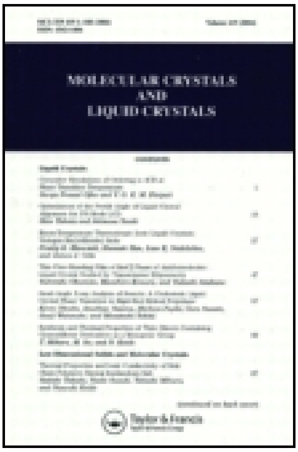

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CONTROL OF CHARGE INSTABILITIES IN QUASI-ONE-DIMENSIONAL HALOGEN-BRIDGED NICKEL COMPOUNDS

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Abstract Quasi-one-dimensional halogen-bridged nickel compounds with nitrate counteranions, $Ni(chxn)_2X(NO_3)_2$ (chxn=cyclohexanediamine ; X=Cl and Br), and with perchlorate counteranions, $Ni(chxn)_2X(ClO_4)_2$ (X=Cl and Br) have been synthesized in order to control the charge instabilities. The $Ni(chxn)_2X(NO_3)_2$ were synthesized by both chemical and electrochemical methods. The crystal structure of $Ni(chxn)_2Br(NO_3)_2$ has been determined by single-crystal X-ray diffraction method. In this compound, the $Ni(chxn)_2$ moieties are bridged by Br^- ions to construct linear-chain structures and the hydrogen-bond networks of NH...O-N-O...HN which hold the chains are extended over the chains two-dimensionally. The bridging Br^- ions are located at the midpoints between neighboring two Ni atoms along the chains with no Peierls distortion. The $Ni(chxn)_2X(ClO_4)_2$ were synthesized by halogenation of 70 % $HClO_4$ solution of $Ni(chxn)_2(ClO_4)_2$. The lattice constants of $Ni(chxn)_2Cl(ClO_4)_2$ were determined by X-ray powder pattern. The Ni-Cl-Ni distance of this compound is almost equal to that of $Ni(chxn)_2Cl_3$, but the inter-chain distance in the direction of counteranions is much longer than that in $Ni(chxn)_2Cl_3$. The electronic structure of $Ni(chxn)_2Cl(ClO_4)_2$ was discussed on the basis of the results of electrical conductivity and temperature-dependence CP/MAS ^{13}C NMR spectra.

INTRODUCTION

Recently quasi-one-dimensional compounds have been attracting much attention since they show very interesting physical properties such as Peierls instabilities, spin-Peierls, charge density wave (CDW) state, spin density wave (SDW) state, superconductivity, etc..[1] Among these compounds, quasi-one-dimensional halogen-bridged mixed-valence compounds (MX chains) have been extensively investigated during this decade, because of their interesting properties such as an intense intervalence charge transfer band, an overtone progression in resonance Raman, a luminescence with a large Stokes-shift, midgap absorptions attributable to a soliton or a polaron, large third-order nonlinear optical susceptibilities, one-dimensional model compounds of high Tc copperoxide superconductors, etc..[2] Theoretically, these compounds can be considered to be a Peierls-Hubbard system where the electron-phonon interaction (S), the electron transfer energy (T), the on-site and inter-site Coulomb interactions (U and V) are cooperated or competitive with one another.[3] Originally, these compounds are considered one-dimensional metal. However, it is well known that the stability of the one-dimensional metallic state is dependent on the degree of the electron-phonon interaction (S) and the on-site Coulomb interaction (U). In most compounds, due to the electron-phonon interaction, the bridging halogens are displaced from the midpoint between neighboring metal atoms, giving a charge density wave state or M^{II}-M^{IV} mixed-valence state. Accordingly, the half-filled metallic band splits into the occupied valence band and the unoccupie conduction band with a finite Peierls gap. These compounds are formulated as $[M(AA)_2][M(AA)_2X_2]Y_4$ (M^{II}-M^{IV} = Pt^{II}-Pt^{IV}, Pd^{II}-Pd^{IV}, Ni^{II}-Ni^{IV}, Pd^{II}-Pt^{IV}, Ni^{II}-Pt^{IV} and Cu^{II}-Pt^{IV}; X=Cl, Br and I; AA=ethylenediamine (en), cyclohexanediamine (chxn), etc.; Y=ClO_4, X, etc.). In the case of the stronger on-site Coulomb interaction (U) compared with the electron-phonon interaction (S), the spin density wave state (SDW) or Mott-Hubbard state is more stable, where the bridging halogens are located at the midpoints between two neighboring metal ions. More recently, only a few compounds in such a state, $Ni(chxn)_2X_3$ (X=Cl, Br and mixed-halide) have been reported.[4] These compounds show very strong antiferromagnetic interaction between spins located on each Ni^{III} site.

