Figure 3. (Left axis): Comparison of carbon-13 spin–lattice relaxation times (T_1, s) vs generation for designated carbons (3, 5, and 6; ▲, □, and O, respectively) in **3** with CHCl₃ solvent and various dendrimer generations. (Right axis): Molecular asymmetry (--●--) vs dendrimer generation (number of Z' groups).

In conclusion, this work describes molecular simulations and physical measurements that suggest starburst branching strategies may be useful for controlling molecular morphogenesis.

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Synthesis and Crystal Structure of a Novel One-Dimensional Halogen-Bridged Ni^{III}–X–Ni^{III} Compound, {[Ni(R,R-chxn)₂Br]Br₂}∞

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Recently, 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.[2] Their
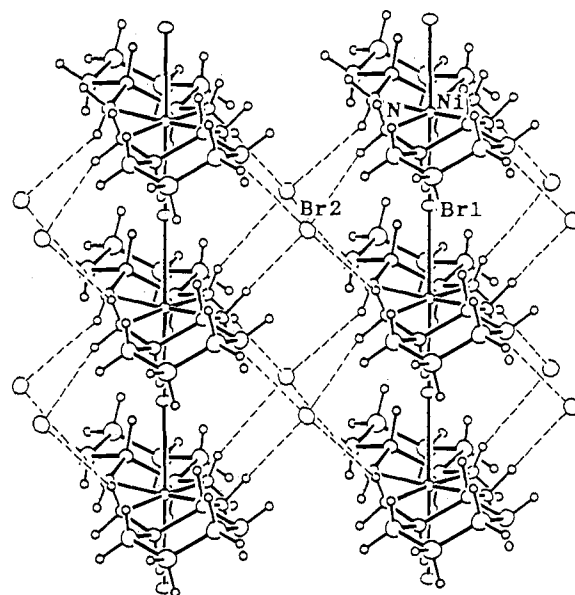
Figure 1. ORTEP drawing of a portion of the infinite chains along *b* with surrounding Br⁻ ions of {[Ni(R,R-chxn)₂Br]Br₂}∞ (**1**) at room temperature. The dashed lines correspond to hydrogen bonds. Thermal ellipsoids are 50% probability surfaces.

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 toward the M^{IV} atom.[2b] They show characteristic physical properties, such as the strong intervalence charge-transfer absorption and the luminescence with large Stokes shift.[2,3] The solid-state properties can be interpreted by using an extended Peierls–Hubbard model which incorporates the electron–electron correlation on intermetal sites.[4] The relation between the Peierls energy gaps and lattice distortions for the compounds has been established by a number of structural[5] and optical studies.[2b] It is expected from this relation that a Ni system should be most suitable to prepare the Ni^{III}–X–Ni^{III} compound,[6] which is one extreme limit of the M^{II}–X–M^{IV} compound and is particularly interesting in its electronic structure and physical properties.[7]

We report here the synthesis, crystal structure, and physical properties of a novel bromo-bridged Ni^{III}–X–Ni^{III} linear chain compound with the (1R,2R)-cyclohexanediamine ligand, {[Ni(R,R-chxn)₂Br]Br₂}∞. It is to our knowledge the first example of a halogen-bridged linear chain metal complex having no Peierls distortion.[8]

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Black prismatic crystals of {[Ni(*R,R*-chxn)$_2$Br]Br$_2$}$_\infty$ (**1**) were grown by slow diffusion of Br$_2$ gas into 2-methoxyethanol solution of [NiBr$_2$(*R,R*-chxn)$_2$] under N$_2$ atmosphere. Orange red crystals of [NiBr$_2$([14]aneN$_4$)]ClO$_4$, **2**,[9] which is the reference compound containing a discrete Ni^{III} complex, were obtained by oxidizing [Ni([14]aneN$_4$)](ClO$_4$)$_2$ with Br$_2$ in aqueous solution.

Single-crystal X-ray structure analyses were carried out at room temperature and −152 °C for **1**[10] and at room temperature for **2**.[11] The structure of **1** was refined by using a full-matrix least-squares technique including occupancy factors of the counter and bridging Br atoms. The stoichiometric structure of **1** was determined by the analysis and confirmed by both the elemental analysis[12] and the observed density.[13]

The chain structure of **1**, which is isomorphous with the mixed-valence compound of [Pt(*R,R*-chxn)$_2$][PtCl$_2$(*R,R*-chxn)$_2$]Cl$_4$[14] except for the position of a bridging halogen atom, is shown in Figure 1. The Ni(*R,R*-chxn)$_2$ moieties, lying on special positions, are bridged by Br atoms and stacked along the *b*-axis, constructing a linear chain structure. The neighboring Ni(*R,R*-chxn)$_2$ moieties on the same chain are linked by four NH···Br$^-$···HN hydrogen bonds (3.415 (12), 3.502 (12) Å). 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 the physical properties of **1**, it is essential to decide whether the bridging Br atom is located at the midpoint between two Ni atoms or just deviated from the midpoint.[15] If the bridging Br atom is shifted slightly from the midpoint, the compound can be regarded as the well-known Peierls distorted halogen-bridged Ni^{II}–X–Ni^{IV} mixed-valence compound. On the other hand, the location of the atom at the midpoint would result in a halogen-bridged Ni^{III}–X–Ni^{III} compound with different properties. On the basis of careful consideration of the X-ray diffraction results,[16] we found that **1** has the Ni^{III}–X–Ni^{III} structure. Firstly, the Ni^{III}–Br distance of the chain compound **1** (2.580 (1) Å) is significantly shorter than that of the discrete compound **2** (2.616 (1) Å). Secondly, the structure analysis of **1** does not indicate positional disorder of the bridging Br atom. The thermal ellipsoid of the bridging Br atom is very small (U_{eq} (−152 °C) = 0.0089 Å^2). Finally, neither diffuse scattering nor satellite peak relating to a superstructure have been observed on the X-ray oscillation and Weissenberg photographs of **1**.

