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Tuning of Spin Density Wave Strengths in Quasi-One-Dimensional Mixed-Halogen-Bridged Nickel(III) Complexes with Strong Electron Correlation, $[\mathrm{Ni^{III}(chxn)_2Cl_{1-\mathit{x}}Br_{\mathit{x}}](NO_3)_2}$

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This communication describes the syntheses of the quasi-one-dimensional mixed-halogen-bridged $\mathrm{Ni^{III}}$ complexes with strong electron correlation $[\mathrm{Ni(chxn)_2Cl_{1-\mathit{x}}Br_{\mathit{x}}](NO_3)_2}$ and the tuning of the spin density wave strengths of these compounds. If the Cl 3p and Br 4p make one band in the compounds, we should observe a single peak in the electronic spectra. As a result, we should observe the single peak from 1.45 to 2.00 eV depending on the mixing ratios of Cl and Br ions. Therefore, the Cl 3p and Br 4p make one band. Then, we have succeeded in tuning the spin density wave strengths of the $\mathrm{Ni^{III}}$ complexes with the strong electron correlation by mixing the bridging halogen ions successively.

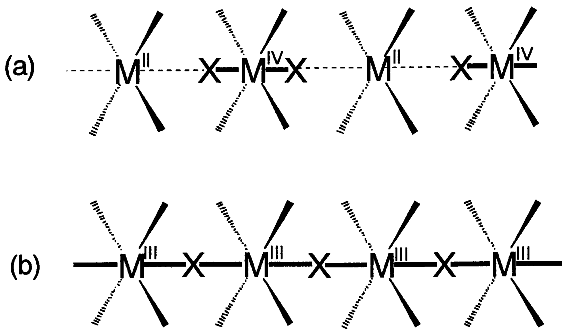

Figure 1. Structures of $\mathrm{M^{II}{-}M^{IV}}$ mixed-valence complexes of Pt and Pd (a), and $\mathrm{M^{III}}$ complexes of Ni (b).

Quasi-one-dimensional halogen-bridged mixed-valence compounds (MX chains) have been extensively investigated during the past 20 years, because of their 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.[1−9] Theoretically these MX chains are considered as Peierls−Hubbard systems, where the electron−phonon interaction (S), the electron transfer (T), the intra- and intersite Coulomb repulsion energies (U and V, respectively) compete or cooperate with each other.[10,11] The Pt and Pd compounds have charge density wave states (CDW) or $\mathrm{M^{II}{-}M^{IV}}$ 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 (Figure 1a).

Accordingly, the half-filled metallic band is split into the occupied valence band and the unoccupied conduction band with finite Peierls gaps. Therefore, these compounds belong to the class II type of the Robin−Day classification for the mixed-valence complexes.[1] In these compounds, the CDW strengths are tuned by substituting the metal ions, bridging halogens, in-plane ligands, and counteranions.[12] 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 $\mathrm{Ni^{III}}$ Mott−Hubbard states due to the

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strong electron correlation (*U*), where the bridging halogens are located at the midpoints between neighboring two Ni atoms (Figure 1b). Therefore, these Ni complexes belong to the class III type of the Robin−Day classification for the mixed-valence complexes.[1] 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.[13,14] More recently the gigantic third-order nonlinear optical susceptibility ($\chi^{(3)} = \sim 10^{-4}$ esu) has been observed in [Ni^{III}(chxn)$_2$Br]Br$_2$ (chxn = 1*R*,2*R*-diaminocyclohexane) due to the strong electron correlation and the lower CT band.[15]

A new series of MX chains, that is, the Ni−Pd mixed-metal compounds Ni$_{1-x}$Pd$_x$(chxn)$_2$Br$_3$, 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 an 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 (∼5 eV) compared with the electron−phonon interaction on the Pd site (∼1 eV).[16−18]

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 and lower Hubbard band composed of the Ni^{III} d$_{z^2}$. Therefore, the electronic structures of the Ni^{III} complexes are similar to those of the starting materials of high-T_c copper oxide superconductors except for their dimensionalities.[19] The lowest charge-transfer band is attributable to the transition from the bridging halogens to the upper Hubbard bands of Ni^{III} 3d$_{z^2}$. Such CT bands are observed at 1.45 and 2.00 eV for [Ni(chxn)$_2$X](NO$_3$)$_2$ (X = Cl and Br), respectively.[14] In order to investigate their electronic structures, we have synthesized the mixed-halogen-bridged complexes, [Ni^{III}(chxn)$_2$Cl$_{1-x}$Br$_x$](NO$_3$)$_2$, and measured the single-crystal reflectance spectra, XPS, Auger spectra, and X-ray powder patterns.[20]

