photoelectron spectroscopy (XPS), optical absorption spectroscopy, polarized Raman spectroscopy, and SQUID magnetometry measurements.

EXPERIMENTAL

This complex was prepared by the method previously reported[6]. The single crystals were grown by the diffusion technique in CS_2 solution which contained $Ni_2(dta)_4$ and I_2. The qualities of obtained crystals were checked by elemental analysis and X-ray diffraction.

The XPS measurements were carried out on an Ulvac Phi 5600ci with a monochromated Al-Kα X-ray source (1487 eV) at rt.

For optical absorption spectra, powdered samples ground down from single crystals were diluted with KBr and then the mixtures were processed into pellets. The UV-VIS-NIR absorption spectra were recorded in the temperature region 4.0–302 K by a Jasco-V570 spectrometer with an Oxford Optistat^{CF}. IR spectra were measured in the temperature region 4.0–302 K by a ThermoNicolet NEXUS 670 FT-IR spectrometer with an Oxford Microstat^{CF}.

The polarized Raman spectra of single crystals were measured in the temperature region 3.2–300 K by a Jasco NR-1800 subtractive-dispersion triple polychromator using a microscope with an Oxford Microstat^{CF}. A Spectra-Physics model 2017 Ar^+ laser provided the exciting line (514.5 nm). Wavenumber calibration was effected by reference to the emission of Ne lamp.

The magnetic susceptibility measurement of unoriented single crystals was performed in the temperature range of 2-300 K using a Quantum Design MPMS-5 SQUID magnetometer.

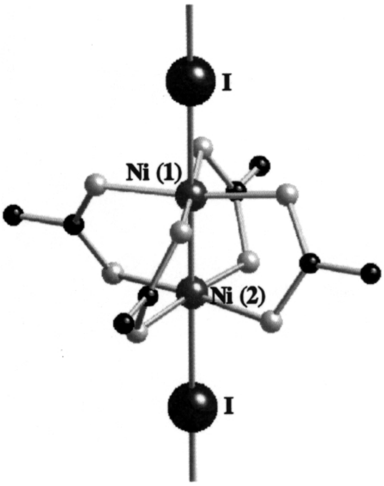

FIGURE 1 Crystal structure of $Ni_2(dta)_4I$.

RESULT AND DISSUCUSSION

The crystal structures of $Ni_2(dta)_4I$ was reported[6,8] as shown in Figure 1, in which each metal-dimer unit $[Ni_2(dta)_4]$ is uniform.

The oxidation state of nickel ions has been investigated from XPS. Figure 2 shows the XPS spectra of Ni $2p_{3/2}$ region for $Ni_2(dta)_4I$ and Ni(II) complex $Ni_2(dta)_4$. As shown Figure 2b, $Ni_2(dta)_4$ was fitted with one component of Ni^{2+}. On the other hand, for the iodine–bridged $Ni_2(dta)_4I$, the spectrum was reasonably fitted with two components of Ni^{2+} and Ni^{3+} (Figure 1a). Binding energies and full widths at half maximum (fwhm) of the components were given in Table 1. Under the time scale of XPS (10^{-16} s), the charges of nickel ions in $Ni_2(dta)_4I$ are detected as Ni^{2+} and Ni^{3+}.

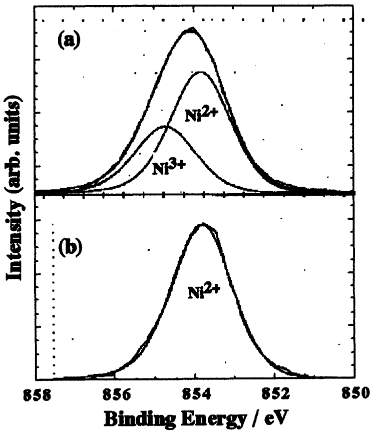

FIGURE 2 XPS spectra of Ni $2p_{3/2}$ region at rt; (a) a fit for the observed spectrum of $Ni_2(dta)_4I$, (b) the Ni(II) complex $Ni_2(dta)_4$.

TABLE 1 Binding energies (eV) for the Ni $2p_{3/2}$ region.

complex	$2p_{3/2}$ Ni^{2+} (fwhm)	 Ni^{3+} (fwhm)
$Ni_2(dta)_4$	853.8 (1.8)	
$Ni_2(dta)_4I$	854.0 (1.8)	855.0 (1.8)

Optical absorption spectra are shown in Figure 3. One of the most important features in $Ni_2(dta)_4I$ is a strong absorption with a maximum centered at 0.65 eV, which is absent in the Ni(II) complex $Ni_2(dta)_4$. This strong band is considered to be attributable to an inter-dimer ($d_{\sigma*} \rightarrow d_{\sigma*}$) transition. The transition energy is roughly equal to the U of $d_{\sigma*}$ in the $[Ni_2(dta)_4]$ dimer units. The splitting of this band was clearly observed below 100 K as shown in Figure 4, which implies some distortion occurring in the 1-D -Ni-Ni-I- chains.

