

# A Novel Tridentate-N,N,S Iminothiolate Ligand That Leads to the Formation of S-Bridged Dinickel(II) and Tetracobalt(III) Structures

Asako Igashira-Kamiyama, Masayuki Saito, and Takumi Konno\*

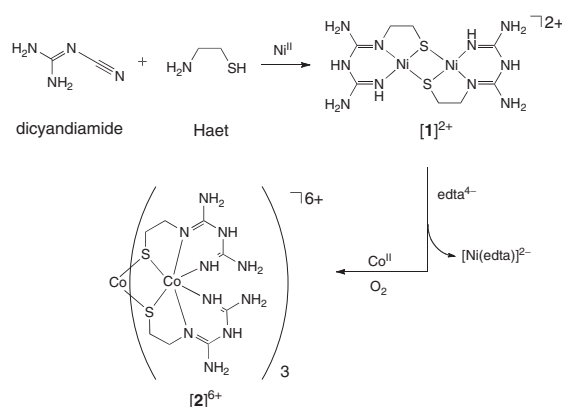
Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043

(Received October 6, 2009; CL-090903; E-mail: konno@chem.sci.osaka-u.ac.jp)

Treatment of dicyandiamide, 2-aminoethanethiol hydrochloride, and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in water gave an S-bridged dinickel(II) complex,  $[\text{Ni}_2(\text{L})_2]\text{Cl}_2$  ( $[\mathbf{1}]\text{Cl}_2$ ), which contains novel tridentate-N,N,S iminothiolate ligands with a biguanide moiety ( $\text{L}^-$ ). Another S-bridged complex containing  $\text{L}^-$ ,  $[\text{Co}\{\text{Co}(\text{L})_2\}_3]^{6+}$  ( $[\mathbf{2}]\text{Cl}_6$ ), which has the first example of a hexol S-bridged structure, was obtained by the stepwise reaction of  $[\mathbf{1}]\text{Cl}_2$  with  $\text{Na}_4\text{edta}$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in water.

It is well known that aliphatic thiolate groups possess a high nucleophilicity to bridge two or three metal centers to form S-bridged multinuclear structures. Utilizing this property, a number of S-bridged multinuclear complexes that show intriguing structures and properties have been prepared from bidentate-N,S thiolate ligands, represented by 2-aminoethanethiolate (aet).<sup>1</sup> To extend the bidentate-N,S ligand system, linear tridentate-N,N,S ligands with an aliphatic thiolate group have also been employed to construct S-bridged multinuclear structures.<sup>2,3</sup> In the tridentate-N,N,S ligand systems so far reported, however, no functional groups available for coordination and/or hydrogen bonding exist in the created multinuclear structures, and the further aggregation of multinuclear complexes into highly organized structures has rarely been achieved. It has been shown that a biguanide ligand bound to one metal ion can coordinate to another metal ion or form hydrogen bonds with another complex unit using free amine groups.<sup>4</sup> Thus, the rational aggregation of multinuclear complexes, as well as the creation of novel S-bridged multinuclear structures, would be promising if one designs aliphatic thiolate ligands bearing a biguanide moiety. Here we report that a desirable tridentate-N,N,S ligand with a biguanide moiety ( $\text{L}^-$ ) is created in a S-bridged dinickel(II) structure in  $[\text{Ni}_2(\text{L})_2]^{2+}$  ( $[\mathbf{1}]^{2+}$ ) from Haet and dicyandiamide in the presence of  $\text{Ni}^{\text{II}}$  ion (Scheme 1). Remarkably, the metal replacement of  $\text{Ni}^{\text{II}}$  in  $[\mathbf{1}]^{2+}$  by  $\text{Co}^{\text{III}}$  led to the formation of a tetracobalt(III) structure in  $[\text{Co}\{\text{Co}(\text{L})_2\}_3]^{6+}$  ( $[\mathbf{2}]^{6+}$ ), which is the first example of a hexol S-bridged tetranuclear complex. The crystal structures of these complexes that show multiple hydrogen bonding networks through amine groups of biguanide moieties are also reported.

Treatment of dicyandiamide, Haet·HCl, and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in water in a 1:1:1 ratio gave a dark purple solution from which purple stick crystals ( $[\mathbf{1}]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ ) were isolated.<sup>5</sup> The electronic absorption spectrum of  $[\mathbf{1}]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  in water exhibits a visible band at 520 nm, which is assignable to  $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$  transition for  $\text{Ni}^{\text{II}}$  with a square-planar coordination environment.<sup>6,7</sup> The formation of an iminothiolate ligand with a biguanide moiety ( $\text{L}^-$ ) in  $[\mathbf{1}]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  is suggested by the  $^1\text{H}$ NMR spectrum giving a single set of signals due to methylene and amine groups, together with the IR spectrum that shows a  $\nu(\text{C}=\text{N})$  band at  $1680\text{ cm}^{-1}$ .<sup>6,8</sup> The structure of  $[\mathbf{1}]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  was determined



Scheme 1. Synthetic roots of  $[\mathbf{1}]^{2+}$  and  $[\mathbf{2}]^{6+}$ .