Table 1. Crystal Parameters (Å) of [Ni(chxn)$_2$Cl$_{1-x}$Br$_x$](NO$_3$)$_2$

x	*a*	*b*	*c*
1.0	22.91	5.21	7.86
0.90	22.85	5.20	7.86
0.79	22.94	5.13	7.91
0.69	22.98	5.13	7.90
0.55	23.03	5.09	7.99
0.32	23.00	5.07	7.94
0.18	22.97	5.04	7.94
0.10	22.94	5.00	7.95
0.02	23.09	4.98	7.96
0	22.99	4.98	8.00

Table 2. XPS and Auger Spectral Data of [Ni(chxn)$_2$Cl$_{1-x}$Br$_x$](NO$_3$)$_2$ (eV)

x	Ni(2p)	Ni(3d)	Ni KLL	*U*
1.0	852.40	2.03	641.64	3.38
0.79	852.99	1.98	641.73	4.16
0.32	852.67	1.56	641.40	4.35
0.10	853.25	2.04	640.88	3.45
0	852.80	1.17	640.64	4.50

The X-ray powder patterns of [Ni^{III}(chxn)$_2$Cl$_{1-x}$Br$_x$](NO$_3$)$_2$ are similar to one another and to those of [Ni(chxn)$_2$X](NO$_3$)$_2$ (X = Cl and Br), where their structures were determined previously by single-crystal X-ray diffraction methods, that is, a space group of *I*222.[14] Therefore the structures are assumed to have the halogen-bridged linear chain structures, where the planar [Ni(chxn)$_2$] are stacked with the axial bridging halogen ions. The NO$_3^-$ counterions exist along the chains, forming the two-dimensional hydrogen-bond networks as observed in [Ni(chxn)$_2$X](NO$_3$)$_2$ (X = Cl and Br).[14] The results of the X-ray powder patterns are listed in Table 1. The *b*-axes and *c*-axes correspond to the Ni−Ni distances along the chain and the interchain distances in the direction of the hydrogen bonds, respectively. As shown in Table 1, the *b*-axes increase with increasing Br contents, due to the larger ionic radius of Br compared with that of Cl. Therefore, the mixing of the bridging halogen ions was considered to be carried out successfully. On the other hand, the *c*-axis decreases with increasing Br content. Such a negative correlation between *a*- and *b*-axes has been observed in [Ni(chxn)$_2$X]Y$_2$ (X = Cl and Br; Y = Cl, Br, NO$_3$, and ClO$_4$).[14]

In order to evaluate the on-site Coulomb repulsion energies of Ni components, we have measured the XPS and Auger spectra of these compounds. The results are listed in Table 2.

The broad Ni 3d signals are observed at ca. 1−2 eV. The Ni 2p$_{3/2}$ signals are observed at ca. 852−853.5 eV. The Ni KLL signals are observed at ca. 640.5−641.7 eV. By using the previous methods, we have obtained the on-site Coulomb repulsion energies (*U*).[19] The values range from 3.5 to 5 eV. These values are almost equal to those of [Ni(chxn)$_2$X]X$_2$ (X = Cl and Br). Therefore, these Ni complexes have strong electron correlation energy (*U*).

By Kramers−Kronig transformations of the single-crystal reflectance spectra, we have obtained the absorption spectra (Figure 3).

No intense absorptions are observed in the light perpendicular to the chain axis. On the other hand, in the light

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(20) The experimental procedures are as follows. The chemical reagents were purchased from Wako Pure Chemical Industry Co. Ltd., and all procedures were performed in N$_2$ atmosphere. Ni^{II}(chxn)$_2$X$_2$ (X = Cl and Br) were synthesized by the methods described previously (ref 14). The title compounds [Ni^{III}(chxn)$_2$Cl$_{1-x}$Br$_x$](NO$_3$)$_2$ were obtained by the electrochemical oxidation methods of various mixing ratios of Ni(chxn)$_2$Cl$_2$ and Ni(chxn)$_2$Br$_2$ in methanol solutions (ca. 1 mmol) including ca. 1 g of NH$_4$NO$_3$ as an electrolyte at room temperature with electric current of 20 μA using an H-shaped cell.

