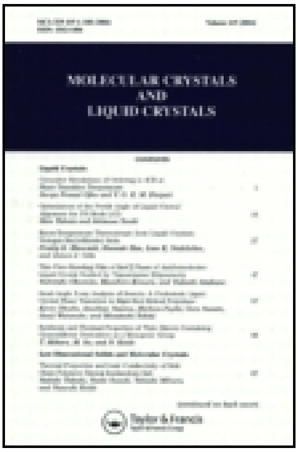

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Syntheses, Structures, and Solid State Properties of One-Dimensional Halogen-Bridged Ni^{111}-X-Ni^{111} Compounds (X=Cl and Br)

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SYNTHESES, STRUCTURES, AND SOLID STATE PROPERTIES OF ONE-DIMENSIONAL HALOGEN-BRIDGED Ni^{III}-X-Ni^{III} COMPOUNDS (X=Cl and Br)

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Abstract Halogen-bridged linear-chain compounds, $\{[Ni(R,R\text{-}chxn)_2X]X_2\}_\infty$ (X=Cl and Br), were synthesized and their structures have been determined by low-temperature X-ray diffraction analyses. The novel one-dimensional Ni^{III}-X-Ni^{III} structure with no Peierls distortion, which is an extreme limit of the M^{II}-X-M^{IV} mixed-valence structure, has been confirmed on the basis of careful consideration of X-ray diffraction results. The optical energy gaps of 1.9 eV and 1.28 eV for the chloro- and bromo-bridged compounds reveal the semiconductive character. Temperature independent small magnetic susceptibility for the bromo-bridged compound implies the strong antiferromagnetic coupling between electronic spins (S=1/2) localized on the Ni^{III}.

INTRODUCTION

For the last decade, the series of halogen-bridged M^{II}-X-M^{IV} mixed valence compounds (M=Pt, Pd and Ni) has attracted much interest from solid state physicists and chemists as one-dimensional materials having strong electron-lattice interaction.[1-3] The compounds consist of the square-planar four-coordinate M^{II} and the octahedral six-coordinate M^{IV} complexes which are stacked alternately to construct a linear chain.[4-12] Their structures are well described as Peierls distorted linear chains with repeating unit ...M^{II}...X-M^{IV}-X..., in which the Peierls distortion is defined by the displacement of the bridging halogen atom, X, from the midpoint between the two metal atoms towards the M^{IV} atom.[2] They show characteristic physical properties, such as the strong intervalence charge transfer absorption,[1-3] the luminescence with large Stokes-shift,[1-2] and the long overtone progression in the resonance Raman spectrum.[13-16] The relation between the Peierls energy gaps and the lattice distortions has been established by a number of the structural[5-12] and optical studies.[1-3] It was expected that a Ni system should be most suitable to prepare the M^{III}-X-M^{III} compound,[17-21] which is one extreme limit of the M^{II}-X-M^{IV} compound and is particularly interesting in its electronic structure and physical properties.[22-25]

Recently, we successfully synthesized a novel halogen-bridged Ni^{III}-Br-Ni^{III} linear chain compounds with the (1R,2R)-cyclohexanediamine ligand, $\{[Ni(R,R\text{-chxn})_2Br]Br_2\}_\infty$ **2** and reported the halogen-bridged linear chain structure with no Peierls distortion which was to our knowledge the first example.[26,27] We report here the synthesis and crystal structure of a chloro-bridged analogue, $\{[Ni(R,R\text{-chxn})_2Cl]Cl_2\}_\infty$ **1**, and the physical properties of both the novel compounds.

