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Mott-Hubbard State in One-Dimensional Iodo-Bridged Binuclear Metal Dithioacetato Complexes, $M_2(dta)_4I$ (M=Pt and Ni)

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MOTT-HUBBARD STATE IN ONE-DIMENSIONAL IODO-BRIDGED BINUCLEAR METAL DITHIOACETATO COMPLEXES, $M_2(dta)_4I$ (M=Pt AND Ni)

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Abstract Polarized reflection, electrical conductivity, magnetic susceptibility measurements and X-ray crystal structure redetermination have been carried out on one-dimensional iodo-bridged binuclear metal dithioacetato complexes, $M_2(dta)_4I$ (M=Pt and Ni; dta=$CH_3CS_2^-$) in order to elucidate their electronic property. The chain structure consists of $-M^{2.5+}-M^{2.5+}-I-M^{2.5+}-M^{2.5+}-$ with no Peierls distortion, and two metal atoms in binuclear moieties are bridged by four dithioacetato ligands to give a cage structure. The magnetic behavior of these compounds revealed very strong antiferromagnetic coupling between electronic spins (S=1/2) localized on the M-M dimers. They show semiconducting behavior with high conductivities and small activation energies compared with those of the MX compounds. From these results, it may be concluded that the compounds are one-dimensional Mott-Hubbard insulators, in contrast to Peierls insulators of $R_4[Pt_2(pop)_4X].nH_2O$ complexes ($...M^{2+}-M^{2+}...X-M^{3+}-M^{3+}-X..$).

INTRODUCTION

Halogen-bridged one-dimensional $M^{2+}-X-M^{4+}$ mixed-valence compounds (MX) show the interesting physical properties relating to the strong electron-lattice interaction such as the intense charge transfer absorption, the luminescence with a large Stokes-shift, the overtone progression in the resonance Raman spectra, and the midgap absorptions attributed to polaron or soliton.[1-4] The physical properties have been extensively investigated to clarify the nature

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of the ground state, the excited state, and the relaxation process in one-dimensional electronic system with the strong electon-lattice interaction. Recently novel one-dimensional Ni^{3+}-X-Ni^{3+}complexes, $Ni(chxn)_2X_3$ (X=Cl and Br) with no Peierls distortion were synthesized. They show very strong antiferromagnetic coupling between electronic spins (S=1/2) localized on the Ni^{3+}, and are assigned to Mott-Hubbard insulators.[5,6]

As a development of new halogen-bridged one-dimensional compounds, a MMX type of one-dimensional halogen-bridged binuclear metal complexes, $R_4[Pt_2(pop)_4X].nH_2O$ (R=K and NH_4; X=Cl, Br and I; n=0, 2 and 3; pop=$P_2O_5H_2^{2-}$)[7-9] and $M_2(dta)_4I$ (M=Pt and Ni; dta=$CH_3CS_2^-$) were synthesized. These new MMX type compounds have some characteristics compared with the MX compound as follows; (i) the electronic structure of metal ions are strongly coupled with each other in the M-M dimer in the chain, (ii) the difference of oxidation states of metal ions is smaller, (iii) three structures are possible as shown below. The optical, magnetical and electrical conductivities of $R_4[Pt_2(pop)_4X].nH_2O$

$$\cdots M^{2+}-M^{2+}\cdots X-M^{3+}-M^{3+}-X\cdots$$
$$\cdots M^{2+}-M^{3+}-X\cdots M^{2+}-M^{3+}-X\cdots$$
$$-M^{2.5+}-M^{2.5+}-X-M^{2.5+}-M^{2.5+}-X-$$

(hereafter abbreviated as pop compound) so far measured seem to indicate that the compounds form a Peierls-type chain structure, Pt^{2+}-Pt^{2+}...X-Pt^{3+}-Pt^{3+}-X. On the other hand, the crystal structures of $M_2(dta)_4I$ show that the bridging iodine is located at the middle point between two M-M dimers in a chain. Their electronic structures are, however, not so clear because their physical properties were measured by using polycrystalline samples only. In order to make clear the electronic structure of $M_2(dta)_4I$, we have measured polarized reflectance spectra, single crystal electrical conductivities, and magnetic susceptibilities, together with more careful redetermination of the crystal structure of $Ni_2(dta)_4I$.

