CHEMISTRY LETTERS, pp. 1133-1136, 1985.

THE CHLORO-BRIDGED ONE-DIMENSIONAL NICKEL(II)-NICKEL(IV) MIXED-VALENCE COMPLEX OBTAINED FROM DISPROPORTIONATION REACTION OF THE NICKEL(III) COMPLEX IN $(CH_3OCH_3)(HBF_4)$

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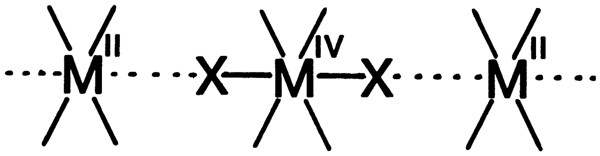
The chloro-bridged one-dimensional Ni^{II}-Ni^{IV} mixed-valence complex with 3,7-diazanonane-1,9-diamine (L), $[Ni^{II}L][Ni^{IV}Cl_2L](BF_4)_4$, was prepared by the disproportionation reaction of the Ni^{III} complex, $[Ni^{III}Cl_2L]Cl$, using $(CH_3OCH_3)(HBF_4)$ as a solvent and reactant. The authenticity was evidenced by the X-ray photoelectron spectra, electronic spectrum, and electrical conductivity.

Halogen-bridged M^{II}-M^{IV} mixed-valence complexes of Pt, Pd and Ni with amines as in-plane ligand(s) are known to adopt a linear chain structure shown below, where the square planar four-coordinate M^{II} and six-coordinate M^{IV} are stacked alternately.$^{1)}$ They show a variety of interesting phenomena such as the Peierls distortion, charge density wave (CDW), and electron-phonon coupling.$^{2)}$ So far, many Pt and Pd mixed-valence complexes have been prepared and characterized by various physical measurements such as X-ray analyses,$^{3)}$ X-ray photoelectron spectra,$^{4)}$ electrical conductivities,$^{5)}$ electronic spectra,$^{6)}$ Raman spectra,$^{7)}$ and XANES.$^{8)}$ However, only a few one-dimensional Ni complexes are known because in the case of Ni system a Ni^{IV} state is very unstable in general.$^{9)}$ In order to acquire an understanding of the effect of metal ions upon the physical and chemical properties of the entire family of compounds, the Ni homologs need to be studied. In this paper, we describe the preparation and characterization of a new Ni^{II}-Ni^{IV} mixed-valence complex.



A starting Ni^{III} complex, $[Ni^{III}Cl_2L]Cl$, was obtained by bubbling dry Cl_2 through the absolute methanol solution of $[Ni^{II}Cl_2L]$.$^{10)}$ When well dried $[Ni^{III}Cl_2L]Cl$ was treated in $(CH_3OCH_3)(HBF_4)$ under N_2 atmosphere, its yellow-brown color turned immediately purple and then almost black precipitates were obtained.

The elemental analysis of the product was consistent with $NiLCl(BF_4)_2$, which is apparently tervalent, but diamagnetic and ESR silent.[11)]

Figure 1 shows an X-ray photoelectron spectrum of $Ni2p_{3/2}$ of $NiLCl(BF_4)_2$ along with those of $[Ni^{II}Cl_2L]$ and $[Ni^{III}Cl_2L]Cl$.[12)] The $[NiCl_2L]Cl$ and $NiLCl(BF_4)_2$ were very susceptible to X-ray irradiation damage and the spectra changed gradually with time during the measurements as reported previously for analogous Ni^{III} and Ni^{II}-Ni^{IV} complexes.[4)] Therefore, the spectral measurements were carried out as quick as possible at a lower voltage. In the spectrum of $NiLCl(BF_4)_2$, its half-width is wider than that of the discrete Ni^{II} or Ni^{III} complex, and the spectrum could be resolved into two components with equal intensity by the computer simulation. The binding energy of the lower component was almost the same as that of the discrete Ni^{II} complex, however, that of the higher one is 1.1 eV higher than that of the Ni^{III} complex (Table 1). The observed fact, supplemented with the diamagnetism and elemental analysis, provides evidence that the compound is not a tervalent Ni complex but a Ni^{II}-Ni^{IV} mixed-valence complex formulated as $[Ni^{II}L][Ni^{IV}Cl_2L](BF_4)_4$.