EXPERIMENTAL

Lustrous-red needle crystals of $\{[Ni(R,R\text{-chxn})_2Cl]Cl_2\}_\infty$ **1** were grown by slow diffusion of chlorine gas into 2-methoxy-ethanol solution of $[NiCl_2(R,R\text{-chxn})_2]$ under N_2 atmosphere. Black prismatic crystals of $\{[Ni(R,R\text{-chxn})_2Br]Br_2\}_\infty$ **2** were prepared by the similar way as **1** by using bromine gas. Elemental analysis for **2**. Calcd for $C_{12}H_{28}N_4NiBr_3$: C, 27.36; H, 5.36; N, 10.64; Ni, 11.14; Br, 45.51%. Found: C, 27.27; H, 5.40; N, 10.41; Ni, 10.55; Br, 45.00%.

Single crystal X-ray structure analyses were carried out at room and low temperatures for **1** and **2**. Intensity data were collected on Enraf-Nonius CAD4 and Rigaku AFC-5 four-circle diffractometers with graphite monochromated Mo Kα radiation, equipped with a variable temperature apparatus based on a cold nitrogen gas stream method. A needle crystal of **1** with dimensions of 0.67x0.09x0.04 mm and a prismatic crystal of **2** with dimensions of 0.19x0.18x0.10 mm were used for the measurements. The density of **2** was determined by flotation using a mixture of $C_2H_4Br_2$ and CCl_4. Crystal data are: (**1**) $C_{12}H_{28}N_4NiCl_3$, orthorhombic, I222, Z=2, at -151°C, a=23.975(5), b=4.894(1), c=6.913(1) Å, V=811.1(3) Å^3, D_x=1.611 g cm^{-3}, μ(Mo Kα) =16.78 cm^{-1}; (**2**) $C_{12}H_{28}N_4NiBr_3$, orthorhombic, I222, Z=2; at 25°C, a=23.587(5), b=5.161(2), c=7.121(1) Å, V=866.8(4) Å^3, D_x=2.018 g cm^{-3}, D_m=1.988 g cm^{-3}, μ(Mo Kα)=84.50 cm^{-1}; at -152°C, a=23.501(4), b=5.157(1), c=7.090(1) Å, V=859.3(3) Å^3, D_x=2.036 g cm^{-3}, μ(Mo Kα) =85.24 cm^{-1}.

The structures were solved by a heavy atom method and refined by a full-matrix least-squares technique including occupancy factors of the counter and bridging halogen atoms. Weighting scheme employed were $w=[\sigma_c^2+(0.015|Fo|)^2]^{-1}$. Final R and R_w values for **1** are 0.032 and 0.048 for 1974 low-temperature data (-151°C) ($2\theta<80°$, $|Fo|>3\sigma(F_0)$), and for **2** are 0.035 and 0.034 for 1043 room temperature data ($2\theta<65°$, $|Fo|>3\sigma(F_0)$), and 0.037 and 0.034 for 1261 low temperature data ($2\theta<90°$, $|Fo|>3\sigma(F_0)$), respectively.

The reflectivity measurements were made at room temperature on flat shiny surfaces 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. The optical conductivity spectra were obtained by applying the Kramers-Kronig transformation to the reflectivity spectra. The Roessler correction was employed in the transformation.[28] Single crystal electrical conductivities were measured by four probe technique, in which the electrical contacts were made with carbon paint. The magnetic susceptibility measurement for 2 was made in the temperature range 2-300 K by an Oxford Faladay-type magnetic balance system equipped with a superconducting magnet. Many small single crystals of ca. 4 mg, of which the b-axes were aligned parallel to each other on a small high quality quartz plate by apiezon grease, were used for the measurements of anisotropy of magnetic susceptibility. All data were corrected by diamagnetism. The single crystal EPR spectra of 2 were measured at 10 K with a JEOL FE2XG, X-band (100 KHz field modulation) spectrometer by using the aligned crystals. The resonance Raman spectra of 2 were measured at ca. 80 K with a variety of exciting lines between 457.9 and 752 nm. The sample was used in the form of a pressed disc cooled in a liquid nitrogen cryostat.

