

シアナミド架橋ニッケル二核錯体の合成と磁氣的性質

Synthesis of NCNH-Bridged Dinuclear Nickel(II) Complexes
and Their Magnetic Properties

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【Introduction】

Owing to the resonance between cyanoimido/amido ($\text{N}=\text{C}-\text{N}^{2-}/\text{N}=\text{C}-\text{NH}^-$) and carbodiimido ($\text{N}=\text{C}=\text{N}^-/\text{N}=\text{C}=\text{NH}$) structures, the cyanamide anions can adopt a variety of coordination modes. The cyanamide-carbodiimide resonance also leads to their exceptionally soft nature as an imide/amide anion, which enables the cyanamido ligand to form stable complexes with both early and late metals.

In our previous study, we have synthesized d^6 cyanamido-bridged complexes of (Ru(II), Ir(III))¹ and d^8 (Pd(II), Pt(II))² metals. In particular, a series of cyanamido-bridged tri-, tetra-, and pentanuclear complexes have been obtained with Pd(II) ions, while a dinuclear complex has been synthesized with Pt(II) which was further utilized as a starting material for heterometallic cluster synthesis. Now we have synthesized NHCN-bridged dinuclear Ni(II) complexes and revealed their magnetic properties.

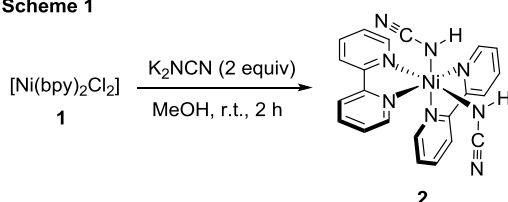
【Experimental Section】

All manipulations were carried out under an inert atmosphere by using standard Schlenk techniques. Nickel complexes were characterized by IR, X-ray diffraction, SQUID, and elemental analyses.

【Results and Discussion】

Synthesis of $[\text{Ni}(\text{NHCN})_2(\text{bpy})_2]$ (2)

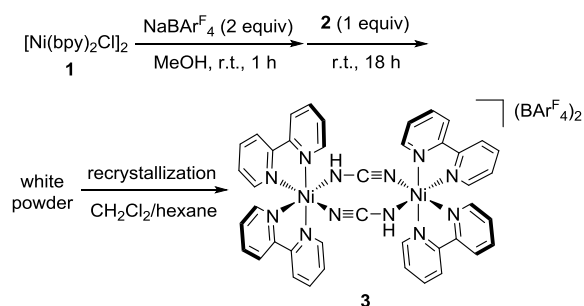
Scheme 1



A MeOH solution of $[\text{Ni}(\text{bpy})_2\text{Cl}_2]$ (**1**, bpy = 2,2'-bipyridine) and K_2NCN (2 equiv), was stirred for 2 h at r.t. The resulting green-brown solution was filtered, and the filtrate was concentrated. Slow diffusion of Et_2O into the MeOH solution afforded $[\text{Ni}(\text{NHCN})_2(\text{bpy})_2] \cdot 2\text{MeOH}$ (**2**:2MeOH) as black crystals (83% yield). Complex **2** exhibits IR absorption at 2154 cm^{-1} assignable to the NCN stretching vibrations. The molecular structure of **2** was determined by an X-ray diffraction study to confirm that the nickel center adopts a distorted octahedral structure and is coordinated by two mutually *cis* cyanamido (1-) ligands. The short terminal N-C bond distances (ca. 1.18 Å) clearly indicate that these cyanamide ligands possess a cyanamido (1-) type ($\text{Ni}-\text{NH}-\text{C}\equiv\text{N}$) structure.

Synthesis of $[\{\text{Ni}(\text{bpy})_2\}_2(\mu_2-\text{NCNH}-N,N')_2][\text{BAR}^{\text{F}}_4]_2$ (3)

Scheme 2



A MeOH solution of **1** and $\text{NaBAR}_4^{\text{F}}_4$ (2 equiv) was stirred for 1 h at r.t. The resulting blue solution was filtered, and complex **2** (1 equiv) was added to the filtrate. The mixture was stirred for 18 h at r.t. The resulting pale violet suspension was filtered, and the precipitate was collected and washed with hexane. The crude product was extracted with CH_2Cl_2 , and slow diffusion of hexane afforded $[\{\text{Ni}(\text{bpy})_2\}_2(\mu_2-\text{NCNH}-N,N')_2][\text{BAR}_4^{\text{F}}]_2$ (**3**) as violet crystals (52% yield). Complex **3** exhibits IR

absorption at 2171 cm^{-1} assignable to the NCN stretching vibration. The molecular structure of **3** was determined by an X-ray diffraction study to confirm that the two octahedral nickel centers are doubly bridged by two NHCN- N,N' ligands. The short terminal N2-C1* bond distance (1.18 Å) and the large Ni1-N2-C1* bond angle (150.7°) clearly indicate that the bridges are regarded as cyanamido (1-) ligands.

