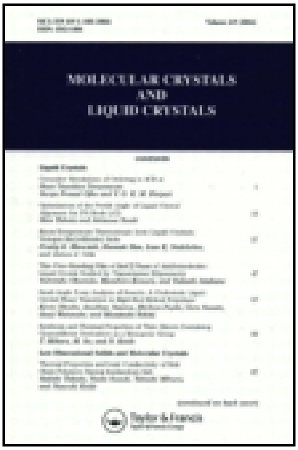

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Electrocrystallization, Crystal Structure, and Solid State Properties of Halogen-Bridged One-Dimensional Compound, $\{[Ni(en)_2Br](ClO_4)_2)\propto$, Having an Elongated Ni $\cdots$ Ni Distance

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ELECTROCRYSTALLIZATION, CRYSTAL STRUCTURE, AND SOLID STATE PROPERTIES OF HALOGEN-BRIDGED ONE-DIMENSIONAL COMPOUND, $\{[Ni(en)_2Br](ClO_4)_2\}_\infty$, HAVING AN ELONGATED Ni•••Ni DISTANCE

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Abstract Two crystal forms (α and β) of a novel halogen bridged one-dimensional Ni^{III}–Br–Ni^{III} compound, $\{[Ni(en)_2Br](ClO_4)_2\}_\infty$ (en=$C_2H_8N_2$), have been prepared by electrochemical oxidation. X-ray crystal structure analysis of the α form revealed that a bridging Br ion is located on the midpoint between two Ni atoms and the Ni—Br distance of 2.640(1) Å is significantly elongated by introducing a bulky ClO_4^- ion as a counter anion. An average Ni–Br distance of 2.693(2) Å for the β form can be estimated from the lattice parameter along the chain. X-ray photoelectron spectra indicate that both forms have the Ni^{III}–X–Ni^{III} structure. Magnetic susceptibility data for both forms show strong antiferromagnetic coupling (J=-1700) between electronic spins (S=1/2) localized on the Ni^{III} on the linear chain.

INTRODUCTION

Halogen-bridged mixed-valence complexes, which have a linear chain structure with a repeating unit of $\cdots M^{II}\cdots X–M^{IV}–X\cdots$ (M=Pt or Pd), have been extensively studied as a typical one-dimensional system having strong electron-lattice interaction.[1,2] They show characteristic physical properties such as the strong intervalence charge-transfer absorption and the luminescence with large Stokes-shift.[1-5] Recently, we succeeded in preparing novel Ni^{III}–X–Ni^{III} compounds which have one-dimensional chain structures with no Peierls distortion.[6-9] Their magnetic behavior implies extremely strong antiferromagnetic coupling between electronic spins localized on the Ni atoms.[6,7]

The one-dimensional M–X–M compounds are classified into either the M^{III}–X–M^{III} mono-valence compound or the M^{II}–X–M^{IV} mixed-valence one depending on whether the bridging halogen is located on the midpoint between two metal atoms or deviated from the center. The electronic structure for the M^{II}–X–M^{IV} compound is well described by a Peierls-Hubbard model as a charge density wave state (CDW) and that for M^{III}–X–M^{III} by a Mott-Hubbard model as a spin density wave state (SDW). From a series of structural and optical studies for the M–X–M compounds, the linear relation between CT excitation energy (Peierls gap) and magnitude of the displacement of a bridging halogen from the midpoint (Peierls distortion) has been elucidated.[10] It should be noted that amplitude of the Peierls distortion can be controlled by modifying the chemical parameters, such as changing central metal (M), bridging halogens (X), organic ligands, and counter anions.[10]

For the M^{II}–X–M^{IV} mixed-valence compounds, the Peierls energy gaps decrease monotonously with decrease of the amplitudes of Peierls distortion. However, E_{CT} observed for the Ni^{III}–X–Ni^{III} compounds (1.2 eV for X=Br and 1.9 eV for Cl) seem to be unusually large compared with the values expected from the relation.[6,7] Recently, Okamoto et al. reported that the strong absorption bands were assigned not to the intervalence charge transfer band from Ni^{III}–X–Ni^{III} to Ni^{II}–X–Ni^{IV} but to the ligand-to-metal charge transfer band from a bridging halogen X^- to Ni^{III}.[11] However, it may be reasonable to point out that there is a phase transition between the Ni^{III}–X–Ni^{III} and Ni^{II}–X–Ni^{IV} states. In order to explore this phase transition, it should be necessary to prepare a Ni^{II}–X–Ni^{IV} compound having a very small Peierls distortion. The interesting compound would be obtained by introducing a bulky anion such as ClO_4^- into a crystal to elongate the Ni•••Ni distance stereochemically.

