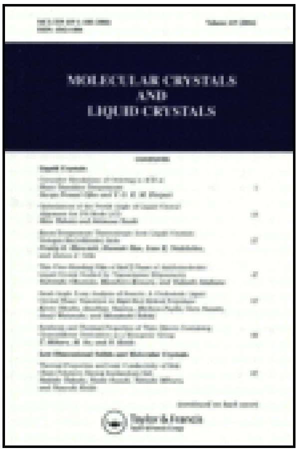

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Physical Properties of Quasi-One-Dimensional Mixed-Metal and Mixed-Halogen Complexese, Ni 1 - x Pd x (chxn) 2 Cl y Br 1 - y Y 2

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Version of record first published: 18 Oct 2010

To cite this article: Toshio Manabe, Kouhei Yokoyama, Tomohiko Ishii, Hitoshi Miyasaka, Hiroyuki Matsuzaka, Masahiro Yamashita, Takuya Kawashima, Hiroyuki Matsuzaki, Hideo Kishida, Hiroshi Okamoto, Kazuhiro Marumoto, Hisaaki Tanaka, Hiroshi Itoh & Sin-Ichi Kuroda (2002): Physical Properties of Quasi-One-Dimensional Mixed-Metal and Mixed-Halogen Complexese, Ni 1 - x Pd x (chxn) 2 Cl y Br 1 - y Y 2, Molecular Crystals and Liquid Crystals, 376:1, 165-170

To link to this article: http://dx.doi.org/10.1080/713738467

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 165-170

1058-725X/02 $12.00 + .00

Physical Properties of Quasi-One-Dimensional Mixed-Metal and Mixed-Halogen Complexese, $Ni_{1-x}Pd_x (chxn)_2Cl_yBr_{1-y}Y_2$

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A series of single crystals of quasi-one-dimensional Ni-Pd mixed-metal MX-chain compounds, $Ni_{1-x}Pd_x(chxn)_2Br_3$, and mixed-halogen MX-chain compounds, $Ni(chxn)_2Cl_yBr_{1-y}(NO_3)_2$ have been obtained by electrochemical oxidation methods. In order to investigate the electronic states of these compounds, the optical conductivity spectra have been measured. These results indicate that the electronic states of the Ni compounds can be controlled by forming the mixed-metal or mixed-halogen systems.

Keywords: Halogen bridged complexes, Electron correlation, Reflection spectroscopy

INTRODUCTION

There have been various investigations of quasi-one-dimensional halogen-bridged metal complexes. Among these compounds, Ni^{III} compounds are of particular current interest. They take Mott-Hubbard states due to the stronger electron-correlation (U) compared with electron-phonon interaction (S) [1, 2]. Therefore, the electronic structure of the Ni^{III} compounds is analogous to that of the copper oxide superconductors. Recentry, it is found that Ni^{III} complexes show gigantic third-order nonlinear susceptibilities, χ^3 [3].

Accordingly, the Ni-Pd mixed-metal systems are very interesting because in the systems the electron-correlation of Ni^{III} and the electron-phonon interaction of Pd^{II}-Pd^{IV} can compete with each other, depending on their mixing ratios. In the previous works, we have obtained a series of mixed-metal complexes, $Ni_{1-x}Pd_x(chxn)_2Br_3$ (chxn = 1R,2R-diaminocyclohexane) and physical properties have been investigated by IR, Raman spectra and ESR (Figure 1). These results suggested that Pd in mixed-metal is influenced with Ni^{III} and gradually approaching to the Pd^{III} state with the increase of the Ni^{III} components [4, 5].

On the other hand, to substitute the bridging halogens is as well useful in order to control the electronic structures of MX-chain compounds. The transfer energy (T) between metal ions increases with increasing halogen ion radius in the order Cl, Br and I [6]. Therefore, in the Cl-Br mixed-halogen systems, the charge-transfer (CT) transition energy could be controlled continuously.

