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An Extended Metal Chain with the 2,7-Bis(dipyridyldiamino)-1,8-naphthyridine (H_4bdpdany) Ligand – The Longest Even-Numbered Metal Chain Complex

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A decanickel extended metal atom chain (EMAC) complex with a new pyridyl- and naphthyridyl-modulated ligand (H_4bdpdany) was synthesized. Analysis of the crystal structure of complex $[Ni_{10}(\mu_{10}\text{-bdpdany})_4(NCS)_2](PF_6)_2$ (**1**) shows that all of the bdpdany^{4-} ligands bind the metal in an all-*syn* conformation, and structural data reveals short Ni···Ni distances in the range 2.36–2.23 Å. Temperature-dependent magnetic measurements performed on two independent high-spin nickel(II) ions of complex $[Ni_{10}(\mu_{10}\text{-bdpdany})_4(NCS)_2](PF_6)_2$ (**1**) demonstrate that the metal chain is antiferromagnetic. The longer distance between the two terminal high-spin nickel(II) ions relative to those in tetranickel and hexanickel strings causes a decrease in the magnitude of the antiferromagnetic interaction.

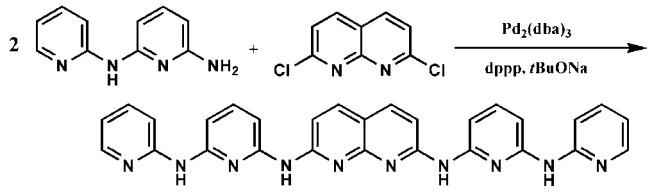
Introduction

Extended metal atom chains (EMACs)[1] are very important, because they provide a fundamental understanding of metal–metal interactions. They also hold potential for use as molecular metal wires and switches.[2] Typical EMACs consist of a linear metal chain and four supporting N ligands helically wrapped around a metal core such that all the pyridine and amido nitrogen atoms are coordinated in a *syn* conformation. Tri-, tetra-, penta-, hepta-,[3] and nonanuclear[4] EMACs wrapped by oligo-α-pyridylamino ligands were synthesized and studied over ten years ago, and it is possible to extend the system to an infinite one-dimensional molecule. Synthesis of EMACs longer than those currently available is one of our research targets; however, as the number of metal atoms in EMACs increases, the difficulty of their synthesis increases and their yield decreases. Meanwhile, it is more difficult to synthesize even-numbered metal-chains than odd-numbered metal-chains. Despite these difficulties, we have previously reported tetranickel,[5] hexanickel,[6] and octanickel chains.[7]

Here we report the synthesis and magnetic properties of a decanickel metal chain, $[Ni_{10}(\mu_{10}\text{-bdpdany})_4(NCS)_2](PF_6)_2$ (**1**), generated by treatment of H_4bdpdany with $Ni(OAc)_2{\cdot}4H_2O$ and $NiCl_2$ in the presence of boiling naphthalene. The molecular structure reveals the presence of a dicationic decanuclear Ni^{II} core $[Ni_{10}(\mu_{10}\text{-bdpdany})_4(NCS)_2]^{2+}$ assembled by four spiral and deprotonated ligands.

Results and Discussion

The ligand, H_4bdpdany, was synthesized by palladium-catalyzed cross-coupling of 2,7-dichloro-1,8-naphthyridine[8] and N^2-(pyridin-2-yl)pyridine-2,6-diamine, by a procedure based on that reported by Buchwald et al.[9] (Scheme 1). According to the NMR spectroscopic and mass spectrometric data, the ligand (H_4bdpdany) was successfully synthesized.



Scheme 1. Synthesis of H_4bdpdany.

The coordination chemistry of the H_4bdpdany ligand can be divided into two types of conformation, the all-*syn* form (complex **1**) and the all-*anti* form (complex **2**), (Scheme 2). Unfortunately, we failed to obtain a good quality crystal of complex **2**. The *R* value is high as a result of serious solvent disorder. The structure of complex **2** (Supporting Information) shows that the all-*anti* form of the H_4bdpdany ligand coordinates with two copper(II) cations (Figure S1).

