

Weak antiferromagnetic coupling for novel linear hexanuclear nickel(II) string complexes (Ni_6^{12+}) and partial metal–metal bonds in their one-electron reduction products (Ni_6^{11+})[†]

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Received 28th November 2005, Accepted 21st March 2006

First published as an Advance Article on the web 11th April 2006

DOI: 10.1039/b516749c

The preparation, crystal structures, magnetic properties and electrochemistry of novel linear hexanuclear nickel string complexes (Ni_6^{12+}) and their corresponding 1- e^- reduction products (Ni_6^{11+}) are reported. In these complexes, the hexanickel chain is in a symmetrical arrangement (approximately D_4 symmetry) and is helically supported by four bpyany(2-) ligands [bpyany(2-) = the dianion of 2,7-bis(*a*-pyridylamino)-1,8-naphthyridine]. The Ni_6^{12+} complexes show that the two terminal nickel ions have high-spin states ($S = 1$) and the four inner ones have low-spin states ($S = 0$). The two terminal nickel ions exhibit weak antiferromagnetic coupling of *ca.* -5 cm^{-1} . All of Ni_6^{12+} complexes display three reversible redox couples at about -0.70 , -0.20 and $+1.10 \text{ V}$ (*vs.* Ag/AgCl). The first reduction wave at about -0.20 V suggests facility of 1- e^- reduction for the Ni_6^{12+} compounds. The reaction of Ni_6^{12+} complexes with hydrazine afforded the 1- e^- reduction products (Ni_6^{11+}). As far as we are aware, the shortest bond distance of 2.202 \AA with a partial metal–metal bond was observed in Ni_6^{11+} compounds. The magnetic results of these Ni_6^{11+} compounds are in agreement with a localized model, in which the two terminal nickel ions are in a spin state of $S = 1$ whereas the central Ni(3)–Ni(4) pair in a spin state of $S = 1/2$. The Ni_6^{11+} compounds show relatively strong antiferromagnetic coupling of about 60 cm^{-1} between the terminal and the central dinickel ions.

Introduction

Metal–Metal bonding in multinuclear metal complexes has attracted much attention due to their peculiar electronic, electrochemical and magnetic properties. Numerous dinuclear metal complexes have been synthesized and their physical and chemical properties have been intensively studied.^{1–4} In the past decade, a number of multinuclear metal chains have been investigated.^{5–18} A systematic research on linear one-dimensional (*e.g.* tri-, tetra-, penta-, hepta-, nonanuclear) metal string complexes wrapped by four oligo(*a*-pyridyl)amido ligands has been studied for their delightful physical and chemical properties.^{10–18} Our STM (scanning tunneling microscopy) study¹⁵ of the one-dimensional chains suggests the promising applications as molecular wires and molecular switches as a result of bonding changes from the neutral complexes to 1- e^- oxidized ones. However, examples of 1- e^- reduction products of multinuclear complexes are rare, presumably, due

to their instability. It is well-known that the dinuclear compound of 1,8-naphthyridine (ny), $[\text{Ni}_2(\text{ny})_4\text{Br}_2](\text{BPh}_4)$, is a mixed-valence complex with nickel ions having an average charge of $+1.5$.¹⁹ This $[\text{Ni}_2(\text{ny})_4\text{Br}_2]^+$ ion may be regarded as an 1- e^- reduction product. Recently, numerous polynuclear metal complexes of naphthyridine derivatives have been synthesized and investigated, for instance, the dinuclear metal complexes with 2-pyridyl-1,8-naphthyridine (pyny) and 2,7-bispyridyl-1,8-naphthyridine (bpny).²⁰ Another interesting example is the tetranuclear molybdenum complex, $[\text{Mo}_4(\text{O}_2\text{C}(t\text{-Bu}))_6(\mu_4\text{-dhny})(\text{THF})_2]$ (dhny = dianion of 2,7-dihydroxy-1,8-naphthyridine), in which the Mo(II) ions group up to form two Mo_2 units.²¹ The structures of some naphthyridine derivatives are shown in Scheme 1.

2,7-Bis(*a*-pyridylamino)-1,8-naphthyridine (H_2bpyany) used in this paper is a hexadentate ligand and hence can support a linear chain of six metals. We have explored the linear hexacobalt complexes (Co_6^{12+}), supported by four helical bpyany(2-) ligands and their corresponding 1- e^- reduction products (Co_6^{11+}).²² There are no significant structural changes upon 1- e^- reduction of the Co_6^{12+} chain.

In the present study, we report the synthesis of the hexanuclear nickel(II) complexes wrapped by bpyany(2-) ligands and their corresponding 1- e^- reduction products. Their crystal structures and magnetic and electrochemical properties are also presented.

For clarity, the complexes described in this paper are listed as follows: $[\text{Ni}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2](\text{Y})_n$ ($n = 2$; $\text{Y} = \text{PF}_6^-$ (**1a**); $n = 2$, $\text{Y} = \text{BPh}_4^-$ (**1b**); $n = 1$, $\text{Y} = \text{PF}_6^-$ (**2**)), $[\text{Ni}_6(\mu_6\text{-bpyany})_4\text{Cl}_2](\text{PF}_6)_n$ ($n = 2$ (**3**); $n = 1$ (**4**)).