RESULTS AND DISCUSSION

Crystal Structures

Both the crystal structures of **1** and **2** are isomorphous with the mixed valence compound of $[Pt(R,R\text{-chxn})_2][PtCl_2(R,R\text{-chxn})_2]Cl_4$[29] except for the positions of bridging halogen atoms. The chain structure of **1** is shown in Figure 1. In Table 1, the relevant bond distances of **1** and **2** are compared with the corresponding values of the discrete Ni^{III} and Ni^{II} complexes. The $Ni(R,R\text{-chxn})_2$ moieties, lying on special positions of 222, are bridged by halogen atoms and stacked along b-axis, constructing a linear chain structure. The neighboring $Ni(R,R\text{-chxn})_2$ moieties on the same chain are linked by four $NH...X^-...HN$ hydrogen bonds (3.235(3) and 3.314(3) Å for **1**; 3.415(12) and 3.502(12) Å for **2**). As shown in Figure 1, the hydrogen bond network extended over the chains constructs a two-dimensional structure parallel to the bc plane.

In order to discuss their electronic and magnetic structures, it is essential to decide whether the bridging halogen atoms are located at the midpoints between two Ni atoms (Ni^{III}-X-Ni^{III} structure) or just deviated from the midpoints (Ni^{II}-X-Ni^{IV} structure).[32] On the basis of careful consideration of the X-ray diffraction results, we found that **1** and **2** have the linear-chain Ni^{III}-X-Ni^{III} structures.

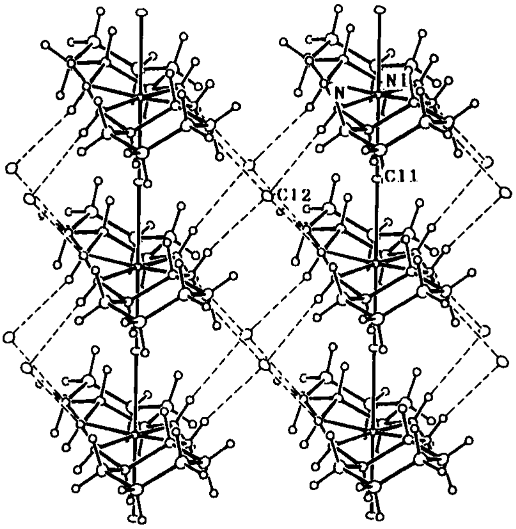

FIGURE 1. ORTEP drawing of a portion of the infinite chains along b with surrounding Cl^- ions of $\{[Ni(R,R\text{-}chxn)_2Cl]Cl_2\}_\infty$ **1** at -151°C. The dashed lines correspond to hydrogen bonds. Thermal ellipsoids are 50% probability surfaces.

Firstly, as shown in Table 1, both the Ni^{III}-X distances of the chain compound **1** and **2** are significantly shorter than those of the discrete Ni^{III} compounds, respectively. Secondly, the structure analyses of **1** and **2** do not indicate positional disorders of the bridging halogen atoms. The thermal ellipsoids of the bridging halogen atoms are very

TABLE I Comparison of the averaged bond distances (Å).

	Ni-X	Ni-N	Ref.
$\{[Ni(R,R\text{-}chxn)_2Cl]Cl_2\}_\infty$	2.447(1)	1.944(1)	this work
$[Ni^{III}Cl_2L]ClO_4$ •	2.452(5)	1.970(7)	30
$[Ni^{II}Cl_2L]$	2.510(1)	2.067(1)	31
$\{[Ni(R,R\text{-}chxn)_2Br]Br_2\}_\infty$	2.578(1)	1.944(3)	26
$[Ni^{III}Br_2L]ClO_4$	2.616(1)	1.971(7)	26
$[Ni^{II}Br_2L]$	2.694(1)	2.063(5)	21

• L=1,4,8,11-tetraazacyclotetradecane.

small. Finally, neither diffuse scattering nor satellite peak relating to a superstructure have been observed on the X-ray oscillation and Weissenberg photographs of **1** or **2**. It is also important to elucidate whether the crystals of **1** and **2** are nonstoichiometric or stoichiometric compounds, that is, partially oxidized compounds or not. The full-matrix least-squares refinements including occupancy factors of the bridging and counter halogen atoms revealed the stoichiometric structures of **1** and **2**. Both the elemental analysis and the observed density for **2** confirmed the results.

