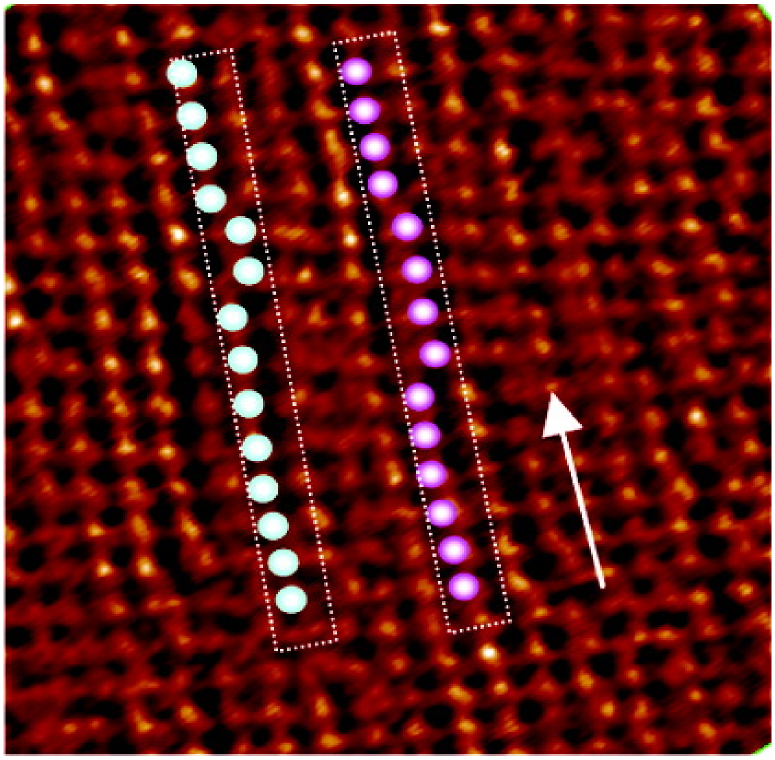
Communication

Direct Observation of the Disorder of the Methyl Group of (*R*)-1,2-Diaminopropane Ligand in the Quasi-1D Bromo-Bridged Ni(III) Complex by STM

Mari Sasaki, Shinya Takaishi, Hitoshi Miyasaka, Ken-ichi Sugiura, and Masahiro Yamashita

J. Am. Chem. Soc., **2005**, 127 (43), 14958-14959• DOI: 10.1021/ja053715g • Publication Date (Web): 05 October 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Direct Observation of the Disorder of the Methyl Group of (*R*)-1,2-Diaminopropane Ligand in the Quasi-1D Bromo-Bridged Ni(III) Complex by STM

Mari Sasaki,† Shinya Takaishi,‡ Hitoshi Miyasaka,† Ken-ichi Sugiura,† and Masahiro Yamashita*,‡

Department of Chemistry, Tokyo Metropolitan University, Hachioji 192-0097, Japan, and Department of Chemistry, Tohoku University, Sendai 980-8578, Japan

Received June 6, 2005; E-mail: yamasita@agnus.chem.tohoku.ac.jp

In recent years, one-dimensional (1D) electronic systems have been attracting much attention in both applied and pure sciences. From the viewpoints of applied sciences, these systems are very promising in the field of nonlinear optics and nanoelectronics, while from the viewpoints of pure sciences, many characteristic physical properties have been observed, such as spin-density wave (SDW) and charge-density wave (CDW) states in organic conductors,[1,2] solitons, polarons, and bipolarons in π-conjugated polymers,[3,4] and slow relaxation of magnetization in several ferro- and ferrimagnetic quantum compounds.[5−7] Among these compounds, quasi-1D halogen-bridged complexes (MX chains) have recently attracted the interest of many chemists and physicists as 1D electronic materials because they show marked physical properties, such as intense intervalence charge-transfer bands,[8] overtone progression of resonance Raman spectra,[9,10] luminescence spectra with large Stokes shifts,[11] large third-order nonlinear optical properties,[12] mid-gap absorptions attributable to solitons and polarons,[13,14] 1D model compounds of high T_c copper oxide superconductors,[15] etc. From theoretical viewpoints, electronic structures of 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.[16,17] The Pt and Pd compounds form 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.[18] On the other hand, the Ni compounds form the $Ni^{III}-Ni^{III}$ Mott-Hubbard states due to the strong electron correlation (U), where the bridging halogens are located at the midpoints between neighboring two Ni atoms.[19] Quite strong antiferromagnetic interactions among the spins located on the Ni^{III} d_{z^2} orbitals through the p_z orbitals of bridging halogen ions are observed in these compounds ($J \approx -3600$ K).[20] Recently, the gigantic third-order nonlinear optical susceptibility ($\chi^{(3)} \approx 10^{-4}$ esu) has been observed in $[Ni(chxn)_2Br]Br_2$ (chxn = (1*R*,2*R*)-diaminocyclohexane).[12]