Over a hundred of M^{II}–X–M^{IV} mixed-valence compounds have been synthesized for the Pt and Pd complexes. On the other hand, only a few Ni^{III}–X–Ni^{III} compounds have been prepared.[6-9] This is owing to marked differences in the crystal preparation as follows. Crystals of the Pt and Pd compounds are easily obtained by adding excess amount of counteranion to an aqueous solution containing M^{II} and M^{IV} complexes, since M^{IV} complexes are stable in an aqueous solution.[12] For the Ni compound, however, both the oxidation and crystallization processes should be made simultaneously since a Ni^{IV} complex could not be isolated yet. The Ni^{III}–X–Ni^{III} compounds previously reported were obtained by chemical oxidation of Ni^{II} monomeric complexes using halogen gas.[6,7] The halogen oxidation procedure enable only a few compounds, since halogen atoms are introduced not only as bridging ions but also as counteranions. On the other hand, the electrochemical oxidation technique seems to be much favorable for preparing many types of M–X–M compounds, since various combination of bridging ion and counteranion becomes possible and the rate of crystallization can be controlled.[8]

We report here the electrochemical crystallization, crystal structure, and magnetic properties of a bromo-bridged $\mathrm{Ni^{III}}$–X–$\mathrm{Ni^{III}}$ compound, $\{[\mathrm{Ni(en)_2Br}](\mathrm{ClO_4})_2\}_\infty$. This is the first example of the $\mathrm{Ni^{III}}$–X–$\mathrm{Ni^{III}}$ compounds having a stereochemically elongated Ni•••Ni distance, though the $\mathrm{Ni^{II}}$–X–$\mathrm{Ni^{IV}}$ compound could not be prepared yet.

EXPERIMENTAL

Sample Preparation

A mixture of 0.042 g (0.12 mmol) of $\mathrm{Ni(en)_2Br_2}$ and a 0.600 g (5.64 mmol) of $\mathrm{LiClO_4}$ in 20 $\mathrm{cm^3}$ of 2-propanol were heated to reflux for 4 h. The solution was filtered and electrochemically oxidized using Pt electrode by galvanostat at 23 °C. Deep brown prismatic crystals with gold luster of $\{[\mathrm{Ni(en)_2Br}](\mathrm{ClO_4})_2\}_\infty$ (α form) were grown on the cathode after several days with continuous electrolysis at 5 μA.

A mixture of 0.085 g (0.25 mmol) of $\mathrm{Ni(en)_2Br_2}$ and a 0.400 g (3.75 mmol) of $\mathrm{LiClO_4}$ were dissolved in 20 $\mathrm{cm^3}$ of dried methanol-ethanol (1:4) mixed solvent. The mixture was filtered and electrochemically oxidized at the same condition as that for α form. Dark brown crystals of $\{[\mathrm{Ni(en)_2Br}](\mathrm{ClO_4})_2\}_\infty$ (β form) were obtained. Found: C, 10.68; H, 3.40; N, 12.41%. Calcd for $\mathrm{C_4H_{16}N_4O_8BrCl_2Ni}$: C, 10.50; H, 3.52; N, 12.24%.

X-ray Crystal Structure Analysis

X-ray diffraction data of $\{[\mathrm{Ni(en)_2Br}](\mathrm{ClO_4})_2\}_\infty$ were measured at room temperature on an Enraf-Nonius CAD4 diffractometer, graphite monochromated MoKα radiation (λ=0.71073Å), θ-2θ scan technique. A square prismatic crystal of the α form elongated along b with dimensions of 0.25x0.08x0.08 mm was used for the data collection. Lattice parameters were determined from the least-square calculation using 25 centered reflections in the range $12.5° \le \theta \le 15°$. Crystallographic data for the α form are: orthorhombic, *Icma*, a=13.737(2), b=10.559(3), c=9.553(2) Å, Z=4. Total 2017 intensities up to θ=30° were measured and corrected for Lorentz-polarization effects and absorption based on the numerical Gaussian integration method. 642 observed unique reflections with $|F|>3\sigma(F)$ were used for structure determination and refinement. The structure was solved by the Patterson method. All non-hydrogen atoms were found and refined anisotropically. The R(F) and R_w(F) values are 0.067 and 0.068, respectively. All the calculations were carried out by using the Xtal3.2 program package.[13]

Oscillation and Weissenberg photographs were taken for a square prismatic crystal of the β form, showing many weak Bragg reflections corresponding to a commensurate superstructure. Crystallographic parameters for the fundamental cell, which was determined by excluding weak reflections, are: orthorhombic, *Pnab*, a=15.710(3), b=16.259(4), c=10.773(6) Å. Intensity data were measured for the fundamental lattice, and 1019 observed unique reflections were used for structure analysis. Only the arrangement of $Ni(en)_2$ units and bridging Br ions was determined, though accurate structure analysis could not be achieved. One-dimensional chain structure is parallel to the c axis.