Physical Properties

Semiconductive character of **1** and **2** has been revealed by optical and electrical conductivity measurements. Figure 2 shows the single crystal conductivity spectra for **2**. An intense narrow band observed at 1.28 eV for the parallel component of the spectra can be assigned to the charge transfer transition. It should be noted that the band width is significantly narrower than the charge transfer transition band for the M^{II}-X-M^{IV} mixed valence compounds. The optical energy gap of 1.28 eV for **2** is smaller than the value for the Pt^{II}-Br-Pt^{IV}

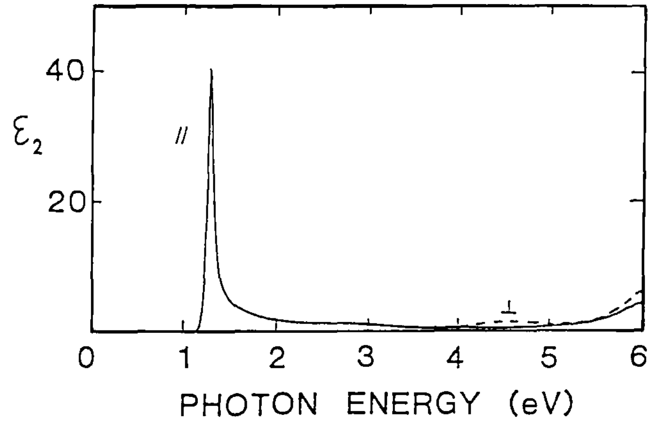

FIGURE 2. The polarized optical conductivity spectra parallel (——) and perpendicular (– – – –) to the chain axis transformed from the reflectivity spectra of $\{[Ni(R,R\text{-}chxn)_2Br]Br_2\}_\infty$ **2**.

mixed valence compound but larger than the Pd^{II}-Br-Pd^{IV} compound.[33] This is not consistent with the relation between the Peierls energy gaps and the lattice distortions for the mixed valence compounds. An optical energy gap of 1.9 eV is also obtained from the optical conductivity spectra for **1**.

Single crystal electrical conductivity measurements, however, show very small activation energies and relatively high conductivities. The room temperature conductivities and activation energies along the chain axes were $1\times10^{-3}\,\Omega^{-1}\mathrm{cm}^{-1}$ and 0.19 eV for **1**, and $2\times10^{-2}\,\Omega^{-1}\mathrm{cm}^{-1}$ and 0.11 eV for **2**, respectively. The low activation energies can not be regarded as intrinsic values for the Ni^{III}-X-Ni^{III} compounds but may be interpreted by the electron transfer mechanism originated from the excess electrons from Ni^{II} species or the electron holes from Ni^{IV} contained in the crystal as impurities.

Resonance Raman spectra of **2** is presented in Figure 3. A peaks at 213 cm^{-1} is strongly enhanced on changing the excitation energies to the far red region. This suggests that the 213 cm^{-1} band should be assigned to the symmetrical Br-Ni^{III}-Br stretching mode, since the charge transfer band is just in the infrared region. The weak band