EXPERIMENTAL

Single crystals of $M_2(dta)_4I$ were obtained by the method previously reported. Intensity data were collected on a Rigaku AFC-5 four-circle diffractometer with graphite monochromated Mo Kα radiation. Crystal data are: $C_8H_{12}S_8INi_2$, monoclinic, P2/n, Z=2, a=12.499(2), b=8.381(1), c=8.930(1) Å, β=106.59(1)°, V=896.5(2) Å^3, μ(Mo Kα)=46.99 mm^{-1}. The structure was solved by a heavy atom method and refined by a full-matrix least-squares technique. Weighting scheme employed was $W=[\sigma_c^2+(0.0151F_o)^2]^{-1}$. Final R and R_w values are 0.026

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and 0.033 for 1340 reflections ($2\theta < 60°$, $|F_o| > 3\sigma(F_o)$), respectively. The reflectivity measurements were made at room temperature on flat shiny surface of the single-crystals using the light polarized parallel and perpendicular to the chain axes, over the photon energy range 0.5-6.5 eV. Single crystal electrical conductivities were measured by the two probe technique, in which the electrical contacts were made with carbon paint. The magnetic susceptibility measurements were made in the temperature range 2-300 K by an Oxford Faraday-type magnetic balance system equiped with a superconducting magnet. All data were corrected by diamagnetism.

RESULTS AND DISCUSSION

The structure of $Ni_2(dta)_4I$ is shown in Fig. 1. The relevant bond distances are listed in Table 1, along with those of corresponding M_2^{2+} and M_2^{3+} dimers. The structure consists of a linear chain of-Ni-Ni-I-Ni-Ni-, where two Ni atoms are bridged by four dithioacetato ligands. The two NiS_4 squares in dimer Ni_2S_8 are twisted from the eclipsed structure. Disorder is observed in the dithioacetato ligands which take two twisted configuration rotated clockwise and counterclockwise around the Ni-Ni axis, where only S atoms are disordered but methyl and quarternary carbons are fixed. Such disorder was not observed in the structure reported previously by Bellitto et al.[11] An essential point

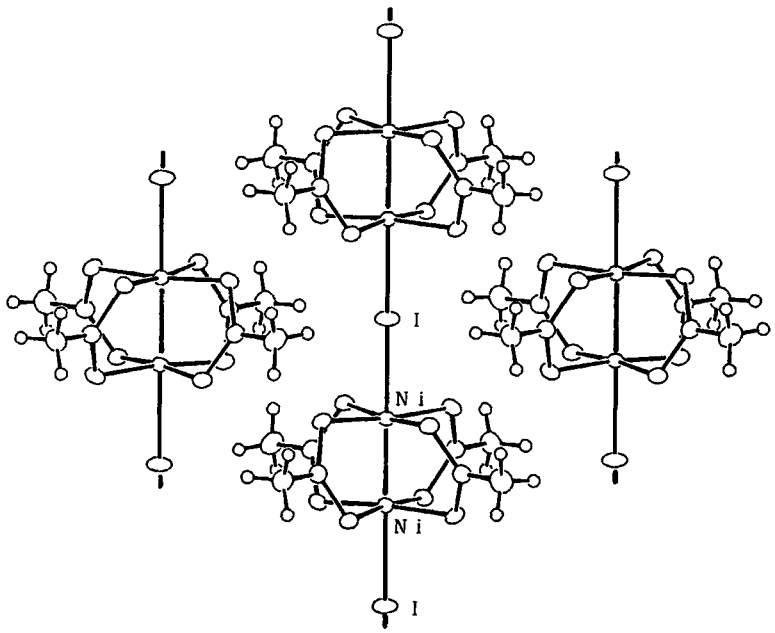

FIGURE 1. ORTEP drawing of the infinite chains of $Ni_2(dta)_4I$.