These MX chains are characteristic in the sense that the band gaps can be tuned by varying chemical factors such as M, X, AA, and Y, and moreover the interchain interaction can be controlled by using the intra- and inter-chain hydrogen bonds between aminohydrogens and counteranions.[5] From the viewpoints of the spin- and charge-fluctuations, the interesting physical properties are expected for the compounds at the interface or with the transition between a M^{III} Mott-Hubbard state and a Ni^{II}-Ni^{IV} mixed-valence state where the S and U are severely competed. Only nickel compounds take both CDW and SDW states, depending on the degree of U and S. In this study, in order to control the charge instabilities or the strengths of U and S, we have synthesized the nickel cyclohexanediamine compounds with nitrate counteranions, and with perchlorate counteranions. Introducing NO_3^- or ClO_4^- instead of halogen ions as counteranions is considered to make influences to this system on the Ni-Ni distances and the hydrogen-bond networks between aminohydrogens and counteranions.

EXPERIMENTAL

The $Ni(chxn)_2X(NO_3)_2$ (X=Cl and Br) were synthesized by adding 61% HNO_3 to the 2-methoxyethanol solutions of $Ni(chxn)_2X_2$. These compounds were also obtained electrochemically by using NH_4NO_3 as an electrolyte. The $Ni(chxn)_2X(ClO_4)_2$ (X=Cl and Br) were synthesized by halogenation of 70% $HClO_4$ solutions of $Ni(chxn)_2(ClO_4)_2$.

Single-crystal X-ray structure analysis was carried out for $Ni(chxn)_2Br(NO_3)_2$ at room temperature. Intensity data were collected on Rigaku AFC-5 four-circle diffractometer using graphite-monochromated Mo-K α radiation. Crystal data are: $C_{12}H_{28}N_6O_6NiBr$, orthorhombic, I222, Z=2, a=22.906(3), b=5.213(1), c=7.855(1) Å, and V=937.9(2) Å^3. The structure was solved by heavy atom method and refined by full-matrix least-squares technique. Final R value is 0.0614.

X-ray powder patterns were measured on MAC Science MPX3 using Cu Kα radiation at room temperature.

The electrical conductivities were measured on single-crystals and pellets by quasi four probe methods using carbon paste.

The ^{13}C CP/MAS NMR spectra were measured by applying proton decoupling using a Bruker MSL-300 spectrometer. The chemical shifts given in ppm are relative to external TMS.

RESULTS AND DISCUSSION

$Ni(chxn)_2X(NO_3)_2$

The $Ni(chxn)_2X(NO_3)_2$ (X=Cl and Br) were prepared by adding 61% HNO_3 to 2-methoxyethanol solutions of $Ni(chxn)_2X_2$, where HNO_3 not only worked as an oxidising reagent but also provided counteranions. These compounds were also obtained by electrochemical oxidation of 2-methoxyethanol solutions of $Ni(chxn)_2X_2$ using NH_4NO_3 as

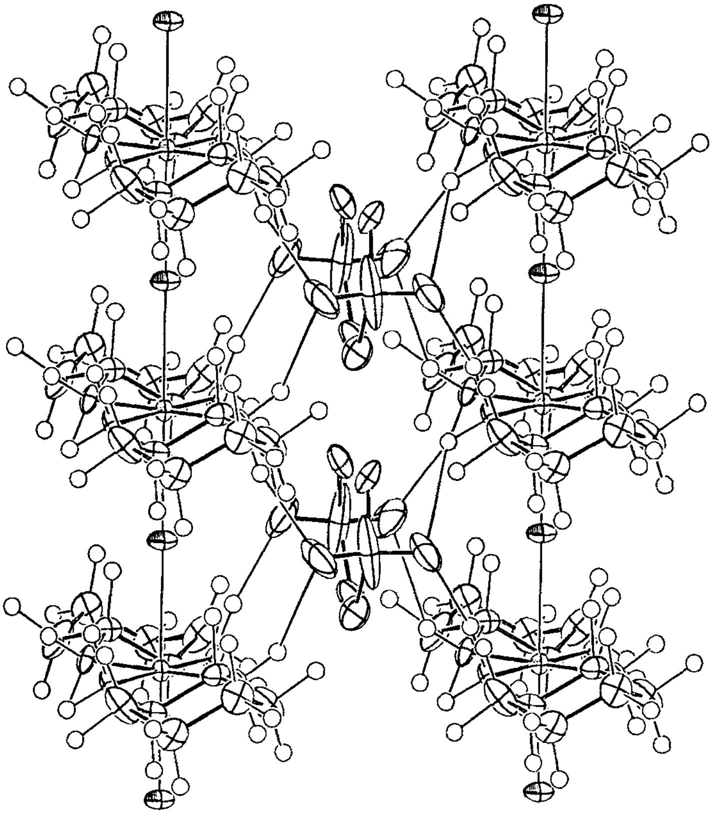

FIGURE 1 ORTEP drawing of $Ni(chxn)_2Br(NO_3)_2$. Ni-Br=2.607(1), Ni-N=1.937(4) Å: $Ni(chxn)_2Br_3$, Ni-Br=2.578(1), Ni-N=1.944(3) Å.

electrolytes. Single-crystals suitable for X-ray analyses and physical measurements were obtaind by the electrochemical method. Therefore, the electrochemical method was proved to be useful to obtain the MX chain compounds.