More recently, a new series of MX chains, that is, the mixed-metal complexes $Ni_{1-\chi}Pd_{\chi}(chxn)_2Br_3$ ($0 \leq \chi \leq 1$), were synthesized,[21] and their local electronic structures, such as the Mott-Hubbard state, CDW state, and spin soliton, have been directly observed by scanning tunneling microscopy (STM) for the first time.[22]

Although many attempts on substituting bridging halogen ions and counterions have so far been made, the substituting effect of the in-plane ligand has not been studied. For the real application of $\chi^{(3)}$ as the optical devices, shortening of the $Ni^{III}-Ni^{III}$ distances is effective in order to increase $\chi^{(3)}$ values. For this purpose, the simpler ligands compared with the chxn are more preferable. According to such a strategy, we have synthesized quasi-1D bromo-bridged Ni^{III} complexes, $[Ni(AA)_2Br]Br_2$ (AA = (*R*)-1,2-diaminopropane(=pn) and (2*R*,3*R*)-diaminobutane(=bn)), and made STM measurements on these complexes. In this paper, we report the real disorder of the methyl group of $[Ni(pn)_2Br]Br_2$ by STM in real space, for the first time, as well as the crystal structures of $[Ni(AA)_2Br]Br_2$ (AA = pn, bn).

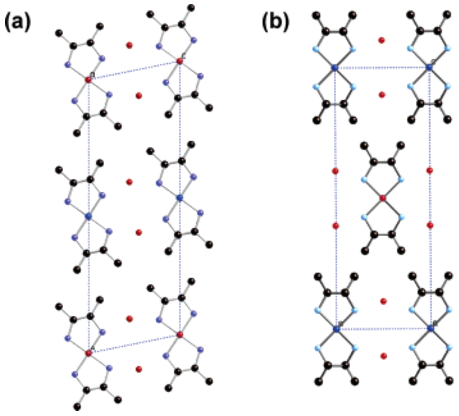


Figure 1. Crystal structures of (a) $[Ni(bn)_2Br]Br_2$ and (b) $[Ni(pn)_2Br]Br_2$ on the *ac* plane.

Figure 1 shows the single-crystal X-ray structure $[Ni(AA)_2Br]Br_2$ (AA = bn, pn). Ni^{III} ions and bromide ions are arranged alternately along the *b* axis, forming the linear chain structures. The Ni−Ni distances at −152 °C determined by X-ray single-crystal structure analysis are 5.136(6) Å for $[Ni(bn)_2Br]Br_2$ and 5.110(7) Å for $[Ni(pn)_2Br]Br_2$. These values are a little shorter than that of $[Ni(chxn)_2Br]Br_2$ (5.157(1) Å).[19] The inter- and intrachain hydrogen bond networks are observed between the amino hydrogen of $[Ni(AA)_2]$ and the counter bromo ions, forming the two-dimensional hydrogen bond networks. The crystal system of the bn compound is monoclinic to avoid steric repulsion in the part of the methyl groups of the bn ligand (Figure 1a). On the other hand, the crystal structure of the pn compound is isomorphous with $[Ni(chxn)_2Br]Br_2$, and the methyl groups of the pn ligands are disordered on both carbon atoms, with half occupancies (Figure 1b).