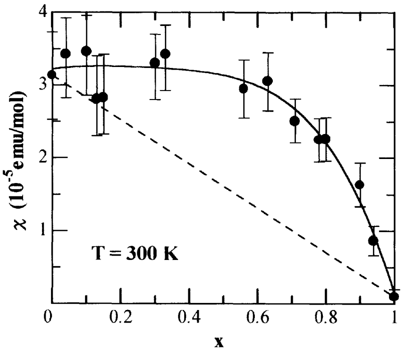

Figure 1. Spin susceptibilities of $Ni_{1-x}Pd_x(chxn)_2Br_3$

In this study, we have investigated the electronic structures of Ni-Pd mixed-metal compounds, $Ni_{1-x}Pd_x(chxn)_2Br_3$ and Cl-Br mixed-halogen compounds, $Ni(chxn)_2Cl_yBr_{1-y}(NO_3)_2$.

EXPERIMENTAL

A series of single crystals of the Ni-Pd mixed-metal compounds, $Ni_{1-x}Pd_x(chxn)_2Br_3$ were obtained by electrochemical oxidation method with the mixed methanol solutions of $Ni(chxn)_2Br_2$ and $[Pd(chxn)_2]Br_2$ with various mixing ratios using tetra-n-butylammonium bromide as electrolyte. A series of crystals of the Cl-Br mixed-halogen compounds, $Ni(chxn)_2Cl_yBr_{1-y}(NO_3)_2$, were obtained by electrochemical oxidation method with the mixed methanol solutions of $Ni(chxn)_2Cl_2$ and $Ni(chxn)_2Br_2$ with various mixing ratios using ammonium nitrate as electrolyte. The mixing ratios of Pd to Ni in $Ni_{1-x}Pd_x(chxn)_2Br_2$ were determined by ICP (inductively coupled plasma) emission spectrometry on a SEIKO SPS 7000 plasma spectrometer. The mixing ratios of Cl to Br in $Ni(chxn)_2Cl_yBr_{1-y}(NO_3)_2$ were estimated by comparing with crystal parameters (a, b, and c axes) and population analysis of Cl and Br using X-ray structure determination on Rigaku R-AXIS RAPID at room temperature. Optical conductivity spectra were obtained by the Kramers-Kronig transformation from the polarized reflectivity spectra, with the electric vector E parallel to the chain axis b (//).

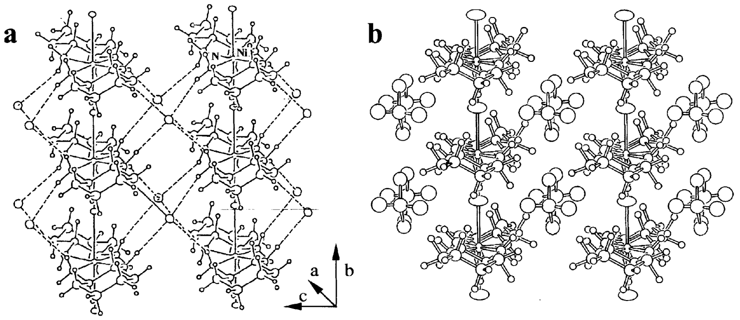

Figure 2. Crystal structures of **a**, $Ni(chxn)_2Br_3$ and **b**, $Ni(chxn)_2Cl_yBr_{1-y}(NO_3)_2$

RESULTS AND DISCUSSION

The crystal structure of $Ni_{1-x}Pd_x(chxn)_2Br_3$ is shown Figure 2a. The compound for x=0 considered to be CT insulator [1]. The optical conductivity spectra along the chain axis b of the series of $Ni_{1-x}Pd_x(chxn)_2Br_3$ are shown Figure 3. In the Ni^{III} system, its spectrum show an absorption peak due to the CT transition from the Br p_z valence band to the Ni $d_z{}^2$ upper Hubbard band. On the other hand, the Pd^{II}-Pd^{IV} system indicates that CT transition occurs from the Pd^{II} ion to the Pd^{IV} ion. In the mixed-metal compounds, the CT-gap energy decrease with increasing of Pd ratio, x.

