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Tuning of Electronic Structures of Quasi-One-Dimensional Bromo-Bridged Ni(III) Complexes with Strong Electron-Correlation by Doping of Co(III) Ions, $[Ni_{1-x}Co_x(Chxn)_2Br]Br_2$

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We have succeeded in synthesizing the Ni^{III} complexes doped by Co^{III} ions, $[Ni_{1-x}Co_x(chxn)_2Br]Br_2$ ($x = 0$, 0.043, 0.093, and 0.118) by using an electrochemical oxidation method. The single-crystal reflectance spectrum of $x = 0.118$ shows an intense CT band about 0.5 eV, which is lower than that of $[Ni(chxn)_2Br]Br_2$ (1.3 eV). The single-crystal electrical conductivities at room temperature of these compounds increase with increase of the amounts of doping of Co^{III} ions. In the ESR spectra, peak-to-peak line widths ΔH_{pp} at room temperature change about 600 G in $[Ni(chxn)_2Br]Br_2$ to 200 G in $x = 0.118$. Such a large x dependence of ΔH_{pp} seems to be ascribed to the increasing contribution from the increasing Curie spins which have smaller line width. Therefore, we have tuned the electronic structures of quasi-one-dimensional bromo-bridged Ni^{III} complexes with strong electron correlations by doping of Co^{III} ions.

Recently quasi-one-dimensional halogen-bridged mixed-valence compounds (MX chains) have been attracting much attention because they show very interesting physical properties such as intense and dichroic intervalence charge-transfer bands, overtone progression of resonance Raman spectra, luminescence spectra with large Stokes shifts, large third-order nonlinear optical properties, midgap absorptions attributable to solitons and polarons, one-dimensional model compounds of high T_c copper oxide superconductors, etc.[1] Theoretically these MX chains are considered as Peierls−Hubbard systems, where the electron−phonon interaction (S), the electron transfer (T), and the intra- and intersite Coulomb repulsion energies (U and V, respectively) compete or cooperate with each other.[2] The Pt and Pd compounds have charge density wave states (CDW) or $M^{II}-M^{IV}$ mixed-valence states due to the electron−phonon interaction (S), where the bridging halogens are displaced from the midpoints between the neighboring two metal ions. Therefore, these compounds belong to the class II type of the Robin−Day classification for the mixed-valence complexes.[1a] In these compounds, the CDW strengths are tuned by substituting the metal ions, bridging halogens, in-plane ligands, and counteranions.[3] Moreover, the dimensionalities of the CDW can be controlled by using the intra- and interchain hydrogen-bond networks. On the other hand, the Ni compounds have spin density wave states (SDW) or Ni^{III} Mott−Hubbard states due to the strong electron correlation (U), where the bridging halogens are located at the midpoints between two neighboring Ni atoms. Therefore, these Ni complexes belong to the class III type of the Robin−Day classification for the mixed-

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(1) (a) Robin, M. B.; Day, P. *Adv. Inorg. Radiochem*. **1967**, *10*, 247. (b) Bishop, A. R.; Swanson, B. I. *Los Alamos Sci*. **1993**, *21*, 133. (c) Clark, R. J. H. *Adv. Infrared Raman Spectrosc*. **1983**, *11*, 133. (d) Okamoto, H.; Yamashita, M. *Bull. Chem. Soc. Jpn*. **1998**, *71*, 2023. (e) Yamashita, M.; Manabe, T.; Kawashima, T.; Okamoto, H.; Kitagawa, H. *Coord. Chem. Rev*. **1999**, *190−192*, 309. (f) Iwasa, Y.; Funatsu, E.; Koda, T.; Yamashita, M. *Appl. Phys. Lett*. **1991**, *59*, 2219. (g) Kuroda, N.; Sakai, M.; Nishina, Y.; Tanaka, M.; Kurita, S. *Phys. Rev. Lett*. **1987**, *58*, 3808. (h) Okamoto, H.; Mitani, T.; Toriumi, K.; Yamashita, M. *Phys. Rev. Lett*. **1982**, *69*, 2248. (i) *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1982; Vols. I−III.

