

Electrochemical Synthesis and Crystal Structure of a Novel One-Dimensional Halogen-Bridged Nickel(III) Complex

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A novel halogen-bridged one-dimensional Ni^{III}-X-Ni^{III} compound, {[Ni^{III}(en)₂Cl]Cl₂}_∞ (en = C₂H₈N₂) has been synthesized by electrochemical oxidation. Single crystal X-ray crystallography revealed that a bridging halogen ion is located on the midpoint between two Ni(III) atoms with Ni-Cl 2.438 (1) Å. This is the first example for electrocrystallization of halogen-bridged 1-D metal complexes.

Halogen-bridged M^{II}-X-M^{IV} (M = Pt, Pd, and Ni) mixed-valence complexes have been investigated as a typical one-dimensional (1-D) system having strong electron-lattice interaction.¹ Their 1-D sequences are described as Peierls distorted charge density wave (CDW) state. The periodicity of 1-D sequence and the amplitude of the CDW state can be controlled by modification of the chemical parameters,² such as changing metal (M), bridging halogen (X), ligands, and counteranions. Especially for Ni complexes, the bridging halogen is located at the midpoint between two Ni(III) atoms on the linear chain, indicating no Peierls distortion.^{3,4} Since the Ni^{III}-X-Ni^{III} system is an extreme limit of M^{II}-X-M^{IV} compound, its electronic structure and physical properties attract much attention. Although hundreds of analogous Pt compounds have been synthesized for various combination of chemical parameters, a few examples have been prepared for Ni analogs. Crystals of Pt compounds are easily obtained by adding excess counteranion to an aqueous solution containing equal amount of Pt(II) and Pt(IV) complexes. For Ni compounds, both the oxidation of Ni(II) complex and crystallization processes should be made simultaneously because no stable Ni(IV) complex could be prepared. The Ni^{III}-X-Ni^{III} compounds previously reported were obtained by chemical oxidation of the Ni(II) monomeric complex using slow diffusion of halogen gas. This oxidation procedure enables only a few combination of chemical parameters for these Ni compounds, because halogen atoms are introduced into 1-D system not only as bridging atoms but also as counteranions. We report here the synthesis and crystal structure of a novel one-dimensional Ni compound

Table 1. Selected interatomic distances (Å) and angles (°)

Ni-Cl(1)	2.438 (1)	Ni-N	1.933 (2)
N-C	1.504 (5)	C-C ⁱ	1.486 (6)
Cl(2) ... N	3.2410 (5)		
N-Ni-N ⁱⁱ	87.08 (7)	Ni-N-C	108.7 (2)
N-C-C ⁱ	107.1 (3)		

* symmetry codes: i) x, -y, -z; ii) -x, -y, z;

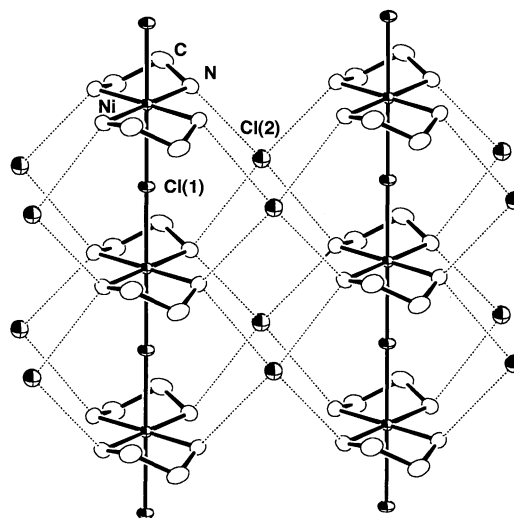


Figure 1. ORTEP drawing of {[Ni(en)₂Cl]Cl₂}_∞ 1-D chain structure along *b* axis. Dashed lines indicate hydrogen bonds between Cl⁻ anions and amino-groups of ethylenediamine ligands. Thermal ellipsoids are at 50% probability levels.

{[Ni(en)₂Cl]Cl₂}_∞ which was prepared by a new approach, electrocrystallization. In contrast to the chemical oxidation technique this method is favorable for controlling the rate of crystal growth, and for introduction of various bridging atoms and counteranions. This is the first example for preparing the halogen-bridged Ni 1-D compound by electrochemical oxidation.