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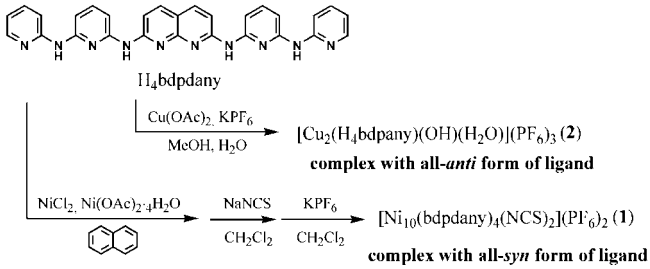
Single-crystal X-ray diffraction study of $[Ni_{10}(\mu_{10}\text{-bdpdany})_4(NCS)_2](PF_6)_2$ (**1**) reveals that the asymmetric unit contains half of the complex. The dication of **1** is located at an inversion center with 50% disorder of a spiral set of four bdpdany^{4-} ligands. (Figure 1) The decanuclear linear metal chain is helically wrapped by four all-*syn*-form-type bdpdany^{4-} ligands. All of the nickel ions and two axial N atoms are nearly collinear. Metal–metal distances decrease upon going from the end to the center of the chain. Nitrogen atoms at the amido positions have larger negative charge than the other nitrogen atoms. Therefore, the Ni2–N_{av} and Ni4–N_{av} distances are the shortest among the other Ni–N_{av} bond lengths (Table 1). In general, the bond orders of C–C and C–N bonds are inversely proportional to the bond lengths. It should be noted that the torsion angles of the naphthyridyl group are smaller than those of the pyridyl group, because the naphthyridyl unit is more rigid than the pyridyl unit. The coordination geometries of terminal nickel atoms and inner nickel atoms are square-pyramidal and square-planar, respectively. The average Ni1–N_{av} bond length is 2.077(18) Å, which is longer than the Ni–N distances for the internal Ni ions, which suggests that the terminal Ni ions are in a high-spin state, $S = 1$, and the other Ni ions are in a low-spin state, $S = 0$ (Scheme 3).

Table 1. Selected bond lengths (Å) of compound **1**.[a]

Ni1–Ni2	2.3635(18)	Ni2–Ni3	2.2749(17)
Ni3–Ni4	2.2475(17)	Ni4–Ni5	2.2329(17)
Ni5–Ni5A	2.235(2)	Ni1–N_{av}	2.077(18)
Ni2–N_{av}	1.869(17)	Ni3–N_{av}	1.902(8)
Ni4–N_{av}	1.900(15)	Ni5–N_{av}	1.937(9)

[a] Ni–N_{av}: average value for the four wrapping ligands. Symmetry operation for compound **1**: A: $-x + 2$, $-y$, $-z + 1$.



Scheme 2. The coordination chemistry of H_4bdpdany.

Redox properties of EMACs are important for research on metal–metal bonding and for potential applications of EMACs as molecular devices. Electrochemical studies of compounds **1** were performed in CH_2Cl_2 solution with TBAP as the electrolyte. Compound **1** displays rich features in its cyclic voltammogram, as shown in Figure S2. In the last analysis, the low intensity is probably caused by its poor solubility. Compound **1** exhibits four reversible redox couples at $E_{1/2}$ = –0.07, +0.52, +0.93, and +1.30 V and one irreversible redox couple at E_{pa} = –0.98 V (vs. Ag/AgCl).

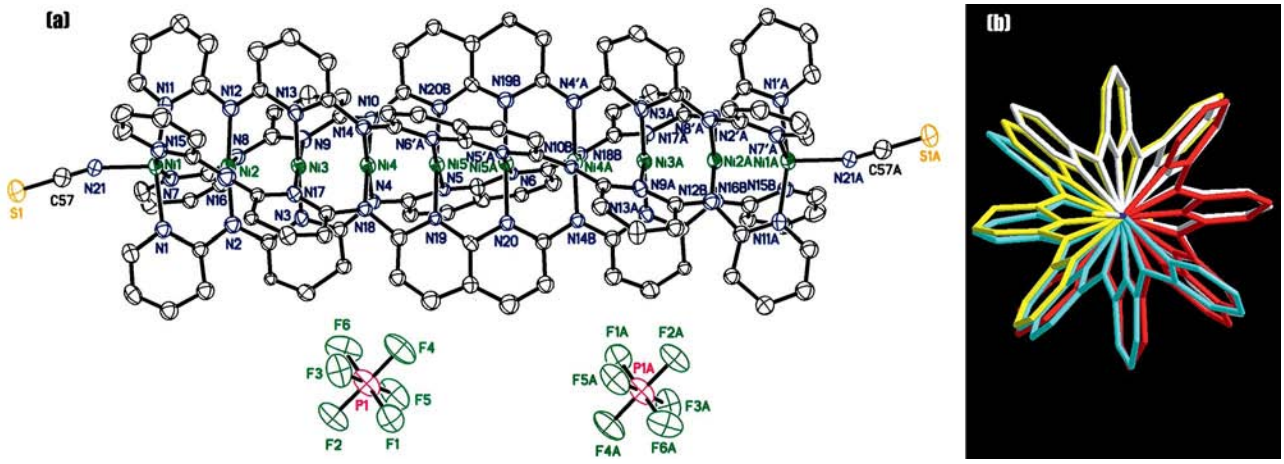
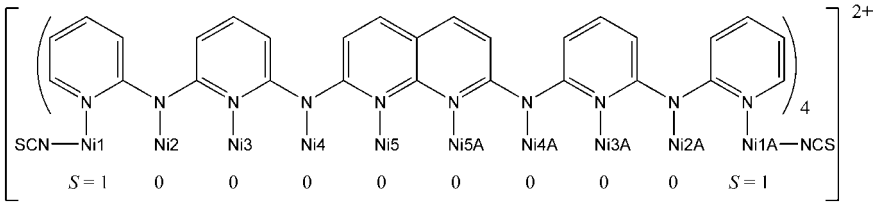


