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Bromination of $[Ni^{II}(diamine)_2Br_2]$ Complexes. Crystal Structure of *trans*-Dibromobis(ethylenediamine)nickel(III) Bromide, $[Ni(en)_2Br_2]Br$

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Introduction

The chemistry of Ni^{III} has attracted much attention in several fields. This arises from its unusual oxidation state,[2] its presence as a trace bioelement,[3] its use in the study of the kinetics and mechanisms of the oxidation reactions of organic molecules or metal ions,[4] and the interesting solid-state properties displayed by some of its compounds.[5] However, not all compounds which appear to contain nickel(III) on the basis of their empirical formula do in fact contain this ion and may belong to one of the following groups: (a) discrete d^7 nickel(III) complexes, e.g. $[Ni([14]aneN_4)Cl_2]ClO_4$[6] ($[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane); (b) nickel(II) complexes with cation radical ligands, e.g. $[Ni(pdma)_2Cl_2]Cl$[7] (pdma = *o*-phenylenebis(dimethylarsine)); (c) halide-bridged one-dimensional Ni^{II}–Ni^{IV} mixed-valence complexes, e.g. $Ni(en)_2Cl(ClO_4)_2$[8] (en = ethylenediamine); (d) halide-bridged one-dimensional nickel(III) complexes, e.g. $[Ni(chxn)_2Br]Br_2$[5] (chxn = 1(*R*),2(*R*)-diaminocyclohexane); (e) partially oxidized complexes, e.g. $Ni(Hdpg)_2I$[9] (H_2dpg = diphenylglyoxime).

So far, the compounds with diamine ligands appearing to contain nickel(III) on the basis of their empirical formula have been synthesized and characterized by various physicochemical techniques. The sensitivity to preparative conditions, in-plane diamines, and anions for this class of complexes have been investigated. In the case of ethylenediamine (en) as a ligand, rapid bubbling of Cl_2 into an ethanol solution of $[Ni(en)_2Cl_2]$ produces a discrete Ni^{III} complex, $[Ni(en)_2Cl_2]Cl$,[8a,b,10] while a chloro-bridged one-dimensional mixed-valence compound, $[Ni(en)_2][Ni(en)_2Cl_2]Cl_4$, is prepared by passing a slow stream of Cl_2 diluted with a large amount of N_2 through a MeOH–EtOH (1:1 v/v) solution of $[Ni(en)_2Cl_2]$.[10] Interestingly, $[Ni(en)_2Cl_2]Cl$ is gradually disproportioned into $[Ni(en)_2][Ni(en)_2Cl_2]Cl_4$ by moisture in the solid state.[11] $[Ni(en)_2Cl_2]Cl$ is also disproportioned into $[Ni(en)_2][Ni(en)_2Cl_2](ClO_4)_4$ by using 70% $HClO_4$ as a solvent and reactant.[8] Bromination of $[Ni(en)_2Br_2]$ produces $[Ni(en)_2Br_2]Br$,[8a] which is not disproportioned into a Ni^{II}–Ni^{IV} mixed-valence complex.[12]

On the other hand, in the case of 1(*R*),2(*R*)-diaminocyclohexane (chxn) as a ligand, novel halide-bridged one-dimensional Ni^{III} compounds, $[Ni(chxn)_2X]X_2$ (X = Cl, Br, or mixed halides), were obtained by halogenation of $[Ni(chxn)_2X_2]$ in ethanol or 2-methoxyethanol.[5] In spite of the same preparative conditions in bromination, two types of compounds were obtained depending on the in-plane diamines. In order to investigate the sensitivity to the in-plane ligands for this class of complexes, we have measured the recorded voltammograms of $[Ni(AA)_2Br_2]$ (AA = en, chxn) and have determined the crystal structure of $[Ni(en)_2Br_2]Br$ and compared it with those of $[Ni(chxn)_2Br]Br_2$ and $[Ni(N_4\text{-macrocycle})Br_2]Y$.[5,13]

Experimental Section

The cyclic voltammograms of $[Ni(AA)_2Br_2]$ (AA = en, chxn) were recorded with a digital universal signal processing system (HECS-328B, Huso Co. Ltd.). A Pt disk electrode (diameter 1.0 mm) was used as a working electrode. The reference electrode was a Ag/AgCl electrode in aqueous solution (saturated KCl), which was used with a double-junction assembly.