(2) (a) Nasu. K. *J. Phys. Soc. Jpn*. **1983**, *52*, 3865. (b) Gammel, J. T.; Saxena, A.; Batstic, I.; Bishop, A. R.; Phillpot, S. R. *Phys. Rev. B* **1992**, *45*, 6408.

(3) Okamoto, H.; Toriumi, K.; Okaniwa, K.; Mitani, T.; Yamashita, M. *Mater. Sci. Eng*. **1992**, *B13*, L9.

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valence complexes.[1a] The very strong antiferromagnetic interactions among the spins located on the Ni^{III} d_{z^2} orbitals through the bridging halogen ions are observed in these compounds.[4] More recently the gigantic third-order nonlinear optical susceptibility ($\sim10^{-4}$ esu) has been observed in $[Ni^{III}(chxn)_2Br]Br_2$ (chxn = 1(*R*),2(*R*)-diaminocyclohexane) due to the strong electron correlation and the lower CT band.[5] New series of MX chains, that is, the Ni−Pd mixed-metal compounds $Ni_{1-x}Pd_x(chxn)_2Br_3$, have been synthesized, where the electron−phonon interaction (S) on the Pd sites and the electron correlation (U) on the Ni sites compete with each other. With increase of the Ni component, the Pd^{II}−Pd^{IV} mixed-valence state is gradually changed into the Pd^{III} state due to the stronger electron correlation on the Ni site ($\sim$5 eV) compared with the electron−phonon interaction on the Pd site ($\sim$1 eV).[6]

Correctly speaking, the Ni^{III} complexes are not Mott insulators but charge-transfer insulators where the energy levels of the bridging halogens are located between the upper-Hubbard band (LUMO-like) and lower-Hubbard band (HOMO-like) composed of the Ni^{III} d_{z^2}. Therefore, the electronic structures of the Ni^{III} complexes are similar to those of high-T_c copper oxide superconductors except for their dimensionalities.[7] Then the doping into the Ni^{III} complex is very interesting. Since the Ni^{III} has d^7 and the Co^{III} has d^6 configurations, the Ni−Co systems mean the hole doping. According to such a strategy, we have synthesized single crystals of the complexes, $[Ni_{1-x}Co_x(chxn)_2Br]Br$ ($x = 0.043$, 0.093, and 0.118), by an electrochemical method of the mixed methanol solution of $Ni(chxn)_2Br_2$ and $[Co(chxn)_2Br_2]Br$. The elemental analyses of Ni and Co ions were carried out by an ICP method.

The X-ray powder patterns of $[Ni(chxn)_2Br]Br_2$ and $[Ni_{1-x}Co_x(chxn)_2Br]Br_2$ are similar to each other. Therefore, the crystal structures of $[Ni_{1-x}Co_x(chxn)_2Br]Br_2$ are similar to that of $[Ni^{III}(chxn)_2Br]Br_2$, where the planar $[M(chxn)_2]$ are bridged by the Br^- ions, forming the linear chain structures. Moreover, each linear chain is hydrogen-bonded by the counteranion Br^-, forming a two-dimensional hydrogen-bond network (Figure 1). Thus the Co^{III} ions are successfully incorporated into the one-dimensional Ni^{III} chain systems.