TABLE I Comparison of the Averaged bond distances (Å)

	M-M	M-X	Oxd.	Ref.
$Pt_2(dta)_4$	2.767(1)	------	+2	10
$Pt_2(dta)_4I$	2.677(2)	2.975(3), 2.981(3)	+2.5	10
$Pt_2(dta)_4Br_2$	2.571(1)	2.572(1)	+3	12
$Ni_2(dta)_4$	2.564(1)	------	+2	11
$Ni_2(dta)_4I$	2.538(4)	2.920(4), 2.923(4)	+2.5	This work
	2.514(5)	2.928(4), 2.940(4)	+2.5	11

related to the physical properties is whether or not the bridging iodine is just located at the midpoint between two Ni dimers. The Ni-I distances are 2.920(4) and 2.923(4) Å, which are equal within the standard deviation. Similarly, in the $Pt_2(dta)_4I$ the bridging iodine atoms are located at middle point between two Pt_2 dimers as reported by Bellitto et al..[10] The M-M distances are in the order $M_2^{2+} > M_2^{2.5+} > M_2^{3+}$, which is quite consistent with the depopulation of the $d\sigma^*$ level, that is, $(d)^2(d\sigma^*)^2$, $(d)^2(d\sigma^*)^1$, and $(d)^2$, respectively.

As shown in Fig. 2, the magnetic susceptibility of $Ni_2(dta)_4I$ is independent of temperature down to about 50 K (ca. 10^{-6} emu/gr) and then rapidly increases at lower temperature. Such behavior is very similar to that of

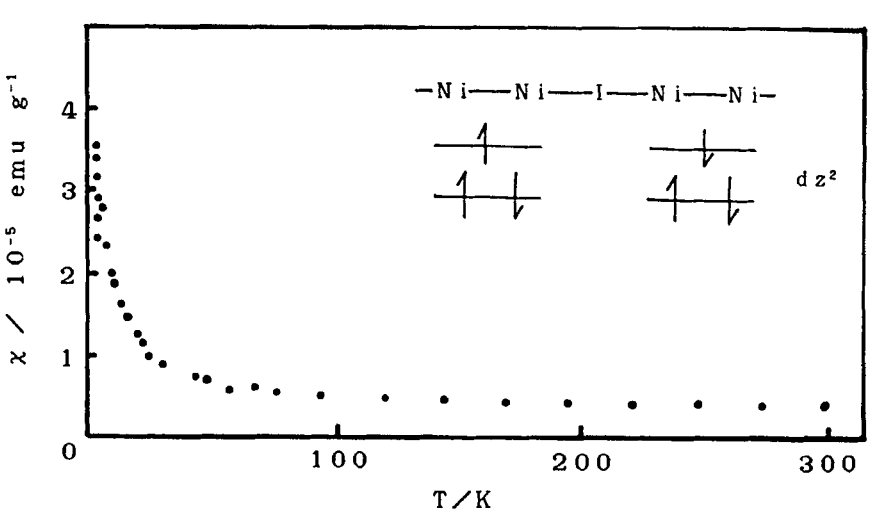

FIGURE 2. Magnetic susceptibilities as a function of temperature of $Ni_2(dta)_4I$

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$Ni(chxn)_2Br_3$ consisting of $-Ni^{3+}-Br-Ni^{3+}-$, where the temperature independent behavior is due to the very strong antiferromagnetic coupling between electron spins (S=1/2) on the Ni^{3+} and the rapid increase at lower temperature is attributable to a small amount of impurity obeying the Curie low.[6] Thus, the essential feature of $Pt_2(dta)_4I$ is similar to that of $Ni_2(dta)_4I$; the very strong antiferromagnetic coupling between electronic spins (S=1/2) on the M-M dimers exists in the $M_2(dta)_4I$ complexes in common.