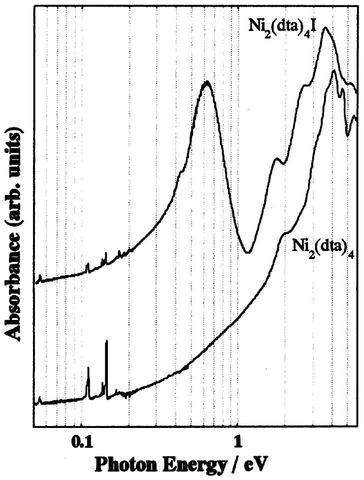

FIGURE 3 Absorption spectra of $Ni_2(dta)_4I$ and $Ni_2(dta)_4$.

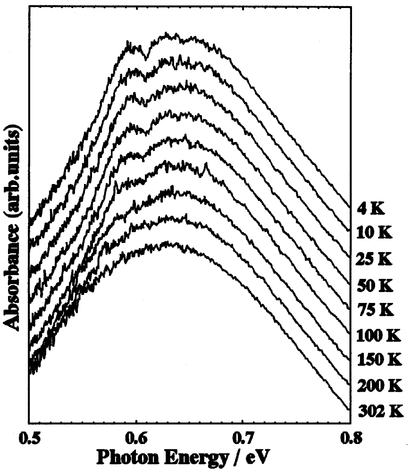

FIGURE 4 Temperature dependence of the interdimer charge-transfer band.

Raman spectroscopy has been widely used to study the vibrational and structural properties, since Raman modes are very sensitive to the symmetry of metal complexes[15]. Temperature dependence of Raman spectra in the low-frequency region for $Ni_2(dta)_4I$ is shown in Figure 5. The stretching mode of υ(Ni-Ni) around 90 cm^{-1} shows a shoulder at the higher wavenumber side at 300 K, although it was reported that $[Ni_2(dta)_4]$ units were uniform[6,8]. This υ(Ni-Ni) mode was clearly split into a doublet and shifted slightly to the high-frequency side at low temperatures. In addition, the Ni-I stretching mode υ(Ni-I) around 125 cm^{-1} was gradually activated below 100 K, which would be Raman-inactive if the iodine ions were centrally placed between $[Ni_2(dta)_4]$ dimer units. The splitting of the υ(Ni-Ni) mode and the appearance of the υ(Ni-I) mode also imply a distortion of the 1-D chains.

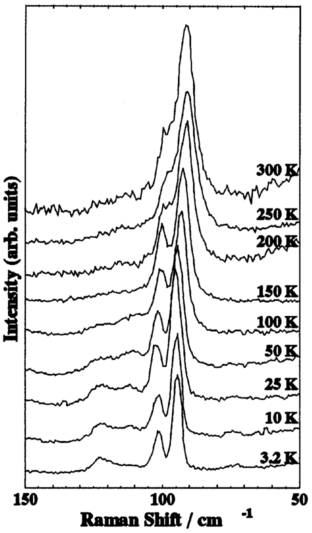

FIGURE 5 Temperature dependence of Raman spectra (*E* // Chain) of the Ni-Ni stretching mode in $Ni_2(dta)_4I$.

To clarify the spin state of $Ni_2(dta)_4I$, the temperature dependence of magnetic susceptibility was measured. The spin concentration of $Ni_2(dta)_4I$ was estimated to be ~ 1/3 from Curie constant or Bonner-Fisher equation. From the optical and magnetic measurements, a model for the distorted 1-D chain can be led as shown in Figure 6. Two structurally independent sites of $[Ni_2(dta)_4]$ units should exist in 1-D chain. Considering the spin concentration ~ 1/3, two thirds $[Ni_2(dta)_4]$ units must be dimerized, resulting in spin-singlet being formed and one

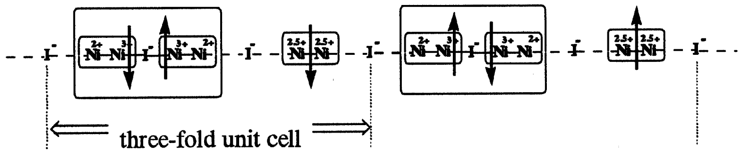

FIGURE 6 A proposed model for 1-D charge-ordering state of $Ni_2(dta)_4I$.

third spins surviving. In the present model, the unit cell would be three-fold. To examine this model, X-ray diffuse scattering measurements are underway.

Acknowledgments

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