In order to investigate the electronic structure and obtain the on-site Coulomb repulsion energies (U), the XP spectra and Auger spectra have been measured for $[Ni_{0.882}Co_{0.118}(chxn)_2Br]Br_2$ along with $[Ni(chxn)_2Br]Br_2$ and $[Co(chxn)_2Br_2]Br$. The $2p_{3/2}$ and $2p_{1/2}$ binding energies of the Ni component of $[Ni_{0.882}Co_{0.118}(chxn)_2Br]Br_2$ are almost same as those of $[Ni(chxn)_2Br]Br_2$. By using the energies of the Auger spectra of $[Ni_{0.882}Co_{0.118}(chxn)_2Br]Br_2$ as described elsewhere,[7a] the on-site Coulomb energy is estimated to be $\sim$5 eV, which is almost same as that of $[Ni(chxn)_2Br]Br_2$. The $2p_{3/2}$ and $2p_{1/2}$ binding energies of the Co ion in $[Ni_{0.882}Co_{0.118}(chxn)_2Br]Br_2$ are almost same as those of $[Co(chxn)_2Br_2]Br$. Therefore, the hole doping is successfully carried out in $[Ni_{0.882}Co_{0.118}(chxn)_2Br]Br_2$.

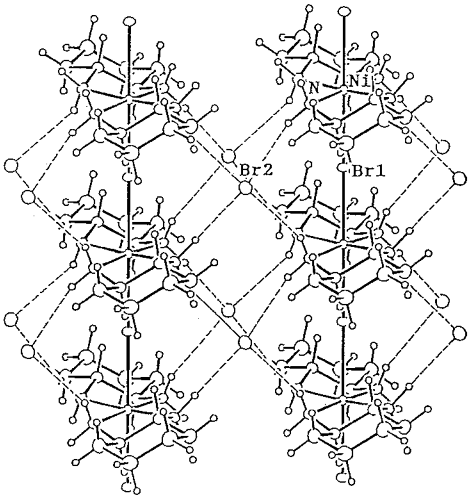

Figure 1. Crystal structure of $[Ni^{III}(chxn)_2Br]Br_2$[3].

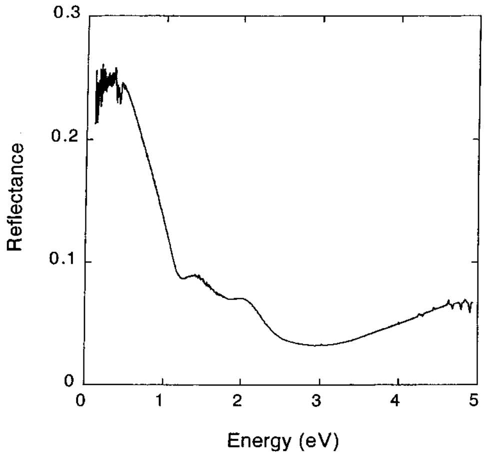

Figure 2. Single-crystal reflectance spectrum of $[Ni_{0.882}Co_{0.118}(chxn)_2Br]Br_2$ along chain axis.

The single-crystal reflectance spectrum of $[Ni_{0.882}Co_{0.118}(chxn)_2Br]Br_2$ shows the intense CT band about 0.5 eV (Figure 2). Since the parent $[Ni^{III}(chxn)_2Br]Br_2$ compound shows the CT band about 1.3 eV, the hole doping seems to be successful. Thus, the new electronic structures have been created in the $[Ni_{1-x}Co_x(chxn)_2Br]Br_2$.

The single-crystal electrical conductivity measurements have been carried out for $[Ni_{1-x}Co_x(chxn)_2Br]Br_2$ ($x = 0.049$, 0.093, and 0.118) along with parent $[Ni^{III}(chxn)_2Br]Br_2$ by a four-probe method (Figure 3). We admit ambiguity in the absolute value of the conductivity by 1 order of magnitude due to the sample shape irregularity. All compounds show

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(4) (a) Toriumi, K.; Wada, Y.; Mitani, T.; Bandow, S.; Yamashita, M.; Fujii. *J. Am. Chem. Soc.* **1989**, *111*, 2341. (b) Okamoto, H.; Toriumi, K.; Mitani, T.; Yamashita, M. *Phys. Rev. B* **1990**, *42*, 10381. (c) Yamashita, M.; Manabe, T.; Inoue, K.; Kawashima, T.; Okamoto, H.; Kitagawa, H.; Mitani, T.; Toriumi, K.; Miyamae, H.; Ikeda, R. *Inorg. Chem.* **1999**, *38*, 1894.