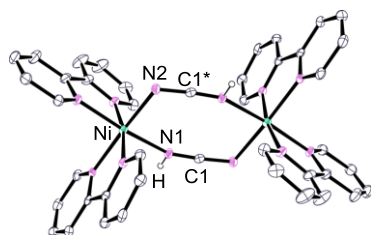
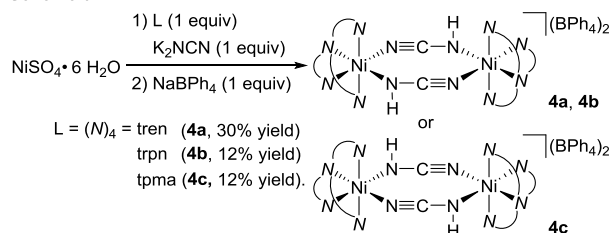


Figure 1. Molecular structure of the cationic part of **3**.

Selected bond lengths [Å] and angles [deg]: Ni-N1, 2.090(4); Ni-N2, 2.087(1); N1-C1, 1.287(6); N2-C1*, 1.180(4); Ni1-N1-C1, 121.2(4); Ni1-N2-C1*, 150.7(3); N1-C1-N2*, 175.8(5).

Synthesis of $[\{\text{Ni}(\text{L})\}_2(\mu_2\text{-NHCN-}N,N')_2][\text{BPh}_4]_2$ ($\text{L} = \text{tren}$ (4a**), trpn (**4b**), tpma (**4c**))**

Scheme 3



A mixture of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, tetradentate ligand (1 equiv, tris(2-aminoethyl)amine (tren), tris(3-aminopropyl)amine (trpn), or tris(2-pyridylmethyl)amine (tpma)), and K_2NCN (1 equiv) in H_2O was stirred for 2 h at r.t. The resulting blue solution was filtered, and NaBPh_4 (1 equiv) in H_2O was added to the filtrate. The mixture was stirred for 1 h at r.t. The resulting pale violet suspension was filtered, and the precipitate was washed with H_2O and Et_2O . The crude material was dissolved in MeCN, and slow diffusion of Et_2O into the MeCN solution afforded $[\{\text{Ni}(\text{L})\}_2(\mu_2\text{-NHCN-}N,N')_2][\text{BPh}_4]_2$ ($\text{L} = \text{tren}$ (**4a**, Figure 2), trpn (**4b**), tpma (**4c**)) in 12-30% yield. Complex **4a-c** exhibits IR absorptions at 2161-2165 cm^{-1} assignable to the NCN stretching vibration. The molecular structures of **4a-c** were determined by X-ray diffraction studies to confirm that the structure of these complexes are basically similar to that of **3**. However, the

structure of the tetradentate ligand was found to control the direction of the NHCN bridged in the dinuclear core.

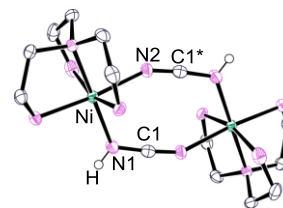


Figure 2. Molecular structure of the cationic part of **4a**.

Selected bond lengths [Å] and angles [deg]: Ni-N1, 2.066(2); Ni-N2, 2.146(2); N1-C1, 1.289(3); N2-C1*, 1.1772(1); Ni1-N1-C1, 119.69(16); Ni1-N2-C1*, 151.2(2); N1-C1-N2*, 174.7(3).

SQUID measurements of **3 and **4a-c****

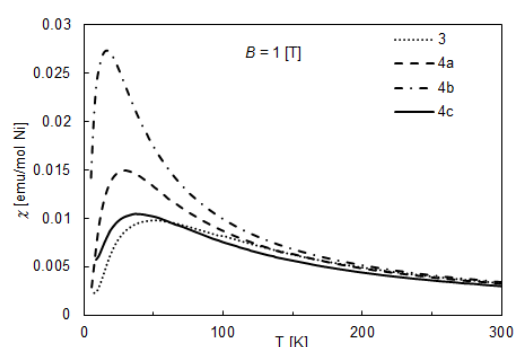


Figure 3. Temperature dependence of χ for **3**, **4a-c**.

The SQUID measurements of **3** and **4a-c** throughout the temperature range of 5-300 K are given in Figure 3. The exchange interaction constants $J = -16.7$ (**3**, < 53 K), -9.7 (**4a**, < 30 K), -5.6 (**4b**, < 17 K), and -9.7 (**4c**, < 35 K) cm^{-1} indicated that these compounds exhibit antiferromagnetism at low temperatures.

【Conclusion】

We successfully synthesized Ni(II) cyanamido mononuclear complex **2** and Ni(II) dinuclear complexes **3** and **4** with NHCN ligands. The dinuclear complexes exhibit antiferromagnetism at low temperature.

【Reference】

- 1) a) Ishii, Y. *et al. Dalton Trans.* **2007**, 4701; *Inorg. Chem.* **2009**, 48, 773.
- 2) Ishii, Y. *et al. 41st ICCS*, **2014**, FP-4.

【Presentation】

- 66th and 67th JSCC Conf. (2016, 1PA-026; 2017, 3PA-069), 97th CSJ Annual Meeting (2017, 4G5-43).