Figure 1. (a) Molecular structure of complex $[Ni_{10}(\mu_{10}\text{-bdpdany})_4(NCS)_2](PF_6)_2$ (**1**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. (b) Another view illustrating the quadruple helix along the metal chain axis.



Scheme 3. Proposed nickel spin state representations for **1**.

The first reversible redox couple at $E_{1/2}$ = –0.07 V is assigned to the reduction of Ni_{10}^{20+} to form Ni_{10}^{19+} (**1** to **1**$^{-}$), the second reversible redox couple at $E_{1/2}$ = +0.52 V is assigned to the oxidation of Ni_{10}^{20+} to form Ni_{10}^{21+} (**1** to **1**$^{+}$), and the third reversible redox couple at $E_{1/2}$ = +0.93 V is assigned to the oxidation of Ni_{10}^{21+} to form Ni_{10}^{22+} (**1**$^{+}$ to **1**$^{2+}$) (Supporting Information). All of above electrochemical processes are reversible and involve one-electron abstraction as evidenced by thin-layer spectroelectrochemical measurements. The electrochemical behavior of $[Ni_6(\mu_6\text{-bpyany})_4(NCS)_2](PF_6)_2$ shows a different result compared with compound **1**, and its cyclic voltammogram reveals that there are three redox couples at $E_{1/2}$ = –0.70, –0.22, and +1.08 V. In summary, the extended distance of metal strings resulting from modified ligands leads to greater ease in their reduction.

According to the X-ray diffraction results, we propose a spin state representation of compound **1** as shown in Scheme 3. The plot of molar susceptibility (χ_M) and effective magnetic moments (μ_{eff}/μ_B) vs. absolute temperature [K] for compound **1** are given in Figure 2. The susceptibility (χ_M) curve shows a very weak antiferromagnetic coupling between the two terminal Ni^{II} ions. Compound **1** has an effective magnetic moment of 4.71 μ_B at 300 K, which is not so consistent with the fact that the two terminal nickel ions are in a high-spin state (S = 1) and the eight internal nickel ions are in a low-spin state (S = 0). Compound **1** maintains $\mu_{eff.}$ = 4.71 μ_B from 300 K to 50 K, then slightly decreases to $\mu_{eff.}$ = 4.5 μ_B. The antiferromagnetic behavior is constant from 300 K to 50 K, revealing that the long distance between two terminal Ni atoms will decrease the antiferromagnetic interaction. The simulated results for compound **1** are as follows: $J_{1,(1A)}$ = –0.14 cm^{-1}, g = 2.35, P = 0.055 (Supporting Information). Comparing it with $[Ni_6(\mu_6\text{-bpyany})_4(NCS)_2](PF_6)_2$ and $[Ni_4(\mu_4\text{-DAniDANy})_4(H_2O)_2]$, the coupling constants increase from J = –0.14 cm^{-1} to –5.1 cm^{-1} and –40 cm^{-1}, respectively.[5,6a]

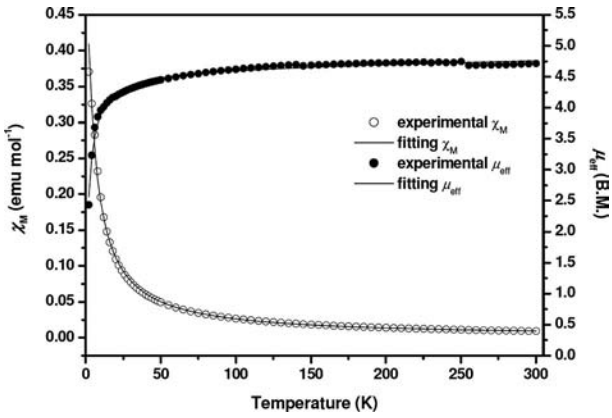


Figure 2. Magnetic behavior for compound **1**: molar magnetic susceptibility χ_M (○), temperature-dependent effective magnetic moments μ_{eff} (●), and simulations (–).