XPS and Magnetic Susceptibility Measurement

The X-ray photoelectron spectra were measured for the powdered sample of α and β forms by VG ESCALAB MKII at the Instrument Center of the Institute for Molecular Science. Weak MgKα radiation operated by 15 kV 5mA was irradiated to the sample. By comparing the initial and final spectra, it was confirmed that sample deterioration did not occur. Binding energies for $Ni2p_{3/2}$ were calibrated for C1s peaks of the ethylendiamine ligand.

The magnetic susceptibility was measured in the temperature range of 2-300 K with a Faraday balance (CAHN 2000) equipped with a superconducting magnet (Oxford Instruments). The magnetic field and the gradient were 1 T and 0.1 T/cm, respectively. Small needle-like crystals of ca. 10 mg were laid onto the bottom of a cylindrical quartz cell, so that the chain-direction of the crystals is roughly perpendicular to the magnetic field. Diamagnetic correction was made by Pascal's method.

RESULTS AND DISCUSSION

Electrochemical Oxidation

Remarkably different compounds were obtained by changing the conditions of electrochemical oxidation process such as solvent, temperature, electric current, and concentrations of Ni complex and supporting electrolyte. The α form of $\{[Ni(en)_2Br](ClO_4)_2\}_\infty$ was obtained from 2-propanol, while the β form was from methanol-ethanol mixed solvent. Although both the crystals have the same stoichiometry, the α form has a regular structure except for disorder of ClO_4^-, but the β form show many satellite peaks corresponding to a superstructure. On the other hand, deep brown crystals with green luster of $[\{Ni^{III}(en)_2\}_2Br_3][Ni^{III}Br_2(en)_2](ClO_4)_4$ were obtained from the methanol-ethanol (1:1) solvent.[14] It should be noted that there contains the Ni^{III} dimer complex having the portion of an infinite Ni^{III}–Br–Ni^{III} chain

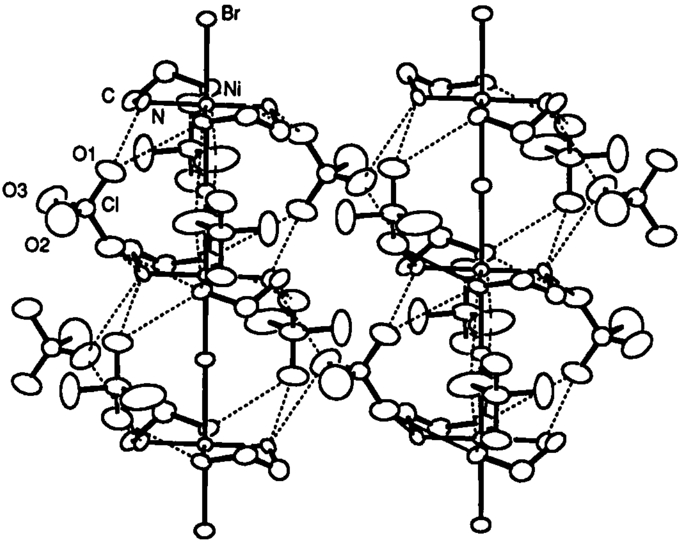

FIGURE 1 ORTEP drawing of the infinite linear chains of $\{[Ni(en)_2Br](ClO_4)_2\}_\infty$ (α form). Dashed lines indicate hydrogen bonds between ClO_4^- and NH_2 of ethylenediamine ligands. Thermal ellipsoids are at 50% probability level.

structure. In addition, red crystals of Ni^{III} monomer complex of $[Ni^{III}Br_2(en)_2]ClO_4$ were grown from the methanol-ethanol solvent (excess methanol).