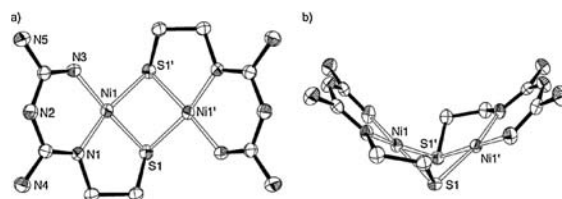
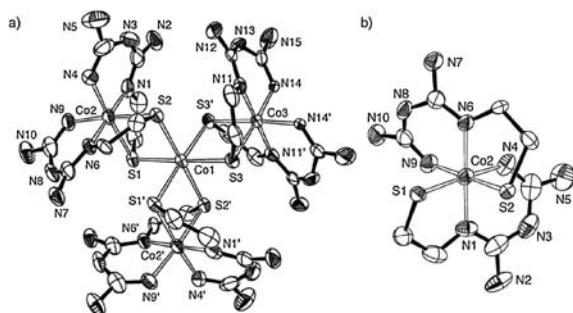


Figure 1. ORTEP drawings of  $[\mathbf{1}]^{2+}$ . a) Top view and b) side view. Hydrogen atoms are omitted for clarity. Symmetry code: (')  $-x, -y + 1, z$ .

by single-crystal X-ray analysis.<sup>9</sup> As shown in Figure 1, the ligand  $\text{L}^-$  in  $[\mathbf{1}]^{2+}$  is a biguanide derivative with an ethanethiol substituent on an imine group, which coordinates to a  $\text{Ni}^{\text{II}}$  center through a thiolate S and two imine N groups to form a  $[\text{Ni}(\text{L})]^+$  unit. The fourth coordination site of the  $[\text{Ni}(\text{L})]^+$  unit is occupied by a thiolato group from another  $[\text{Ni}(\text{L})]^+$  unit to complete a square-planar geometry with a *cis*- $\text{N}_2\text{S}_2$  donor set (av  $\text{Ni}-\text{S} = 2.181(9)$  and  $\text{Ni}-\text{N} = 1.875(2)$  Å). As a result,  $[\mathbf{1}]^{2+}$  has a S-bridged dinickel(II) structure in  $[\text{Ni}_2(\text{L})_2]^{2+}$ , in which two  $[\text{Ni}(\text{L})]^+$  units are connected to each other through two thiolato groups with a dihedral angle between two  $\text{NiN}_2\text{S}_2$  planes being  $71^\circ$ . It may be interesting to note that all the N–H groups in  $[\mathbf{1}]^{2+}$  are involved in hydrogen bonding with  $\text{Cl}^-$  anions and water molecules (av  $\text{N}\cdots\text{Cl} = 3.395(2)$  and  $\text{N}\cdots\text{O} = 2.923(3)$  Å), constructing a 2D sheet-like structure.<sup>6</sup> While similar S-bridged dinickel(II) complexes with a tridentate-N,N,S ligand have been reported,<sup>2</sup> such a dimensional structure having hydrogen-bonding networks has not been observed.

With the aim of preparing another complex containing  $\text{L}^-$  as a multidentate ligand, an aqueous solution of  $[\mathbf{1}]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  was treated with  $\text{Na}_4\text{edta}$ , followed by reacting with  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in air. When the resulting brown solution was chromatographed on an anion-exchange column (QAE-Sephadex A-25), a major



**Figure 2.** ORTEP drawings of  $[2]^{6+}$ . One of two independent cations with the  $(\Delta)(\Delta)_3(R)_6$  configuration is selected. a) Entire tetranuclear cation, b)  $[\text{Co}(\text{L})_2]^+$  unit of  $[2]^{6+}$ . Hydrogen atoms are omitted for clarity. Symmetry code: (')  $x - y + 1/3, -y + 2/3, -z + 7/6$ .