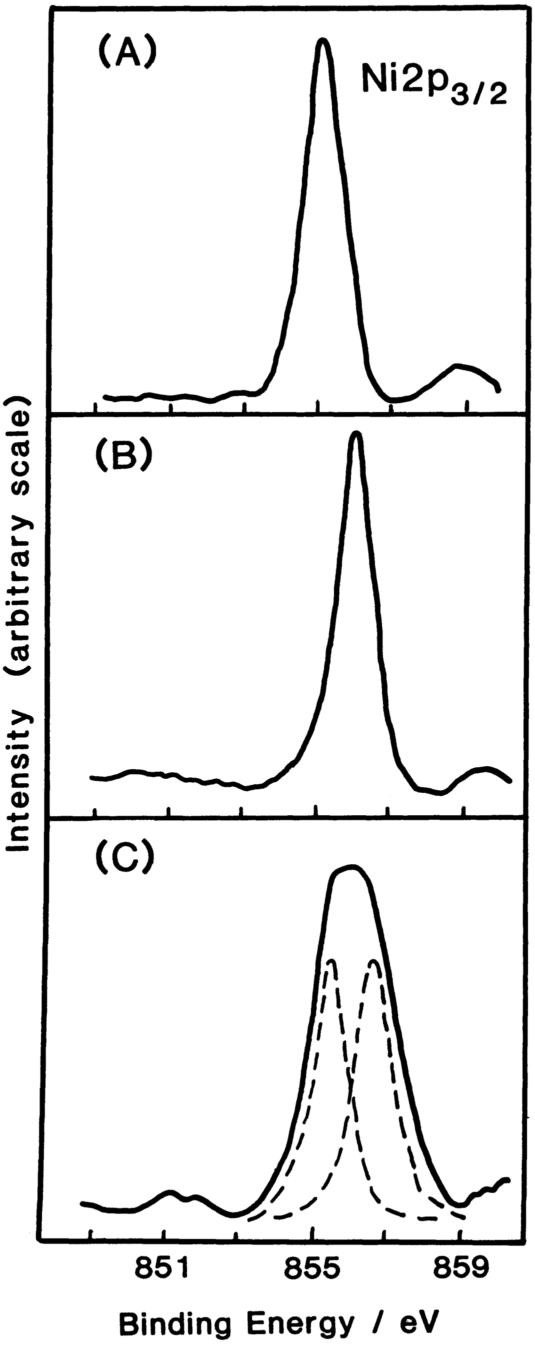


Fig. 1. The X-ray photoelectron spectra. (A) $[Ni^{II}Cl_2L]$; (B) $[Ni^{III}Cl_2L]Cl$; (C) $NiLCl(BF_4)_2$.

Table 1. Binding energy of $Ni2p_{3/2}$ /eV

	Ni^{II}	Ni^{III}	Ni^{IV}
$[Ni^{II}Cl_2L]$	855.2	——	——
$[Ni^{III}Cl_2L]Cl$	——	856.0	——
$NiLCl(BF_4)_2$	855.2	——	857.1

Figure 2 shows the temperature dependence of the electrical conductivity (σ).[13)] The observed relationship is well expressed by a typical equation $\sigma(T) = \sigma_0(-\Delta E/kT)$ for semiconductor where ΔE denotes the thermal activation energy. The conductive data ($\sigma_{300} = 3 \times 10^{-7}\ \Omega^{-1}cm^{-1}$, $\Delta E = 0.45$ eV) are comparable to those of the one-dimensional