Semiconductive character of **1** has been revealed by optical and electrical conductivity measurements.[17,18] The single-crystal reflectivity measurement gave an optical energy gap of 1.28 eV.[19]

The magnetic susceptibility of aligned small crystals of **1** was also measured by a Faraday balance method in the temperature range 2–300 K.[20] The observed temperature independent isotropic magnetic susceptibility, which is less than 10^{-7} emu g^{-1}, does not correspond to a Pauli paramagnetism.[21] The magnetic behavior of **1** 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 two-dimensionality of the hydrogen bond network may play an important role in the magnetic structure. Further studies on the physical properties of **1** are now in progress.

Supplementary Material Available: Listings of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, bond angles, and hydrogen bond distances and ORTEP drawings of crystal and molecular structures (12 pages). Ordering information is given on any current masthead page.

(8) A related Ni compound, which has the same crystal structure but is different in stoichiometry, has been reported: Toftlund, H.; Simonsen, O. *Inorg. Chem.* **1984,** *23,* 4261–4265.

(9) [14]aneN$_4$ denotes a macrocyclic ligand of 1,4,8,11-tetraazacyclotetradecane.

(10) X-ray structure analyses have been carried out by using a black prism with dimensions of 0.19 × 0.18 × 0.10 mm at room temperature and −152 °C. Crystal data are as follows: (**1**) C$_{12}$H$_{28}$N$_4$NiBr$_3$, orthorhombic, *I*222, *Z* = 2; at 25 °C, *a* = 23.587 (5) Å, *b* = 5.161 (2) Å, *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) Å, *b* = 5.157 (1) Å, *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}. Intensity data were collected on a Rigaku AFC-5 four-circle diffractometer with graphite monochromated Mo Kα radiation, equipped with a variable temperature apparatus based on a cold nitrogen gas stream method. The structure was solved by a heavy atom method and refined by a full-matrix least-squares technique. Occupancy factors of Br atoms were included in the calculations. Weighting scheme is $w = [\sigma_c^2 + (0.015 \times |F_o|)^2]^{-1}$. Final *R* and R_w values are 0.035 and 0.034 for 1043 room temperature data (2θ ≤ 65°, |F_o| ≥ 3σ(F_o)), and 0.037 and 0.034 for 1261 low-temperature data (2θ ≤ 90°, |F_o| ≥ 3σ(F_o)), respectively.

(11) X-ray structure analysis has been made by using an orange-red prism with dimensions of 0.36 × 0.11 × 0.08 mm at room temperature. Crystal data are as follows: (**2**) C$_{10}$H$_{24}$N$_4$NiBr$_2$·ClO$_4$, orthorhombic, *P*2$_1$2$_1$2$_1$, *Z* = 4, *a* = 13.282 (2) Å, *b* = 19.451 (4) Å, *c* = 6.745 (1) Å, *V* = 1742.6 (5) Å^3, D_x = 1.976 g cm^{-3}, μ(Mo Kα) = 61.46 cm^{-1}. Intensity data were measured by the same way as in ref 9. The structure was solved by a heavy atom method and refined by a block-diagonal least-squares method. Current *R* and R_w values are 0.042 and 0.037, respectively, for 3663 independent reflections (2θ < 65°, |F_o| ≥ 3σ(F_o)).

(12) Elemental analysis for **1**. Calcd for C$_{12}$H$_{28}$N$_4$NiBr$_3$: 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.

(13) The density of **1** was determined by flotation with a mixture of C$_2$H$_4$Br$_2$ and CCl$_4$.

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(16) An X-ray structure analysis cannot give an unambiguous result with respect to the bridging Br position. This is due to the series-termination effect; atoms which are closer than $\Delta r = 0.61\lambda/(2 \sin \theta_{max})$ are unresolved in a Fourier synthesis and appear as a single atom: James, R. W. *Acta Crystallogr.* **1948,** *1,* 132–134.

(17) Measurements of the single-crystal electrical conductivity by four-probe technique, in which the electrical contacts were made with carbon paint, showed semiconducting behavior with a room temperature conductivity of 2 × 10^{-2} Ω^{-1} cm^{-1} and an activation energy of 0.11 eV along the *b* axis. The high conductivity and the small activation energy may be due to some impurities.

(18) The optical energy gap was obtained from the imaginary part of dielectric constant calculated from the reflectivity spectra by the Kramers–Kronig transformation.

(19) Luminescence or resonance Raman spectra have not yet been observed for **1**.

(20) Small crystals aligned on a quartz plate were used in the measurement.

(21) A small paramagnetic component which obeys the Curie law has been observed in the magnetic susceptibility measurement. The single-crystal EPR spectra, which were measured at 10 K for the aligned crystal of **1**, gave anisotropic *g* values of 2.178 and 2.029 for parallel and perpendicular components, respectively. The number of spins corresponds to 1 wt % of discrete Ni^{III} complex.

The Sonochemistry of Zn Powder

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High-intensity ultrasound can enhance both homogeneous and heterogeneous reactions.[1-13] It has found an important niche in

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