Conclusions

By using the new ligand H_4bdpdany, we successfully obtained single crystals of a decanickel EMAC. Decanickel complex **1** is the longest even-numbered EMAC synthesized to date and has a length of approximately 24.48 Å. The electrochemistry of decanuclear complex **1** demonstrates that the metal chain provides four reversible redox couples at $E_{1/2}$ = –0.07, +0.52, +0.93, and +1.30 V (vs. Ag/AgCl). The coupling constant, $J_{1,(1A)}$ = –0.14 cm^{-1}, reveals very weak interaction between the two terminal nickel atoms.

Experimental Section

Materials: All reagents and solvents were obtained from commercial sources and were used without further purification unless otherwise noted. The CH_2Cl_2 used for electrochemistry was freshly distilled prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized twice from ethyl acetate and dried under vacuum.

Physical Measurements: FAB-MS mass spectra were obtained with a JEOL JMS-700 HF double-focusing spectrometer operating in the positive ion detection mode. Molar magnetic susceptibility was recorded with a SQUID system with 2000 Gauss external magnetic field. Electrochemistry was performed with a three-electrode potentiostat (CH Instruments, Model 750A) in CH_2Cl_2 deoxygenated by purging with prepurified nitrogen gas. Cyclic voltammetry was conducted with the use of a home-made three-electrode cell equipped with a BAS glassy carbon (0.07 cm^2) or platinum (0.02 cm^2) disk as the working electrode, a platinum wire as the auxiliary electrode, and a homemade Ag/AgCl (saturated) reference electrode. The reference electrode was separated from the bulk solution by a double junction filled with electrolyte solution. Potentials are reported vs. Ag/AgCl (saturated) and referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple, which occurs at $E_{1/2}$ = +0.52 V vs. Ag/AgCl (saturated). The working electrode was polished with 0.03 μm aluminum on Buehler felt pads and was put under ultrasonic radiation for 1 min prior to each experiment. The reproducibility of individual potential values was within ±5 mV.

Synthesis of $[Ni_{10}(\mu_{10}\text{-bdpdany})_4(NCS)_2](PF_6)_2$ (1): Anhydrous $NiCl_2$ (320 mg, 2.5 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (620 mg, 2.5 mmol), H_4bdpdany (499 mg, 1.00 mmol), and naphthalene (60 g) were placed in an Erlenmeyer flask. The mixture was heated at reflux (220 °C) for 3.5 h. The solution turned dark brown. After 3.5 h the mixture was treated with hexane to precipitate the metal complexes. The precipitates were collected by suction filtration and rinsed with hexane to remove the residual naphthalene. The metal complexes were extracted with CH_2Cl_2 and treated with NaNCS (162 mg, 2.0 mmol). The solution was stirred for 6 h and then filtered. The solution was treated with KPF_6 (184 mg, 1.0 mmol) and stirred for 6 h. The solvent was removed under vacuum, and the product was extracted with CH_2Cl_2 and crystallized from a CH_2Cl_2 solution by diffusion of ether. Deep brown crystals were obtained. Yield: 73 mg (12%). IR (KBr): $\tilde{\nu}$ = 2067 (m, C≡N), 1597, 1551, 1504, 1427, 1412, 1350 (py), 841 (P–F) cm^{-1}. MS (FAB): m/z = 2681 $[Ni_{10}(\mu_{10}\text{-bdpdany})_4(NCS)_2]^+$.

Crystal Data for 1: $C_{118}H_{84}F_{12}N_{42}Ni_{10}O_2P_2S_2$, M = 3063.43, monoclinic, space group $P2_1/n$, a = 11.1391(12) Å, b = 37.270(4) Å, c = 15.6450(18) Å, β = 110.532(3)°, V = 6082.5(12) Å^3, Z = 2, ρ_{calc} = 1.673 Mg m^{-3}, R_1 = 0.0939, wR_2 = 0.2587.

Crystal Structure Determinations: The chosen crystals were mounted on a glass fiber. Data collection was carried out with a

NONIUS Kappa CCD diffractometer at 150(2) K by using Mo-K_α radiation (λ = 0.71073 Å) and a liquid nitrogen low-temperature controller. Cell parameters were retrieved and refined with the DENZO-SMN[10] software on all reflections. Data reduction was performed with DENZO-SMN software. Semiempirical absorption was based on symmetry-equivalent reflections, and absorption corrections were applied with the DENZO-SMN program. All the structures were solved with SHELXS-97 and refined with SHELXL-97 by full-matrix least-squares on $F2$ values.[11,12] The crystal data for compound **1** is listed in Table S1. CCDC-805476 contains the supplementary crystallographic data of compound **1** for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Synthetic details and magnetic measurements.

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