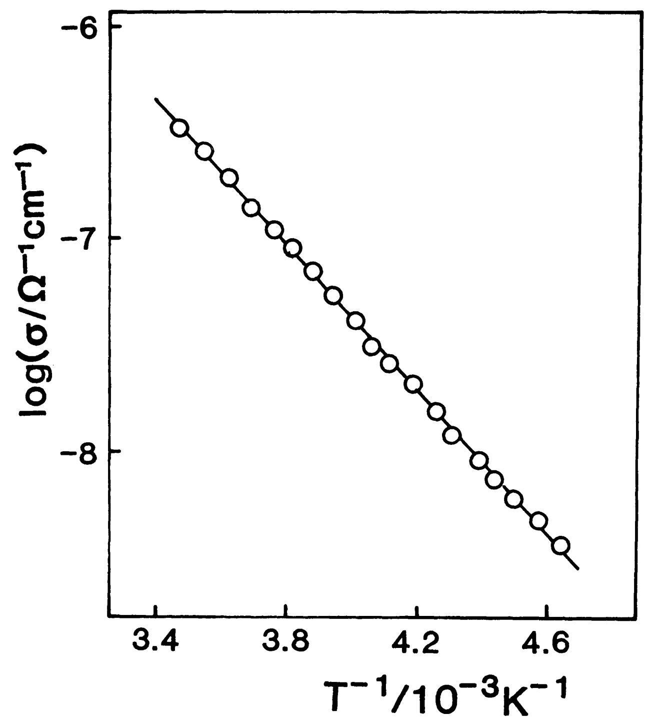


Fig. 2. The temperature dependence of electrical conductivity of $NiLCl(BF_4)_2$.

bromo-bridged Pd^{II}-Pd^{IV} and iodo-bridged Pt^{II}-Pt^{IV} mixed-valence complexes reported previously.[5] The electrical resistance and activation energy with the same chloro-bridges decrease in the order; Pt^{II}-Pt^{IV} > Pd^{II}-Pd^{IV} > Ni^{II}-Ni^{IV}.

The Nujoll mull electronic spectrum of the compound shows a very strong absorption around 15000 cm^{-1}, which would be assigned to an intervalence charge transfer transition from Ni^{II} to Ni^{IV} along the chain. The position of the band maximum is close to that expected from a general trend which has been obtained from data for this class of compounds with various metal ions and various bridging halogens.[14] All the data suggest that the present complex is a new member of the Ni homolog in the family of the halogen-bridged M^{II}-M^{IV} mixed-valence complexes.

Further investigations on the mechanism of the disproportionation reaction, and the structure and electronic state by EXAFS and XANES are now in progress.

This work was supported by the Joint Studies Program (1984) of the Institute for Molecular Science.

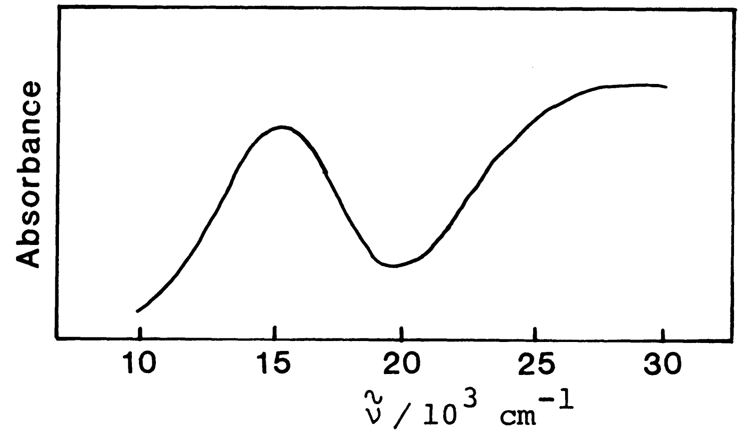


Fig. 3. The Nujoll mull electronic spectrum of $NiLCl(BF_4)_2$.

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10) Found: C, 25.55; H, 6.01; N, 17.03%. Calcd for $NiCl_3C_7H_{20}N_4$: C, 25.85; H, 6.20; N, 17.22%. The magnetic moment of this compound is 1.90 BM at room temperature and the ESR spectrum in a DMSO solution at liquid nitrogen temperature shows a very clear axial symmetry with the parallel feature split into seven almost equally spaced lines (28.6×10^{-4} T) having relative intensity ca. 1:2:3:4:3:2:1. This is due to two axial chloro atoms and the complex is trans-dichloro hexacoordinate $[Ni^{III}Cl_2L]Cl$ with one unpaired electron in d_{z^2} orbital.

11) Found: C, 20.01; H, 4.98; N, 13.31%. Calcd for $NiClB_2F_8C_7H_{20}N_4$: C, 19.64; H, 4.71; N, 13.09%. In the same way, $[Ni(en)_2][NiCl_2(en)_2](BF_4)_4$ and $[NiL_1][NiCl_2L_1](BF_4)_4$ (L_1 = 4,7-diazadeca-1,10-diamine) were obtained.

12) The X-ray photoelectron spectra were obtained with a Mg-Kα exciting irradiation on a SHIMADZU ESCA 750. The spectrometer was calibrated by using C-1s (285.0 eV).

13) The electrical conductivity was measured on a pellet by the two-probe dc method.

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(Received May 10, 1985)