(5) Kishida, H.; Matsuzaki, H.; Okamoto, H.; Manabe, T.; Yamashita, M.; Taguchi, Y.; Tokura, Y. *Nature* **2000**, *405*, 929.

(6) (a) Yamashita, M.; Ishii, T.; Matsuzaka, H.; Manabe, T.; Kawashima, T.; Okamoto, H.; Kitagawa, H.; Mitani, T.; Marumoto, K.; Kuroda, S. *Inorg. Chem.* **1999**, *38*, 5124. (b) Wakabayashi, Y.; Wakabayashi, N.; Yamashita, M.; Manabe, T.; Matsushita, N. *J. Phys. Soc. Jpn.* **1999**, *68*, 3948. (c) Marumoto, K.; Tanaka, H.; Kuroda, S.; Manabe, T.; Yamashita, M. *Phys. Rev. B* **1999**, *60*, 7699.

(7) (a) Okamoto, H.; Shimada, Y.; Oka, Y.; Chainani, A.; Takahashi, T.; Kitagawa, H.; Mitani, T.; Toriumi, K.; Inoue, K.; Manabe, T.; Yamashita, M. *Phys. Rev. B* **1996**, *54*, 8438. (b) Iwano, K. *J. Phys. Soc. Jpn.* **1999**, *68*, 935.

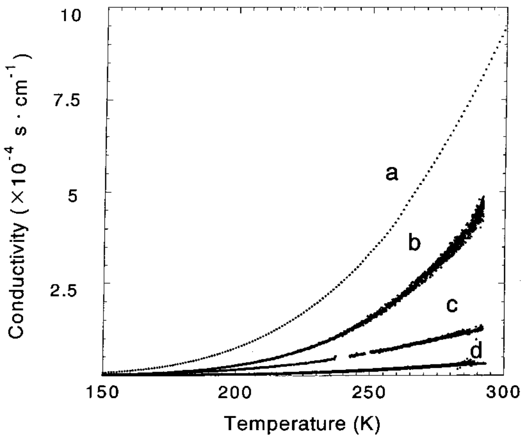

Figure 3. Single-crystal electrical conductivities of $[Ni_{1-x}Co_x(chxn)_2Br]Br_2$: (a) $x = 0.118$, (b) $x = 0.093$, (c) $x = 0.043$, and (d) $x = 0$.

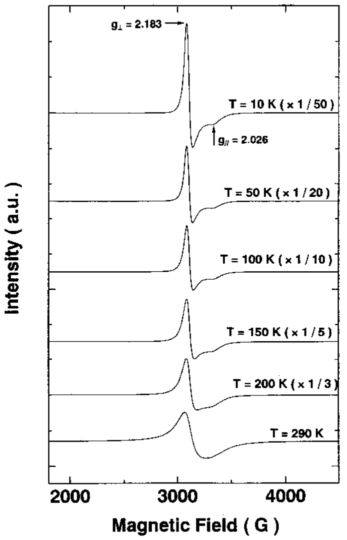

Figure 4. Temperature dependent ESR spectra of $[Ni_{0.882}Co_{0.118}(chxn)_2Br]Br_2$.

the semiconducting behaviors with energy gaps of Eg = 0.11 ∼ 0.16 eV. The energy gaps are much less than the gap found by the reflectance spectrum. However, the electrical conductivities at room temperature of these compounds increase with increase of the amounts of doping of Co^{III} ions. This may indicate the increase of the charge carriers or mobilities by the increase of the amounts of doping of Co^{III} ions.