Figure 2a shows an STM image of in the range of 200 × 200 Å. Bright spots in the image are observed every 5 × 7 Å. Because the Ni−Ni distances along the *b* (1D chain) and *c* axes are 5.136(6) and 7.102(9) Å, respectively, these spots reflect the periodicity of $[Ni(bn)_2]$ units on the *bc* plane. Such an image is similar to that observed in $[Ni(chxn)_2Br]Br_2$. A schematic band structure of $[Ni(bn)_2Br]Br_2$ is shown in Figure 2b. Because the STM measurements were performed with the positive sample bias, the tunnel current is observed from the Fermi energy (E_F) of a tip to a conduction band of the sample. According to the previous studies, the

---

† Tokyo Metropolitan University.
‡ Tohoku University.

10.1021/ja053715g CCC: $30.25 © 2005 American Chemical Society

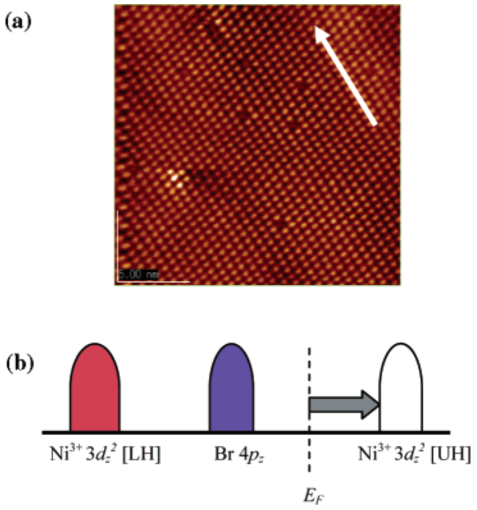


Figure 2. (a) STM image of [Ni(bn)$_2$Br]Br$_2$ on the *bc* plane (200 × 200Å). (b) Schematic band structure of [Ni(bn)$_2$Br]Br$_2$.

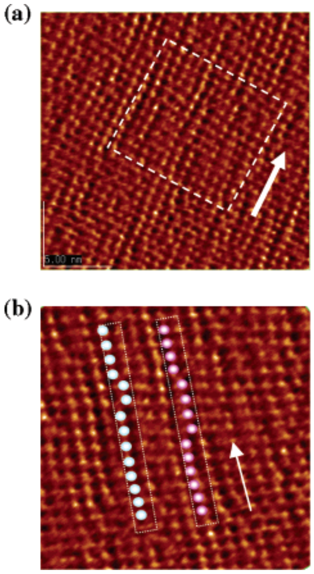


Figure 3. (a) STM image of [Ni(pn)$_2$Br]Br$_2$ (200 × 200 Å) on the *bc* plane. The white arrow shows the 1D chain direction. (b) STM image of magnification of the square part in Figure 3a. The red and blue circles show bright spots arranged in zigzag-fashion, respectively.

conduction bands of the halogen-bridged Ni$^{\mathrm{III}}$ complexes are an unoccupied upper-Hubbard (UH) band composed of the d_{z^2} orbital of Ni. Therefore, in [Ni(bn)$_2$Br]Br$_2$, the tunnel current from the E_{F} of a tip to the UH band of Ni$^{\mathrm{III}}$ is observed as bright spots.

Figure 3a shows an STM image of [Ni(pn)$_2$Br]Br$_2$ in the range of 200 × 200 Å. Bright spots are observed in ca. 5 Å parts. As a result of this and the single-crystal analysis, the [Ni(pn)$_2$Br]Br$_2$ is in a Mott-Hubbard Ni^{3+}−Ni^{3+} state. However, bright spots are not completely one-dimensional, compared with the bn compounds but are arranged in a zigzag-fashion (Figure 3). The image of the pn compound is different from those observed in chxn[22] and bn compounds, as shown in Figure 2a. In our previous paper, we clarified that the tunnel currents strongly reflect the electronic state of the metal ions in the halogen-bridged Ni and Pd compounds.[22] Therefore, in [Ni(pn)$_2$Br]Br$_2$, tunnel currents should be observed through the methyl groups of [Ni(pn)$_2$]. Interestingly, the bright spots, that is, methyl groups, are not arranged on the right- and left-hand alternatively, but in the domain structures or fluctuated structures. As a result, in the X-ray single-crystal structure analysis of [Ni(pn)$_2$Br]Br$_2$, the disorder of the methyl group is observed on the two carbon atoms with half occupancies. Therefore, this is the first direct observation of the disorder of the methyl group of the pn ligands of [Ni(pn)$_2$Br]Br$_2$ in real space. Detailed discussion on the disordered geometry is done in the Supporting Information.