The crystal structure of $Ni(chxn)_2Br(NO_3)_2$ is isomorphous with $Ni(chxn)_2Cl_xBr_{3-x}$.[4] The structure is shown in Fig. 1. The $Ni(chxn)_2$ moieties, lying a special position of 222, are bridged by Br^- ions and stacked along b-axis, constructing a linear-chain structure. The neighboring $Ni(chxn)_2$ moieties along the chains are linked by four NH...O-N-O...HN hydrogen bonds. Moreover, the hydrogen-bond networks are extended over the chains, constructing a two-dimensional hydrogen-bond structure. One of oxygen atoms of NO_3^-, which is not incorporated hydrogen-bond, is disordered at two positions of upper and lower sites. The bridging Br^- ions are located at the midpoint between neighboring two Ni atoms, that is, Ni^{III}-Br-Ni^{III} structure with no Peierls distortion. The Ni-Br-Ni or Ni-Br distance in this compound is a little longer than that of $Ni(chxn)_2Br_3$.[4] This is due to the larger ionic radius of NO_3^- compared with that of Br^-. The electrical conductivity of $Ni(chxn)_2Br(NO_3)_2$ show a semiconducting behavior. The electrical conductivity at room temperature is smaller than that of $Ni(chxn)_2Br_3$ and the activation energy is larger than that of $Ni(chxn)_2Br_3$. These results may be due to the longer Ni-Br-Ni distance in $Ni(chxn)_2Br(NO_3)_2$ compared with that of $Ni(chxn)_2Br_3$. The investigations on their physical properties are now in progress.

$Ni(chxn)_2Cl(ClO_4)_2$

The lattice constants were determined by X-ray powder pattern. The pattern of $Ni(chxn)_2Cl(ClO_4)_2$ is very similar to that of $Ni(chxn)_2Cl_3$, whose structure was already determined by single crystal X-ray analysis. Therefore, assuming the same orthorhombic system as that of $Ni(chxn)_2Cl_3$, the lattice constants of $Ni(chxn)_2Cl(ClO_4)_2$ were determined as listed in Table I, where the b and c axes correspond to the Ni-Ni distance and the interchain distance in the direction of counterions, respectively. In spite of substitution of Cl counterions for ClO_4^- with the larger ionic radius, the Ni-Ni distances are almost constant in both $Ni(chxn)_2Cl_3$ and $Ni(chxn)_2Cl(ClO_4)_2$. On the other hand, the interchain distance c in $Ni(chxn)_2Cl(ClO_4)_2$ becomes much longer compared with that of $Ni(chxn)_2Cl_3$. These results show that the Ni-Cl-Ni bond is considered to be relatively tight and then the

TABLE I Lattice constants obtained by X-ray powder pattern (Å).