Wine-red prismatic single crystals of $[Ni(en)_2Br_2]Br$ were obtained by slow diffusion of Br_2 into an absolute ethanol solution of $[Ni(en)_2Br_2]$ in a desiccator filled with N_2, where the solution was prepared by refluxing a 1:0.5 mixture of $[Ni(en)_3]Br_2$ and $NiBr_2$ in absolute ethanol.

Intensity data were collected on Rigaku AFC-5R diffractometer at 25 °C by use of the θ–2θ scan technique and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A thin platelike crystal of dimensions 0.14 × 0.10 × 0.024 mm was used for the measurement. Among 3568 reflections measured in the range of $2\theta_{max}$ = 60° (h = −22 to +22, k = −10 to +10, l = 0 to +13), 904 independent amplitudes were observed ($|F_o| > 3\sigma(F_o)$). During data collection, intensities of three standard reflections were monitored every 100 measurements, showing no crystal movement or decay. The intensities were corrected for Lorentz–polarization factors and absorption effects, but not for extinction. The absorption correction was made by using a numerical Gaussian integration method, minimum and maximum transmission factors being 0.532 and 0.870. The cell dimensions were determined by a least-squares calculation using 2θ values (25° < 2θ < 30°) measured on the diffractometer.

The structure was solved by a conventional heavy-atom method and refined by a block-diagonal least-squares method. All the hydrogen atoms were located from the difference Fourier map. Maximum and minimum peaks in the difference map were 1.3 and −0.8 e Å^{-3}, respectively. The scattering factors and anomalous corrections were taken from ref 14a. The final atomic parameters are listed in Table II. All calculations were

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(1) (a) Nagoya University. (b) Himeji Institute of Technology.

(2) (a) Busch, D. H.; Pillsbury, C. G.; Lovecchio, F. V.; Tait, A. M.; Hung, Y.; Jackels, S.; Rakowski, M. C.; Schammel, W. P.; Martin, Y. L. *ACS Symp. Ser.* **1977**, *38*, 32. (b) Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* **1979**, *33*, 87. (c) Haines, R. J.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77. (d) Margerum, D. W. *Pure Appl. Chem.* **1983**, *77*, 23.

(3) (a) Albracht, S. J.; Graf, E. C. *FEBS Lett.* **1982**, *140*, 311. (b) Lancaster, J. R. *Science* **1982**, *216*, 1324. (c) Thomson, A. J. *Nature* (*London*) **1982**, *28*, 602.

(4) (a) Brodovitch, J. C.; McAuley, A.; Oswald, T. *Inorg. Chem.* **1982**, *21*, 3442. (b) Wells, C. F.; Fox, D. *J. Chem. Soc., Dalton Trans.* **1977**, 1502. (c) McAuley, A.; Subramanian, S. *Inorg. Chem.* **1991**, *30*, 371.

(5) (a) Toriumi, K.; Wada, Y.; Mitani, T.; Bandow, S.; Yamashita, M.; Fujii, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2341. (b) Okamoto, H.; Toriumi, K.; Mitani, T.; Yamashita, M. *Phys. Rev. B* **1990**, *42*, 10381. (c) Toriumi, K.; Okamoto, H.; Mitani, T.; Bandow, S.; Yamashita, M.; Wada, Y.; Fujii, Y.; Clark, R. J. H.; Michael, D. J.; Edward, A. J. E.; Watkin, D.; Kurmoo, M.; Day, P. *Mol. Cryst. Liq. Cryst.* **1990**, *181*, 333. (d) Ikeda, R.; Tamaru, T.; Yamashita, M. *Chem. Phys. Lett.* **1990**, *173*, 466. (e) Okamoto, H.; Okaniwa, K.; Mitani, T.; Toriumi, K.; Yamashita, M. *Solid State Commun.* **1991**, *77*, 465. (f) Okaniwa, K.; Okamoto, H.; Mitani, T.; Toriumi, K.; Yamashita, M. *J. Phys. Soc. Jpn.* **1991**, *60*, 997. (g) Okamoto, H.; Toriumi, K.; Okaniwa, K.; Mitani, T.; Yamashita, M. *Synth. Met.* **1991**, *41–43*, 2791. (h) Yamashita, M.; Tsuruta, E.; Inoue, K.; Furuta, T.; Okamoto, H.; Mitani, T.; Toriumi, K.; Ohki, H.; Ikeda, R. *Synth. Met.*, in press.