In summary, we succeeded in synthesizing [Ni(AA)$_2$Br]Br$_2$ (AA = bn, pn), and the Ni−Ni distance is shorter than that of chxn compounds. In addition, we have succeeded in visualizing the Mott-Hubbard state in these compounds and the real disorder of the methyl group of pn ligands in [Ni(pn)$_2$Br]Br$_2$ by STM.

Acknowledgment. This work was partly supported by a Grant-in Aid for Creative Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

Supporting Information Available: Complete ref 15, experimental details, crystal structures of the present complexes (CIF), and detailed discussion on the disordered geometry. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Andrieux, A.; Jerome, D.; Bechgaard, K. *J. Phys. Lett.* **1981**, *42*, 87−90.
(2) Forro, L.; Bouffard, S.; Pouget, J. P. *J. Phys. Lett.* **1984**, *45*, 453−459.
(3) Goldberg, I. B.; Crowe, H. R.; Newman, P. R.; Heeger, A. J.; MacDiarmid, A. G. *J. Chem. Phys.* **1979**, *70*, 1132−1136.
(4) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. B* **1980**, *22*, 2099−2111.
(5) Caneschi, A.; Gatteschi, D.; Lalioti, N.; Sangregorio, C.; Sessoli, R.; Venturi, G.; Vindigni, A.; Rettori, A.; Pini, M. G.; Novak, M. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 1760−1763.
(6) Clérac, R.; Miyasaka, H.; Yamashita, M.; Coulon, C. *J. Am. Chem. Soc.* **2002**, *124*, 12837−12844.
(7) Lescouezec, R.; Vaissermann, J.; Ruiz-Perez, C.; Lloret, F.; Carrasco, R.; Julve, M.; Verdaguer, M.; Dromzee, Y.; Gatteschi, D.; Wernsdorfer, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 1483−1486.
(8) Tanaka, M.; Kurita, S.; Kojima, T.; Yamada, Y. *Chem. Phys.* **1984**, *91*, 257−265.
(9) Clark, R. J. H.; Franks, M. L.; Trumble, W. R. *Chem. Phys. Lett.* **1976**, *41*, 287−292.
(10) Clark, R. J. H. *Adv. Infrared Raman Spectrosc.* **1983**, *11*, 95−130.
(11) Tanino, H.; Kobayashi, K. *J. Phys. Soc. Jpn.* **1983**, *52*, 1446−1456.
(12) Kishida, H.; Matsuzaki, H.; Okamoto, H.; Manabe, T.; Yamashita, M.; Taguchi, Y.; Tokura, Y. *Nature* **2000**, *405*, 929−932.
(13) Okamoto, H.; Mitani, T.; Toriumi, K.; Yamashita, M. *Phys. Rev. Lett.* **1992**, *69*, 2248−2251.
(14) Okamoto, H.; Yamashita, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2023−2039.
(15) Yamashita, M. et al. *Inorg. Chem.* **2002**, *41*, 1998−2000.
(16) Baeriswyl, D.; Bishop, A. R. *J. Phys. C: Solid State Phys.* **1988**, *21*, 339−356.
(17) Mishima, A.; Nasu, K. *Phys. Rev. B* **1989**, *40*, 5593−5597.
(18) Hazell, A. *Acta Crystallogr. C* **1991**, *47*, 962−966.
(19) Toriumi, K.; Wada, Y.; Mitani, T.; Bandow, S.; Yamashita, M.; Fujii, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2341−2342.
(20) Okamoto, H.; Toriumi, K.; Mitani, T.; Yamashita, M. *Phys. Rev. B* **1990**, *42*, 10381−10387.
(21) Manabe, T.; Yamashita, M.; Kawashima, T.; Okamoto, H.; Kitagawa, H.; Mitani, T.; Toriumi, K.; Miyamae, H.; Inoue, K.; Yakushi, K. *Proc. of SPIE* **1997**, *3145*, 106−115.
(22) Takaishi, S.; Miyasaka, H.; Sugiura, K.-i.; Yamashita, M.; Matsuzaki, H.; Kishida, H.; Okamoto, H.; Tanaka, H.; Marumoto, K.; Ito, H.; Kuroda, S.; Takami, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 3171−3175.

JA053715G