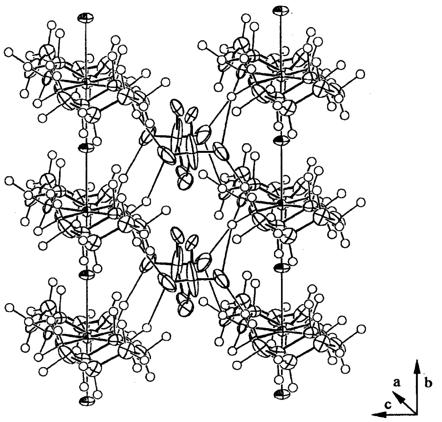

Figure 2. Crystal structure of $[Ni^{III}(chxn)_2Cl](NO_3)_2$.[14]

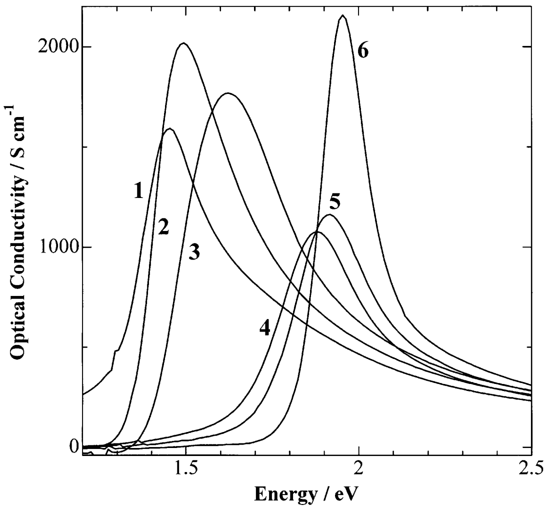

Figure 3. Optical conductive spectra of $[Ni^{III}(chxn)_2Cl_{1-x}Br_x](NO_3)_2$: (1) $x = 1$, (2) $x = 0.82$, (3) $x = 0.68$, (4) $x = 0.46$, (5) $x = 0.21$, and (6) $x = 0$.

parallel to the chain axes, the intense charge-transfer bands are observed from 1.45 to 2.00 eV. Since the on-site Coulomb repulsion energies (U) range from 3.5 to 5 eV and the lowest CT bands range from 1.45 to 2.00 eV, the $[Ni(chxn)_2Cl_{1-x}Br_x](NO_3)_2$ are considered as the CT insulators, where the bridging halogens are located between the upper and lower Hubbard bands of the Ni^{III} d_{z^2}. However, there are two possibilities in their electronic structures as shown in Figure 4.

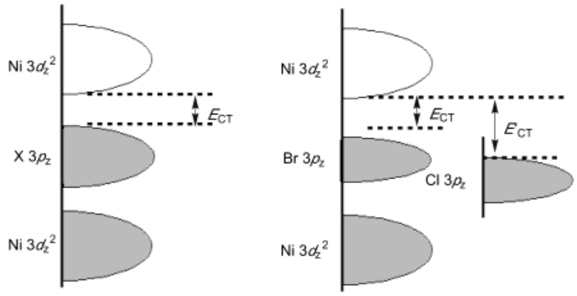

Figure 4. One-band system composed of Cl 3p and Br 4p (a) and two-band system composed of Cl 3p and Br 4p (b).

If the Cl 3p and Br 4p have the different energy states independently in the compounds, we should observe two peaks from Cl 3p and Br 4p to the upper Hubbard band, respectively. If the Cl 3p and Br 4p make one band in the compounds, we should observe one peak. As shown in Figure 3, the single absorption is observed from 1.45 to 2.00 eV depending on the mixing ratios of Cl and Br ions. Therefore, the Cl 3p and Br 4p make one band. Accordingly, the CT bands are attributable to the transitions from the single bridging halogen bands composed of Cl 3p and Br 4p to the upper Hubbard bands of Ni^{III} $3d_{z^2}$. Accordingly, we can tune the spin density wave strengths of Ni^{III} complexes with strong electron correlations by mixing the bridging halogen ions successively.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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