(6) (a) Ito, T.; Sugimoto, M.; Toriumi, K.; Ito, H. *Chem. Lett.* **1981**, 1477. (b) Yamashita, M.; Toriumi, K.; Ito, T. *Acta Crystallogr., Sect. C* **1985**, *41*, 1607. (c) Yamashita, M.; Miyamae, H. *Inorg. Chim. Acta* **1989**, *156*, 71.

(7) Kreisman, P.; Marsh, R.; Preer, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 1067.

(8) (a) Babaeva, A. V.; Baravovaskii, I. B.; Afavaseva, G. G. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1965**, *10*, 686. (b) Yamashita, M.; Nonaka, Y.; Kida, S.; Hamaue, Y.; Aoki, R. *Inorg. Chim. Acta* **1981**, *52*, 43. (c) Yamashita, M.; Ito, T. *Inorg. Chim. Acta* **1984**, *87*, L5. (d) Yamashita, M.; Murase, I.; Ikemoto, I.; Ito, T. *Chem. Lett.* **1985**, 1133.

(9) Cowie, M.; Gleizes, A.; Grynkewich, G. W.; Kalin, D. W.; McIwre, M. S.; Scaringe, R. P.; Teitelbaum, R. C.; Ruby, S. L.; Ibers, A. J.; Kannewurf, C. F.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2922.

(10) Cooper, D. A.; Higgins, S. J.; Levason, W. *J. Chem. Soc., Dalton Trans.* **1983**, 2131.

(11) Yamashita, M.; Murase, I. *Inorg. Chim. Acta* **1985**, *97*, L43.

(12) Yamashita, M. Unpublished results.

(13) Miyamae, H.; Yamauchi, K.; Yamashita, M. *J. Chem. Soc., Dalton Trans.* **1991**, 2921.

(14) (a) Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4, p 74. (b) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Hokoku* **1979**, *55*, 69. (c) Johnson, C. K. ORTEP II. Report ORNL-5138, revised; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

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Table I. Crystallographic Data for $[Ni(en)_2Br_2]Br$

formula	$C_4H_{16}N_4NiBr_3$	Z	4
fw	418.60	μ(Mo Kα), mm^{-1}	12.511
space group	$C2/c$	ρ(calcd), g cm^{-3}	2.384
a, Å	16.125 (6)	T, K	298
b, Å	7.794 (3)	weighting scheme	$[\sigma_o^2 + (0.025\lvert F_o\rvert)^2]^{-1}$
c, Å	9.950 (4)	R,[a] %	3.6
β, deg	111.12 (3)	R_w,[b] %	4.3
V, Å^3	1166.5 (8)		

[a] $R = \sum \lVert F_o\rvert - \lvert F_c\rVert / \sum \lvert F_o\rvert$. [b] $R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \sum w \lvert F_o\rvert^2]^{1/2}$.

Table II. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2) of Non-Hydrogen Atoms for $[Ni(en)_2Br_2]Br$

	x	y	z	B_{eq}[a]
Ni	2500	2500	0	1.9
Br(1)	2697 (1)	2154 (1)	2811 (1)	2.6
Br(2)	0	3853 (2)	2500	5.3
N(1)	3044 (4)	4751 (6)	284 (6)	2.4
N(2)	3651 (4)	1620 (7)	84 (6)	2.6
C(1)	4013 (6)	4561 (11)	824 (11)	5.2
C(2)	4237 (6)	3097 (12)	159 (11)	5.3

[a] $B_{eq} = {}^4/_3 \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

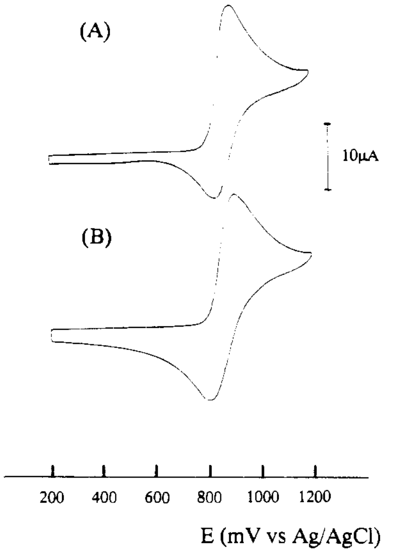

Figure 1. Cyclic voltammograms of $[Ni(en)_2Br_2]$ (A) and $[Ni(chxn)_2Br_2]$ (B) in methanol. The solutions contained 2.0 mM substrate and 0.1 M $(Bu)_4NClO_4$ as a supporting electrolyte. Sweep rate: 500 mV/s.