A mixture of 0.155 g of Ni^{II}(en)₃Cl₂ (0.5 mmol) and 0.032 g of anhydrous NiCl₂ (0.25 mmol) in 20 cm³ of methanol was heated to reflux for 4 h. To a resulting clear blue solution, a 0.168 g (4 mmol) of LiCl was added and electrochemically

Table 2. Comparison of Ni-X (X = Cl and Br) bond distances (Å)

compound	Ni-X	ref.
{[Ni(en) ₂ Cl]Cl ₂ } _∞	2.438 (1)	this work
{[Ni(<i>R,R</i> -chxn) ₂ Cl]Cl ₂ } _∞ ^a	2.447 (1)	3
{[Ni(<i>R,R</i> -chxn) ₂ Br]Br ₂ } _∞	2.580 (1)	4
[Ni ^{III} Cl ₂ L ₂] ClO ₄ ^b	2.452 (4)	5

^achxn = 1,2-diaminocyclohexane;

^bL = 1,4,8,11-tetraazacyclotetradecane

oxidized using Pt electrodes by galvanostat. Black prismatic crystals with gold luster⁶ were grown on the cathode electrode after several days with continuous electrolysis at 5 μ A.

Single crystal X-ray structure analysis⁷ shows that Ni(en)₂ units are linked by Cl atoms as axial ligands to construct 1-D infinite straight chains along *b*-axis. The bridging Cl(1) atom is located at the midpoint between two Ni atoms on the chain.⁸ This chain structure suggests that all Ni atoms have the same oxidation states, identifying no Peierls distortion in the 1-D system. The Ni—Cl distance of 2.438 (1) Å is slightly shorter than that found in {[Ni(*R,R*-chxn)₂Cl]Cl₂}_∞⁴ (Table 2). The counteranion Cl(2) is located between the chains to form two dimensional hydrogen bond network parallel to the *bc* plane with amino-groups (Cl \cdots N 3.241 (1) Å) of ethylenediamine ligands (Figure 1). The single crystal electroconductivity measurement revealed semiconductive character with $\sigma_{RT} = 1 \times 10^{-4}$ S cm⁻¹.⁹

The electrocrystallization technique in preparing 1-D Nickel(III) compounds may be powerful to control the chemical parameters which vary the amplitude of the CDW state. Also large good crystals suitable for measuring physical properties are easily obtained by this method.

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References and Notes

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- 6 Elemental analysis Found: C, 17.06; H, 5.27; N, 19.65%. Calcd for C₄H₁₆Cl₃N₄Ni: C, 16.84; H, 5.65; N, 19.64%. FAB+ mass spectrometry: *e/z* = 213 assigned for C₄H₁₆ClN₄Ni⁺. We thank Chemical Material Center at Institute for Molecular Science for elemental analysis and measuring mass-spectrometry.
- 7 A 0.44 x 0.24 x 0.08 mm dimensions of a single crystal was mounted on an Enraf-Nonius CAD4 diffractometer. Crystal Data : Formula C₄H₁₆Cl₃N₄Ni, *F_w* = 285.25, orthorhombic, *Immm*, *a* = 16.580 (1), *b* = 4.875 (1), *c* = 6.772 (1) Å, *V* = 547.36 (5) Å³, *Z* = 2. *D_x* = 1.731, *D_m* = 1.74 Mg m⁻³, $\mu(\text{Mo } K\alpha) = 2.46$ mm⁻¹, *T* = 294 K. A total of 942 reflections up to $2\theta = 60^\circ$, 763 independent data with *I* > 3.0 $\sigma(I)$ were used for structure determination and refinement. The current *R* value of 0.056 were converged by applying anisotropic thermal factors on non-hydrogen atoms. The Ni(en)₂ moiety is located at *mmm* symmetry position in the crystal, the C atoms of en ligand are disordered at two positions related by a mirror plane.
- 8 The structure analysis shows no positional disorder of the bridging Cl atom. The thermal ellipsoid of Cl(2) atom is not so large (*B_{eq}* = 2.51 (2) Å² at 294K). The X-ray oscillation and Weissenberg photographs showed neither diffuse scattering nor satellite peak which may be caused by mixed valence 1-D chain structure.
- 9 The electroconductivity was measured for the single crystal by four-probe technique in the temperature range 300–350 K. The electrical contacts were made by Au wire with carbon paint. The conductivity of {[Ni(en)₂Cl]Cl₂}_∞ behaves semiconductively ($\sigma_{RT} = 1.3 \times 10^{-4}$ S cm⁻¹; *E_a* = 0.12 eV along *b* axis). Y.O. thanks Dr. T. Mori, Institute for Molecular Science, for measurement and analysis of electroconductivity.