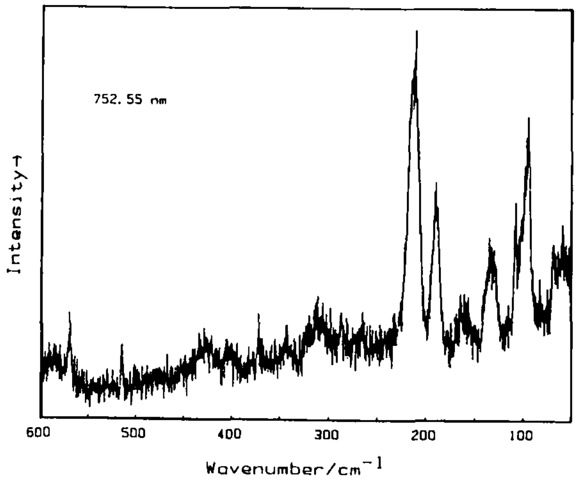

FIGURE 3. Resonance Raman spectrum of $\{[Ni(R,R\text{-}chxn)_2Br]Br_2\}_\infty$ **2** at ca. 80 K with an exciting line of 752.55 nm.

is, however, distinct from the symmetric X-M^{IV}-X stretching band for the halogen-bridged M^{II}-X-M^{IV} mixed-valence compounds which show the characteristic long overtone progressions.[13]

Temperature independent magnetic susceptibility of **2** is shown in Figure 4. No significant anisotropy was observed in the magnetic susceptibility data. A small paramagnetic component which obeys the Curie law was observed. The single crystal EPR spectra, which were measured at 10 K for the aligned crystal of **2**, gave anisotropic g values of 2.178 and 2.029 for parallel and perpendicular components, respectively. The g values are well corresponding to discrete Ni^{III} complexes which may be contained in the crystal as impurities. The number of spins corresponds to 1 wt% of discrete Ni^{III} species. As shown in Figure 4, the temperature independent isotropic magnetic susceptibility is less than 10^{-7} emu g^{-1} and does not correspond to a Pauli paramagnetism.

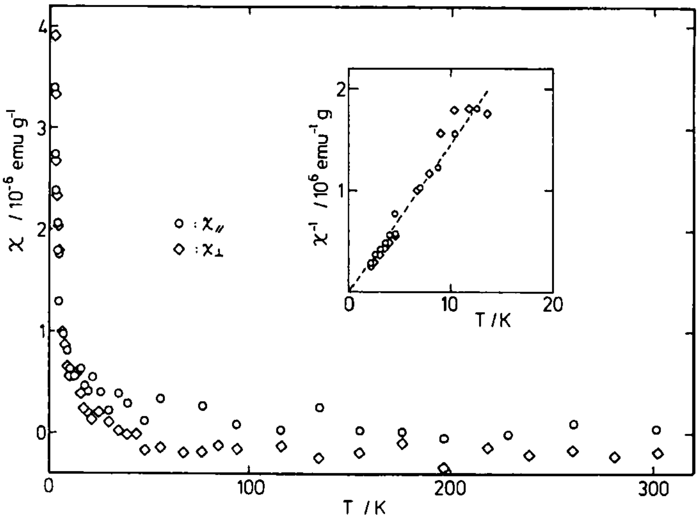

FIGURE 4. Magnetic susceptibility as a function of temperature for $\{[Ni(R,R\text{-}chxn)_2Br]Br_2\}_\infty$ **2**: parallel (○) and perpendicular components (◇).

CONCLUSION

Halogen-bridged linear-chain compounds, $\{[Ni(R,R\text{-}chxn)_2X]X_2\}_\infty$ (X=Cl and Br), were synthesized and the novel one-dimensional Ni^{III}-X-Ni^{III} structure with no Peierls distortion has been determined on the basis of careful consideration of X-ray diffraction results. The optical and electric conductivity data reveal the semiconductive character. The magnetic behavior of **2** implies strong antiferromagnetic coupling between electronic spins (S=1/2) localized on the Ni atoms of the bromo-bridged Ni^{III}-X-Ni^{III} linear chain. The magnetic structures of the compounds are, however, not apparent in detail. The two-dimensionality of the hydrogen bond network may play an important role in the electronic and magnetic structures.

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