The polarized reflection spectra of $M_2(dta)_4I$ crystals (M=Pt and Ni) measured at room temperature are presented in Fig. 3. A strong structure is found in the spectra with an electric vector parallel to the 1-D chain(E//b). Their positions are lower than those of the MX and pop compounds. No prominent structure was observed for the E⊥b spectra. Taking into consideration of their electronic structures, these bands are attributable to the charge transfer excitation from $-M^{2.5+}-M^{2.5+}-I-M^{2.5+}-M^{2.5+}-$ to $-M^{2+}-M^{2+}-I-M^{3+}-M^{3+}-$. The $Ni_2(dta)_4I$ have considerably sharp peak at about 0.6 eV (E_{CT}), while the $Pt_2(dta)_4I$ show no clear edge over the measured range; it seems rather to be metallic-like.

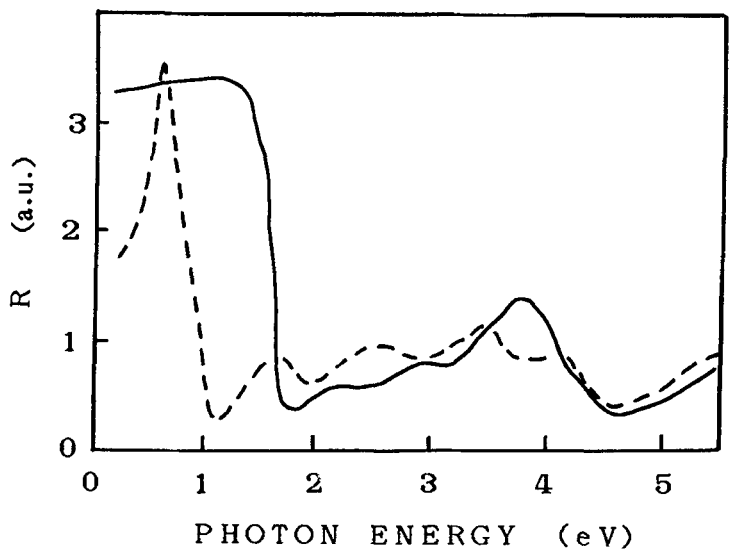

FIGURE 3. The polarized reflectance spectra parallel to the chain axis of $Pt_2(dta)_4I$ (——) and $Ni_2(dta)_4I$ (- - -).

Electrical conductivity measurements on single-crystal of $Ni_2(dta)_4I$ show semiconducting behavior with a small activation energy (ΔE) of 0.10-0.25 eV and a relative high conductivity at room temperature (σ_r) of 2.5×10^{-2} $(\Omega cm)^{-1}$. The electrical conductivity following the relation, $2\Delta E \sim E_{CT}$ can

be explained in terms of thermal excitation of intrinsic carrier (electron-hole). The single-crystal of $Pt_2(dta)_4I$ shows semiconducting-like behavior with σ_r of 2.0 $(\Omega cm)^{-1}$ and ΔE of 0.07 eV below room temperature. It is noticed, however, that the conductivity around room temperature is nearly independent on temperature. These behaviors including the metallic-like spectra of the reflectivity at room temperature could not be explained straightforward.

All of the experimental results of the polarized reflectance spectra, magnetic susceptibilities, electrical conductivities, and X-ray crystal structure of the $M_2(dta)_4I$ support a model of one-dimensional Mott-Hubbard type electronic structure. The larger on-site Coulomb repulsion energy (U) of Ni atom compared with that of Pt atom leads to a larger energy gap in the $Ni_2(dta)_4I$ than that in the $Pt_2(dta)_4I$. Concerning with the electronic state of $Pt_2(dta)_4I$ around room temperature, more detailed investigations are required, which is now in progress.

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