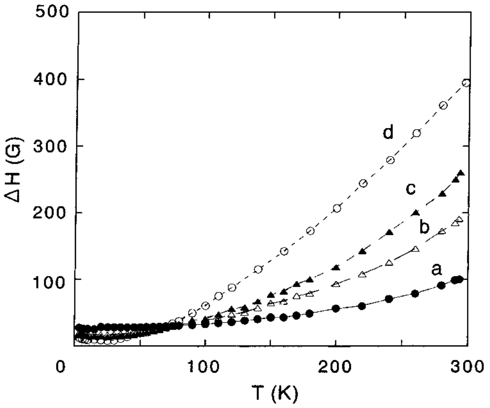

Figure 5. Temperature dependence of peak-to-peak line width ΔH_{pp} of $[Ni_{1-x}Co_x(chxn)_2Br]Br_2$: (a) $x = 0.118$, (b) $x = 0.093$, (c) $x = 0.043$, and (d) $x = 0$.

The ESR spectra have been measured for polycrystalline $[Ni_{1-x}Co_x(chxn)_2Br]Br_2$ ($x = 0$, 0.043, 0.093, and 0.118) down to liquid helium temperature. Figure 4 shows the temperature dependent ESR spectra of $[Ni_{0.882}Co_{0.118}(chxn)_2Br]Br_2$. In the low-temperature region magnetic susceptibility shows Curie-like behavior, while it shows almost temperature independent behavior due to antiferromagnetic spin chains of Ni^{III} in the high-temperature region. The Curie-spin concentration N_c monotonically increases from 0.34% ($[Ni(chxn)_2Br]Br_2$) to 2.07% ($x = 0.118$) as x increases. The Curie-spin component comes from chain ends or finite chain segments which contain odd numbers of spins. Thus monotonic increase of N_c suggests the good substitution of nonmagnetic Co^{III} ions to magnetic Ni^{III} sites in the present materials. The ESR line widths of the polycrystals monotonically increase with temperature in the high-temperature region, which is the same behavior as that of $[Ni(chxn)_2Br]Br_2$ (Figure 5). As x increases, temperature dependence of the line widths become weaker, resulting in the steep drop of their room temperature values. Actually, the peak-to-peak line width ΔH_{pp} at room temperature changes from about 600 G ($[Ni(chxn)_2Br]Br_2$) to 200 G ($x = 0.118$). Such a large x dependence of ΔH_{pp} seems to be ascribed to the increasing contribution from the increasing Curie spins which have smaller line width. Such a systematic change of ESR spectra provides the further evidence of successful doping of Co^{III} into the chain. Such results are in contrast to those of $Ni_{1-x}Pd_x(chxn)_2Br_3$. In $Ni_{1-x}Pd_x(chxn)_2Br_3$, the $Pd^{II}-Pd^{IV}$ mixed-valence states change into the Pd^{III} states with increase of the Ni^{III} components because of the stronger electron correlation (U) of the Ni sites (∼5 eV) compared with the electron−phonon interaction (S) of the Pd sites (∼1 eV). Therefore, the Curie-like spin concentration N_c in $Ni_{1-x}Pd_x(chxn)_2Br_3$ is almost constant, while the N_c in $[Ni_{1-x}Co_x(chxn)_2Br]Br_2$ increases monotonically with increase of the nonmagnetic Co^{III} ions as mentioned above.

In conclusion, we have succeeded in synthesizing of the Ni^{III} complexes doped by Co^{III} ions, $[Ni_{1-x}Co_x(chxn)_2Br]Br_2$, where the new electronic structures are created. The $[Ni(chxn)_2Br]Br_2$ shows a gigantic third-order nonlinear optical susceptibility.[5] This is due to the strong electron correlation (U) and the intense CT band at the low-energy region. As mentioned above, the $[Ni_{0.882}Co_{0.118}(chxn)_2Br]Br_2$ shows the CT band at the lower energy region (0.5 eV) compared with that of the $[Ni(chxn)_2Br]Br_2$ (1.3 eV). Therefore, we can anticipate a larger third-order nonlinear optical susceptibility in the Ni−Co systems.[5] Now, the investigation is in progress.

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