Crystal Structure of $\{[Ni(en)_2Br](ClO_4)_2\}_\infty$ (α Form)

The crystal structure of α form is isomorphous to the analogous halogen-bridged M^{II}–X–M^{IV} mixed valence compounds of $[M(en)_2][MX_2(en)_2](ClO_4)_4$ (M=Pt, Pd; X=Cl, Br).[15] Figure 1 shows the linear chain structure along the b axis. Crystallographically independent $Ni(en)_2$ moieties with square-planar geometry which lie in the special positions of 222, are linked by Br^- ions to construct an infinite linear chain. Neighboring $Ni(en)_2$ moieties on the chain are related by the mirror symmetry perpendicular to the chain and passing through the midpoint between two Ni atoms. The X-ray analysis has revealed that the Br^- ion is just located on the midpoint between two Ni atoms, indicating that all the $Ni(en)_2$ moieties are crystallographically equivalent but not necessarily chemically equivalent. Two possible structures must be considered to interpret this result. The first one is a one-dimensional Ni^{III}–Br–Ni^{III} structure with no Peierls distortion, in which the Br sits strictly on the midpoints between two Ni. The second one is a Ni^{II}-Br-Ni^{IV} mixed-valence structure with a small Peierls distortion.

Because of the positional resolution of X-ray diffractometry (ca. 0.4 Å in this case), we could not distinguish them by the X-ray analysis only.

XPS data for α and β forms revealed that oxidation states of the Ni atoms could be assigned not to the mixed-valence of +2 and +4 but to the mono-valence of +3. From this as well as the magnetic behaviors described below, it is reasonably concluded that $\{[Ni(en)_2Br](ClO_4)_2\}_\infty$ has the Ni^{III}–Br–Ni^{III} linear chain structure with no Peierls distortion.

Relevant interatomic distances for the α form are listed in Table I. In Table II, the Ni^{III}—Br distance are compared to those of the analogous bromo-bridged Ni^{III}–Br–Ni^{III} compounds. The Ni^{III}—Br distance of 2.640(1) Å for the α form is significantly longer than 2.580(1) Å for $\{[Ni(R,R\text{-}chxn)_2Br]Br_2\}_\infty$.[6] More elongated Ni^{III}—Br distance of 2.693(2) Å is observed for the β form. These results strongly indicate that the Ni—Br distance, on which physical properties of the compound depend, can be elongated stereochemically by introducing the bulky counteranion of ClO_4^-. It should, however, be noted that the Ni—Br distance may be elongated farther to obtain a novel Ni^{II}–Br–Ni^{IV} compound.

TABLE I Relevant interatomic distance (Å) and angles (°) for $\{[Ni(en)_2Br](ClO_4)_2\}_\infty$ (α form).

Ni—Br	2.6398(7)	Ni—N	1.928(6)
N—C	1.52(1)	$C—C^i$	1.48(1)
Br-Ni-N	89.7(2)	$N\text{-}C\text{-}C^i$	106.7(6)

symmetry code: i) -x, 1/2-y, z.

TABLE II Comparison of Ni^{III}—Br distances (Å).

compound	Ni—Br	ref.
$\{[Ni(en)_2Br](ClO_4)_2\}_\infty$ (α form)	2.640(1)	this work
$\{[Ni(en)_2Br](ClO_4)_2\}_\infty$ (β form)	2.693(2)	this work
$\{[Ni(R,R\text{-}chxn)_2Br]Br_2\}_\infty$[a]	2.580(1)	16
$[NiBr_2(en)_2]Br$	2.635(1)	16
$[NiBr_2L]ClO_4$[b]	2.616(1)	6

[a] R,R-chxn=(1R,2R)-diaminocyclohexane.
[b] L=1,4,8,11-tetraazacyclotetradecane.