carried out on a HITAC M680 computer at the Computer Center of the Institute for Molecular Science with the programs UNICS III and ORTEP.[14b,c]

Results and Discussion

Bromination of $[Ni^{II}(AA)_2Br_2]$ (AA = en, chxn) was attempted in various solvents such as MeOH, EtOH, 2-methoxyethanol, and CCl_4 (suspension) in order to investigate the effects of the solvents. It was found that, irrespective of the type of solvent, the discrete low-spin d^7 Ni^{III} complex *trans*-$[Ni(en)_2Br_2]Br$ was obtained for AA = en, while the bromide-bridged Ni^{III} complex with an infinite-linear-chain structure was obtained for AA = chxn. In order to investigate redox states in solution, cyclic voltammograms of $[Ni(AA)_2Br_2]$ were recorded in methanol and ethanol. Figure 1 shows the cyclic voltammograms of $[Ni(AA)_2Br_2]$ in methanol. Similar voltammograms with reversible one-electron redox peaks and the same redox potentials were observed for both compounds in methanol and ethanol. The results indicate that the Ni^{III} complexes were generated stably in solutions and reduced to the Ni^{II} complexes reversibly for both compounds. Accordingly, the difference in their solubilities in the solvents, crystal packings, and hydrogen-bond systems, as shown later, may result in the difference in their structures.

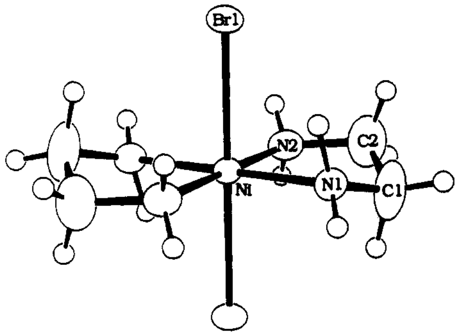

Figure 2. Structure of $[Ni(en)_2Br_2]^+$ with atom numbering. Selected bond distances (Å) and angles (deg): Ni–Br(1) = 2.635 (1), Ni–N(1) = 1.937 (5), Ni–N(2) = 1.951 (7), N(1)–C(1) = 1.466 (11), N(2)–C(2) = 1.475 (12), C(1)–C(2) = 1.429 (15); Br(1)–Ni–N(1) = 89.8 (2), Br(1)–Ni–N(2) = 90.9 (2), N(1)–Ni–N(2) = 86.5 (3), Ni–N(1)–C(1) = 109.2 (4), Ni–N(2)–C(2) = 108.1 (5), N(1)–C(1)–C(2) = 109.0 (7), N(2)–C(2)–C(1) = 112.5 (10).

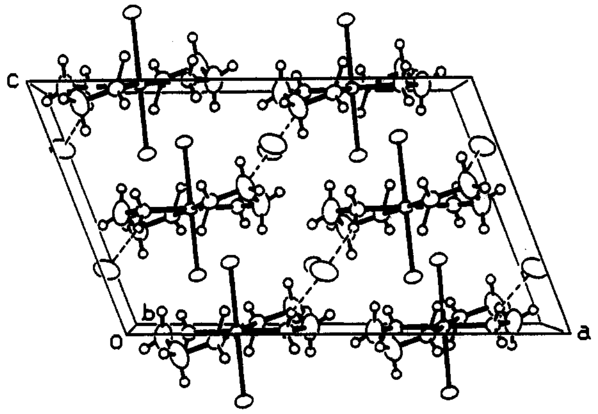

Figure 3. Packing diagram for $[Ni(en)_2Br_2]Br$. The dashed lines correspond to hydrogen bonds (Br(2)···H–N(2) = 3.375 (5) Å [2.55 (10) Å]).