brown band was eluted with water, from which brown crystals ( $[2]\text{Cl}_6 \cdot 6\text{H}_2\text{O}$ ) were obtained.<sup>10</sup> X-ray fluorescence spectroscopy indicated that  $[2]\text{Cl}_6 \cdot 6\text{H}_2\text{O}$  contains only Co as a metal component. The +3 oxidation state of Co ions in  $[2]\text{Cl}_6 \cdot 6\text{H}_2\text{O}$  is induced by its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra that give sharp signals, and the presence of  $\text{L}^-$  in  $[2]\text{Cl}_6 \cdot 6\text{H}_2\text{O}$  is suggested by its IR spectrum that is very similar to the spectrum of  $[1]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ .<sup>6</sup> Single-crystal X-ray analysis revealed that  $[2]^{6+}$  is a tetracobalt(III) complex consisting of three  $[\text{Co}(\text{L})_2]^+$  units that are linked by a central  $\text{Co}^{\text{III}}$  ion (Figure 2).<sup>11</sup> Each  $[\text{Co}(\text{L})_2]^+$  unit in  $[2]^{6+}$  has a *cis*- $\text{N}_4\text{S}_2$  octahedral geometry coordinated by two tridentate-N,N,S ligands ( $\text{L}^-$ ) that adopt a meridional coordination mode (av  $\text{Co}-\text{S} = 2.217(2)$  and  $\text{Co}-\text{N} = 1.930(8)$  Å). The central  $\text{Co}^{\text{III}}$  ion is surrounded by six S atoms from three  $[\text{Co}(\text{L})_2]^+$  units in an octahedral geometry (av  $\text{Co}-\text{S} = 2.285(2)$  Å). While a number of hexol tetranuclear complexes have been reported to date,<sup>12,13</sup> those having bridging atoms other than oxygen are rare,<sup>13</sup> and furthermore,  $[2]^{6+}$  is the first hexol complex having thiolato S as bridging atoms. Crystal  $[2]\text{Cl}_6 \cdot 6\text{H}_2\text{O}$  is a racemic compound consisting of a pair of enantiomers, as indicated by the centrosymmetrical space group  $R\bar{3}c$ . In one enantiomer, the central and the terminal  $\text{Co}^{\text{III}}$  chiral centers adopt  $\Lambda$  and  $\Delta$  configurations, respectively, with bridging S atoms being fixed to R configuration. Thus, the  $(\Lambda)(\Delta)_3(R)_6$  and  $(\Delta)(\Lambda)_3(S)_6$  isomers with a  $D_3$  symmetry exist in crystal  $[2]\text{Cl}_6 \cdot 6\text{H}_2\text{O}$ . Like in  $[1]^{2+}$ , all the N–H groups in  $[2]^{6+}$  form hydrogen bonds with  $\text{Cl}^-$  anions and water molecules (av  $\text{N}\cdots\text{Cl} = 3.35(2)$  and  $\text{N}\cdots\text{O} = 2.95(2)$  Å) to construct a 3D structure.<sup>6</sup>

The  $^1\text{H}$  NMR spectrum of the bulk sample of  $[2]\text{Cl}_6 \cdot 6\text{H}_2\text{O}$  exhibits a single set of signals due to methylene and amine groups.<sup>6</sup> Furthermore, only four carbon signals are observed in its  $^{13}\text{C}$  NMR spectrum.<sup>6</sup> These spectral features imply that a pair of enantiomers,  $(\Lambda)(\Delta)_3(R)_6$  and  $(\Delta)(\Lambda)_3(S)_6$ , found in crystal are selectively formed for  $[2]^{6+}$ . To our knowledge, the selective formation of a pair of enantiomers has not been recognized for any hexol complexes so far reported.<sup>12,13</sup> Molecular model examinations revealed that there exists an unfavorable intramolecular interaction between methylene groups of  $\text{L}^-$  when  $[2]^{6+}$  adopts the other isomers. Complex  $[2]^{6+}$  was partially optically resolved by fractional crystallization with the use of  $\text{K}_2[\text{Sb}_2(\text{R,R-tartrato})_2]$  as a resolving agent, although complete optical resolution has not been achieved yet.<sup>6</sup>

In summary, we succeeded in the creation of a novel tridentate-N,N,S iminothiolate ligand with a biguanide moiety ( $\text{L}^-$ ) in a S-bridged dinickel(II) structure ( $[1]^{2+}$ ) by reacting Haet, dicyandiamide, and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in water. Since a similar reaction using  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  instead of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  did not afford any products containing  $\text{L}^-$ , it is believed that  $\text{Ni}^{\text{II}}$  acts as an effective template available for the nucleophilic addition of an amine group of Haet to a cyano group of dicyandiamide to form  $\text{L}^-$ . Furthermore,  $[1]^{2+}$  was converted to a S-bridged tetracobalt(III) structure in  $[2]^{6+}$  by reacting with  $\text{Co}^{\text{II}}$  in air, after the removal of  $\text{Ni}^{\text{II}}$  with use of  $\text{edta}^{4-}$ . This result indicates that  $[1]^{2+}$  can be used as a starting material for the preparation of other complexes containing  $\text{L}^-$ . Notably,  $[2]^{6+}$  is the first example of a S-bridged tetranuclear complex with a historically important hexol structure that affords selectively a pair of enantiomers. Finally, free amine groups of biguanide moiety in  $[1]^{2+}$  and  $[2]^{6+}$  were found to hydrogen bond, which is suggestive of their coordination ability toward metal ions.