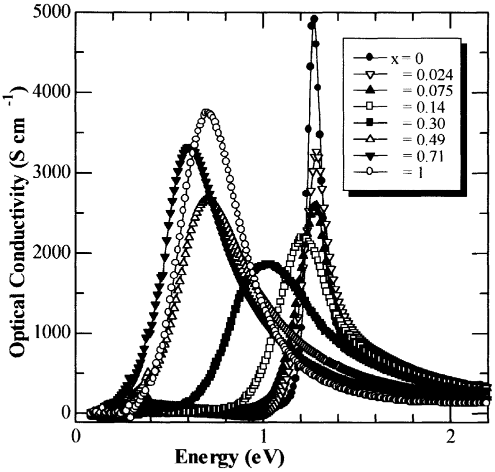

Figure 3. Optical conductivity spectra of $Ni_{1-x}Pd_x(chxn)_2Br_3$

These results suggest that when x < 0.5, Pd ions changes from Pd^{II}-Pd^{IV} state to Pd^{III} state in the mixed-metal compounds, and the

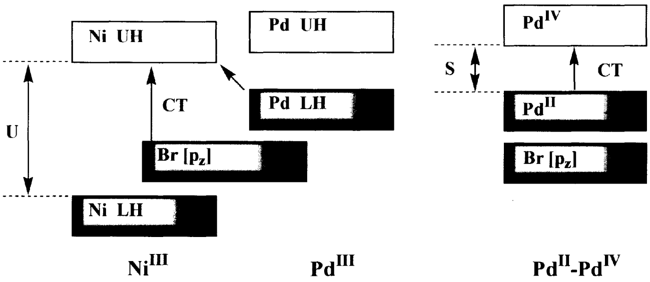

Figure 4. Shcematic electronic structure of $Ni_{1-x}Pd_x(chxn)_2Br_3$

CT-gap energy decrease due to the CT transition from the Pd^{III} lower Hubbard band to the Ni^{III} upper Hubbard band, which is smaller than CT transition from Br p_z to Ni^{III} upper Hubbard band (Figure 4). On the other hand, when x > 0.5, CT transition is dominated by Pd^{II}-Pd^{IV} states.

In the $Ni(chxn)_2Cl_yBr_{1-y}(NO_3)_2$ compounds, crystal structures reveal that only bridging halogens have Cl-Br mixtures because counteranions were NO_3 (Figure 2b). It means that we can estimate the contribution of the bridging halogens. The optical conductivity spectra along the chain axis b of $Ni(chxn)_2Cl_yBr_{1-y}(NO_3)_2$ are shown in Figure 5. Previously, the magnitude of the CT gap energies of the pure Cl-bridged and pure Br-bridged Ni^{III} compounds have been estimated to be about 2 eV ($Ni(chxn)_2Cl_3$), and 1.5 eV ($Ni(chxn)_2Br_3$) respectively [1]. In the mixed-halogen compounds, the CT gap energies which correspond to absorption peaks increase with increase of Cl ratios, y continuously because of the energy difference between $3p_z$ of Cl and $4p_z$ of Br.

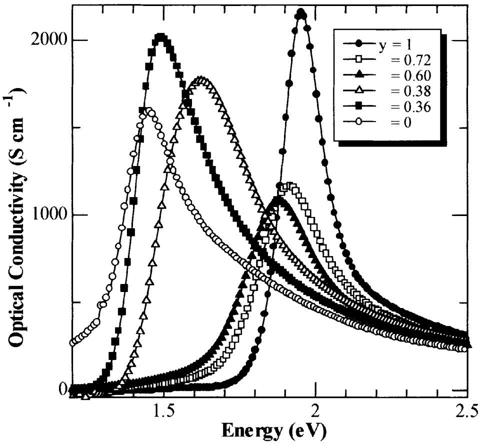

Figure 5. Optical conductivity spectra of $Ni(chxn)_2Cl_yBr_{1-y}(NO_3)_2$

CONCLUSION

We have obtained the single-crystals of the Ni-Pd mixed-metal compounds, $Ni_{1-x}Pd_x(chxn)_2Br_3$ and Cl-Br mixed-halogen compounds, $Ni(chxn)_2Cl_yBr_{1-y}(NO_3)_2$. The former indicates that the red shift of the

CT bands occur due to the Pd^{III} ions created with the decrease of the Pd ratios influenced with the increase of Ni^{III} states. The latter indicates that the CT gap energy can be continuously controlled by mixing halogen ratios.

Thus, the electronic state of the Ni^{III} compounds can be systematically controlled by forming the mixed-metal or mixed-halogen systems.

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