The perspective drawing of the discrete Ni^{III} complex cation $[Ni(en)_2Br_2]^+$ is presented in Figure 2 along with the atom-numbering system. The Ni^{III} ion sits on a center of symmetry and is surrounded pseudooctahedrally by a square-planar array of the four N atoms of the two ethylenediamine ligands and by two Br ions in trans positions. The tetragonal coordination geometry of *trans*-NiN_4Br_2 found in this compound is the same as those of $[Ni([14]aneN_4)Br_2]ClO_4$ and $[Ni([13]aneN_4)Br_2]Br$ ([13]aneN_4 = 1,4,7,10-tetraazacyclotridecane) determined previously by single-crystal X-ray structure analyses.[13] The stereochemistry of the ethylenediamine ligand is the same as that in $Ni^{II}(en)_2(NO_2)(ClO_4)$, but the average Ni–N distance in this compound is 0.14 Å shorter than that in $Ni(en)_2(NO_2)(ClO_4)$.[15] The N–Ni–N angle in this compound (86.5°) is a little larger than that in $Ni(en)_2(NO_2)(ClO_4)$ (82.4°). The bond distances and angles within the ligand are normal.

Compared with those of $[Ni(chxn)_2Br]Br_2$, which has a bromide-bridged one-dimensional chain structure, the Ni–N bond distances in these compounds are almost equal to each other because of the diamines having the same five-membered chelate rings, while the Ni–Br bond distances in $[Ni(en)_2Br_2]Br$ are 0.06 Å longer than those in $[Ni(chxn)_2Br]Br_2$.[5] In $[Ni(chxn)_2Br]Br_2$, there exist not only four NH···Br···HN hydrogen bonds between neighboring $Ni(chxn)_2$ moieties along the chain but also hydrogen bonds over the chains. Previous IR measurements revealed that such hydrogen bonds are very strong and coupled with the electronic state in the one-dimensional structure. Additionally, the magnetic and electronic interactions through

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[15] Meyer, A.; Gleizes, A.; Girered, J. J.; Verdaguer, M.; Kahn, O. *Inorg. Chem.* **1982**, *21*, 1729.

the bridging Br atoms are very strong.[5f] On the other hand, in the $[Ni(en)_2Br_2]Br$, only one hydrogen bond between $[Ni(en)_2Br_2]^+$ and Br^- exists, as shown in Figure 3. Thus, the strong hydrogen bonds and electronic and magnetic interactions are assumed to cause the shorter Ni^{III}–Br distance in $[Ni(chxn)_2Br]Br_2$ compared with that in $[Ni(en)_2Br_2]Br$.

Previously Ito et al.[16] investigated the metal ion characteristics from the viewpoint of a correlation between the axial and in-plane coordination bond distances in tetragonal six-coordinate complexes of the *trans*-MN_4X_2 type, where $M = Zn^{2+}$ (d^{10}), Ni^{2+} (d^8), and Co^{3+} (d^6). Both experimentally and theoretically, it was found that the axial M–X distance decreases as the in-plane M–N distance increases. The degree of the negative correlation is in the order $Zn^{2+} > Ni^{2+} > Co^{3+}$, which is correlated with the electron occupancy of the $d_{x^2-y^2}$ and d_{z^2} orbitals.

In our preceding paper, we have shown the same negative correlation for the first time for Ni^{3+} (d^7), that is, *trans*-$[Ni(N_4\text{-macrocycle})Br_2]^+$, where the N_4-macrocycles were [13]aneN_4 and [14]aneN_4.[13] The average Ni–N and Ni–Br bond distances in $[Ni([13]aneN_4)Br_2]Br$ and $[Ni([14]aneN_4)Br_2]ClO_4$ are listed in Table III, along with those in $[Ni(en)_2Br_2]Br$. In the complexes including macrocyclic ligands, the Ni–N distances vary depending on the hole sizes of the macrocycles. Nevertheless, we can see the negative correlation between the Ni–N and Ni–Br distances in these compounds including macrocycle and diamine ligands. Accordingly, such a negative correlation is concluded to be intrinsic.

Table III. Relevant Average Bond Distances (Å)

	$[Ni([13]aneN_4)Br_2]Br$[a]	$[Ni(en)_2Br_2]Br$	$[Ni([14]aneN_4)Br_2]ClO_4$[b]
Ni–N	1.919 (13)	1.944 (6)	1.971 (7)
Ni–Br	2.664 (1)	2.635 (1)	2.616 (1)

[a] Reference 13. [b] Reference 5a.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles (7 pages). Ordering information is given on any current masthead page.

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(16) (a) Ito, T.; Kato, M.; Ito, H. *Bull, Chem. Soc. Jpn.* **1984**, *57*, 1556. (b) Ito, T.; Kato, M.; Yamashita, M.; Ito, H. *J. Coord. Chem.* **1986**, *15*, 29.