## References and Notes

- a) T. Konno, *Bull. Chem. Soc. Jpn.* **2004**, 77, 627. b) H. Fleischer, S. Hardt, D. Schollmeyer, *Inorg. Chem.* **2006**, 45, 8318. c) Z.-N. Chen, N. Zhao, Y. Fan, J. Ni, *Coord. Chem. Rev.* **2009**, 253, 1.
- a) T. B. Vance, Jr., L. G. Warner, K. Seff, *Inorg. Chem.* **1977**, 16, 2106. b) N. F. Curtis, O. P. Gladhikh, K. R. Morgan, S. L. Heath, *Aust. J. Chem.* **1998**, 51, 49. c) C. A. Grapperhaus, J. A. Bellefeuille, J. H. Reibenspies, M. Y. Darensbourg, *Inorg. Chem.* **1999**, 38, 3698.
- a) M. Mikuriya, F. Adachi, H. Iwasawa, M. Handa, M. Koikawa, H. Okawa, *Bull. Chem. Soc. Jpn.* **1994**, 67, 3263. b) T. Kawahashi, M. Mikuriya, R. Nukada, J.-W. Lim, *Bull. Chem. Soc. Jpn.* **2001**, 74, 323. c) H. L. Jackson, S. C. Shoner, D. Rittenberg, J. A. Cowen, S. Lovell, D. Barnhart, J. A. Kovacs, *Inorg. Chem.* **2001**, 40, 1646.
- a) H. Kitamura, T. Ozawa, K. Jitsukawa, H. Masuda, H. Einaga, *Chem. Lett.* **1999**, 1225. b) A. Igashira-Kamiyama, T. Kajiwarra, T. Konno, T. Ito, *Inorg. Chem.* **2006**, 45, 6460. c) P. Hubberstey, U. Suksangpanya, *Struct. Bond.* **2004**, 111, 33.
- Anal. Calcd for  $[1]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ : C, 17.07; H, 4.66; N, 24.89%. Found: C, 17.34; H, 4.69; N, 24.88%. Yield: 27%. Molar conductivity in water:  $229 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .
- Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- N. Baidya, M. M. Olmstead, P. K. Mascharak, *Inorg. Chem.* **1991**, 30, 3967.
- K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley, Chichester, **1997**.
- Crystal data for  $[1]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ : fw 562.83, orthorhombic,  $P2_12_12_1$ ,  $a = 13.523(6)$ ,  $b = 16.585(6)$ ,  $c = 4.6488(13)$  Å,  $V = 1042.7(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calcd}} = 1.793 \text{ g cm}^{-3}$ , 9740 reflections measured, 2366 independent,  $R_1 = 0.0212$ . CCDC: 749928.
- Anal. Calcd for  $[2]\text{Cl}_6 \cdot 7\text{H}_2\text{O}$ : C, 18.77; H, 4.86; N, 27.36%. Found: C, 18.75; H, 4.72; N, 27.20%. Yield: 31%. Molar conductivity in water:  $787 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .
- Crystal data for  $[2]\text{Cl}_6 \cdot 6\text{H}_2\text{O}$ : fw 1517.90, trigonal,  $R\bar{3}c$ ,  $a = 41.431(5)$ ,  $c = 23.220(4)$  Å,  $V = 34518(8)$  Å<sup>3</sup>,  $Z = 24$ ,  $D_{\text{calcd}} = 1.753 \text{ g cm}^{-3}$ , 29965 reflections measured, 6763 independent,  $R_1 = 0.0733$ . CCDC: 749929. A half of a tetranuclear cation and a sixth of a tetranuclear cation are crystallographically independent. Both cations have the same chiral configurations for Co and S centers.
- For example: a) T. Kudo, Y. Shimura, *Bull. Chem. Soc. Jpn.* **1979**, 52, 3553. b) R. W. Saalfrank, A. Scheurer, I. Bernt, F. W. Heinemann, A. V. Postnikov, V. Schünemann, A. X. Trautwein, M. S. Alam, H. Rupp, P. Müller, *Dalton Trans.* **2006**, 2865. c) I. Bernal, M. T. Gonzalez, J. Cetrullo, J. Cai, *Struct. Chem.* **2001**, 12, 73.
- a) M. Südfeld, W. S. Sheldrick, *Inorg. Chim. Acta* **2000**, 304, 78. b) L. Yang, A. v. Zelewsky, H. Stoeckli-Evans, *Chem. Commun.* **2005**, 4155.