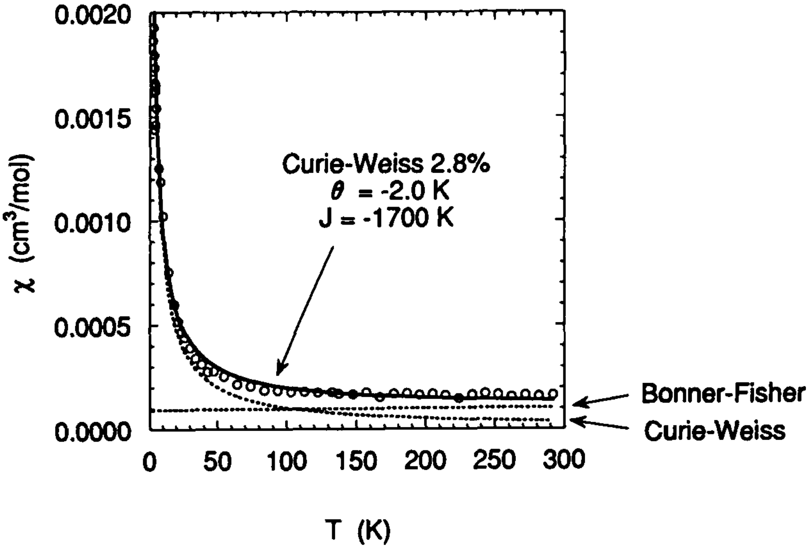

FIGURE 2 The temperature dependence of the magnetic susceptibility of $\{[Ni(en)_2Br](ClO_4)_2\}_\infty$ (α form). The observed data are shown as open circles. The solid line represents the best fit with eq. (2) (see text). Broken lines represent the Curie-Weiss and Bonner-Fisher components.

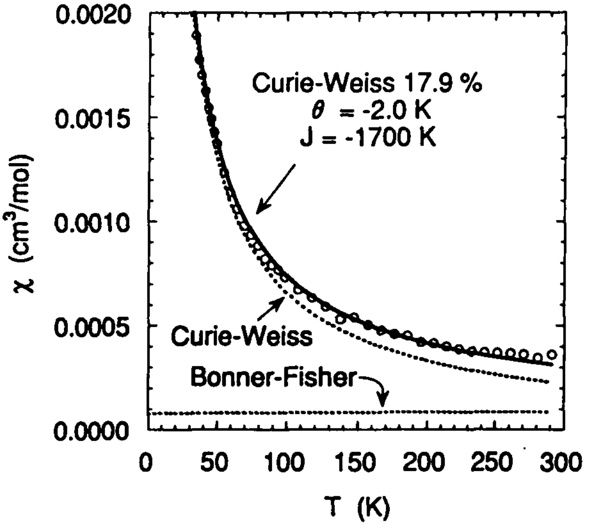

FIGURE 3 The temperature dependence of the magnetic susceptibility of $\{[Ni(en)_2Br](ClO_4)_2\}_\infty$ (β form). The observed data are shown as open circles. The solid line represents the best fit with eq. (2) (see text). Broken lines represent the Curie-Weiss and Bonner-Fisher components.

Magnetic Property

The temperature dependencies of the magnetic susceptibilities of the α and β forms of $\{[Ni(en)_2Br](ClO_4)_2\}_\infty$ are shown in Figs. 2 and 3. Both curves show significant Curie-Weiss-like behaviors in the lower temperature range. It means that the magnetic susceptibility at low temperatures is dominated by weakly coupled isolated spins, which may be originated from (1) small deviation in stoichiometry or (2) a fragment of odd-number Ni atoms derived from a local structural disorder, although neither of them has been proved by chemical analysis or X-ray diffractometry. In the higher temperature range, there still remains temperature-independent paramagnetic susceptibility, which can be seen particularly in the α form in Fig. 2. It is ascribed to the temperature-insensitive paramagnetic susceptibility of the S=1/2 Heisenberg chain with a large antiferromagnetic interaction of the following Hamiltonian,

$$H = -J \Sigma_i S_i \bullet S_{i+1} - g\mu_B H \bullet \Sigma_i S_i \qquad (1)$$

where S_i is the spin operator on the i-th site, and J is the exchange interaction energy. The temperature dependence of the magnetic susceptibility of the above spin system ($\chi_{B\text{-}F}(T,J)$) characterized by the parameter J is well known as Bonner-Fisher curve.[17,18] We adopt the following expression for the total susceptibility,[19]

$$\chi_{obsd}(T) = p \bullet N_g{}^2 \mu_B{}^2 / 4k_B(T-\theta) + (1 - p)\, \chi_{B\text{-}F}(T,J) \qquad (2)$$

where p is molar fraction of the Curie-Weiss spin, and θ the Weiss temperature. When we assume g=2 and treat p, θ and J as variable parameters, the least squares fit of eq. (2) to the observed data results that p=2.8±0.2 % and J=1700±100 K for the α form, and p=17.9±0.5 % and J=-1700±300 K for the β form. The Weiss temperature θ is about -2.0 K in both cases. It has been reported that the intra-chain Ni—Ni distance of an isostructural complex, $\{[Ni(R,R\text{-}chxn)_2Br]Br_2\}_\infty$, is 5.160 Å and J is estimated to be -7200 K by ESR measurement.[20] As compared with this result, we conclude that the antiferromagnetic interaction is significantly weaken in $\{[Ni(en)_2Br\}(ClO_4)_2]_\infty$ complexes, in accord with the increase of the Ni—Ni distance.

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