	a	b	c
$Ni(chxn)_2Cl_3$	24.10	4.91	6.94
$Ni(chxn)_2Cl(ClO_4)_2$	23.78	4.98	8.42

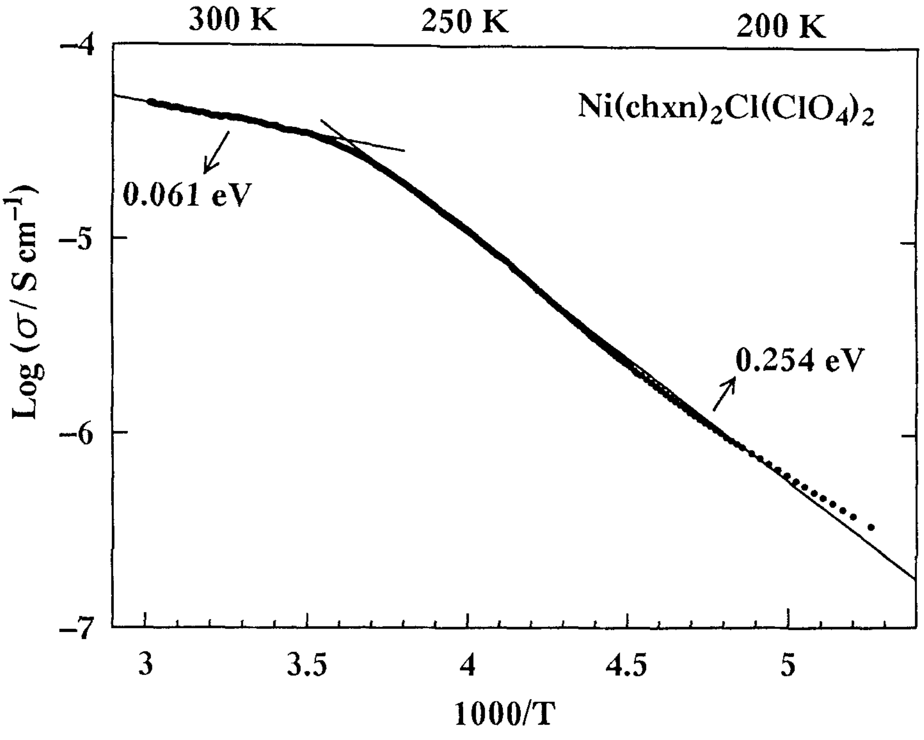

FIGURE 2. Electrical conductivity of $Ni(chxn)_2Cl(ClO_4)_2$.

ClO_4 counteranion can not approach the chains. Accordingly, the interchain distance in the direction of counterions in the ClO_4 compound is much longer than that in the Cl compound.

The electrical conductivity of the polycrystalline by a quasi four probe method using carbon paste shows a semiconducting behavior and corresponding change in activation energies from 0.254 to 0.061 eV arround room temperature, as shown in Fig. 2. In order to evaluate the oxidation states, the solid state ^{13}C NMR spectra were measured at three temperatures, because the splitting patterns of α-carbons in chxn ligands correspond to the oxidation states as shown previously.[4] In the spectrum at 320 K, no splitting in the α-carbon was observed. On the other hand, in the spectrum at 220 K, the α-carbon line is split into doublet with equal intensity components (Fig. 3). From these results, the $Ni(chxn)_2Cl(ClO_4)_2$ might take a Ni^{II}-Ni^{IV} mixed-valence state at 220 K and Ni^{III} Mott-Hubbard state in 320 K. More detail investigations are now in progress.

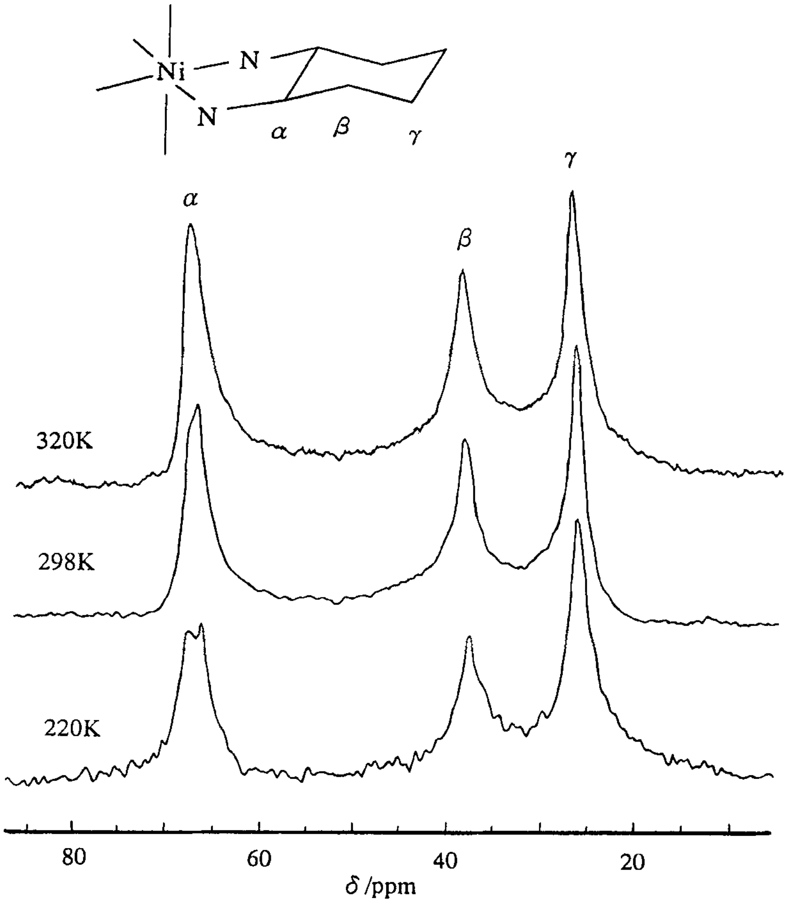

FIGURE 3. CP/MAS ^{13}C NMR spectra of $Ni(chxn)_2Cl(ClO_4)_2$

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