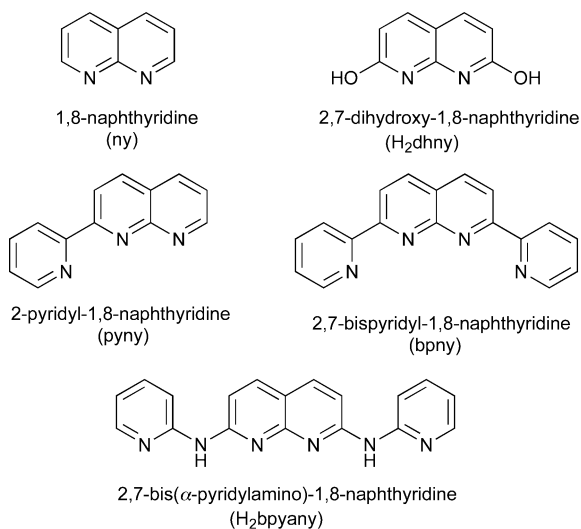
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[†]Electronic supplementary information (ESI) available: Magnetic measurements for compounds **3** and **4** in Fig. S1 and S2, respectively; a linear trinuclear model for compounds **2** and **4** in Scheme S1; EPR spectra for compounds **2** and **4** in Fig. S3 and S4, respectively. See DOI: 10.1039/b516749c

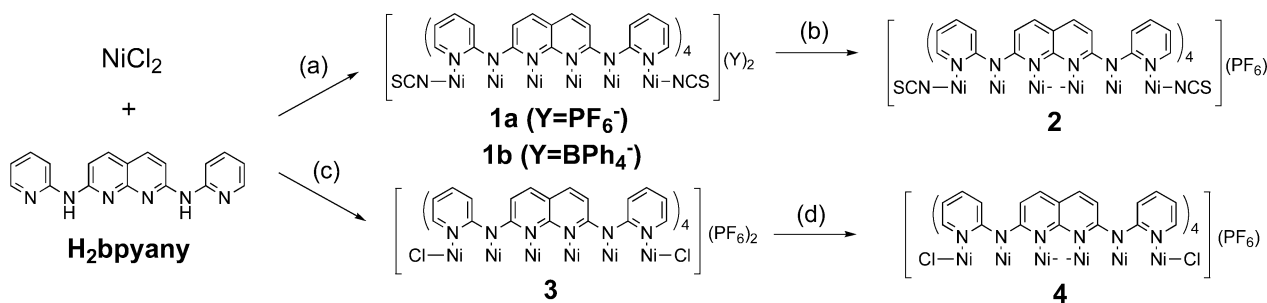


Scheme 1 1,8-Naphthyridine and its derivatives.

Results and discussion

Syntheses

The $H_2bpyany$ ligand was synthesized from the reaction of 2,7-dichloro-1,8-naphthyridine with 2-aminopyridine catalyzed by palladium.²² The synthetic routes for preparation of linear hexanuclear nickel complexes are given in Scheme 2. Treatment of $H_2bpyany$ ligand with $NiCl_2$ in the presence of *t*-BuOK, followed by excess of NaSCN and KPF_6 (or $NaBPh_4$), generated compound **1a** (or **1b**). The one-electron reduction product **2** was obtained by reacting **1a** with $N_2H_4 \cdot H_2O$ in CH_2Cl_2 . Employing a procedure similar to that for **1a** and **2**, compounds **3** and **4** can be produced in fair yields. It should be mentioned that compounds **2** and **4** are air-sensitive and hence the reactions were carried out under an argon atmosphere. Comparing with Co_6^{11+} compounds, $Ni_6^{12+/11+}$ compounds are relatively unstable. These $Ni_6^{12+/11+}$ compounds have been characterized by various spectroscopies. The IR active $C \equiv N$ stretching vibrations of compounds **1a** and **2** were observed at 2067 and 2065 cm^{-1} , respectively. The parent peaks for compounds **1a**, **1b** and **2** are all observed at m/z 1716 in FAB-MS and those for compounds **3** and **4** at m/z 1672. The isotope patterns are all in agreement with the simulation.



Scheme 2 The synthetic routes for the preparation of linear hexanuclear nickel complexes. *Reagents and conditions:* (a) (i) naphthalene/*t*-BuOK; (ii) NaSCN/ KPF_6 or $NaBPh_4$; (b) $N_2H_4 \cdot H_2O$ /anhydrous $MgSO_4$ (s) under Ar; (c) (i) naphthalene/*t*-BuOK; (ii) KPF_6 ; (d) $N_2H_4 \cdot H_2O$ /anhydrous $MgSO_4$ (s) under Ar.

Crystal structures

The crystal data for compounds **1b** and **4** are summarized in Table 1. Compound **1b** crystallizes in the orthorhombic system with space group $Pbca$. The dication of **1b** locates at two-fold symmetry with 50% disorder of a spiral set of four $bpyany(2-)$ ligands. Unfortunately, efforts to obtain good quality crystals of compound **1a**, **2** and **3** were unsuccessful. The dication of **1a** is supposed to be structurally similar to that of **1b**. Compound **4** crystallizes in the tetragonal system with space group $P4/ncc$ locating on a special position of four-fold symmetry passing through the hexanickel chain. Both $[Ni_6(\mu_6-bpyany)_4]^{n+}$ moieties for complexes **1b** ($n = 4$) and **4** ($n = 3$) are roughly in a D_4 symmetry. Thus, the average bond lengths for the both compounds were calculated by D_4 symmetry (Table 2). That is, atom $A(k)$ is equivalent to atom $A(7 - k)$ ($A = Ni, N; k = 1, 2$ or 3). In order to better understand the nature of chemical bonding in these complexes, the resonance structures of the $bpyany(2-)$ ligand have been analysed in our previous report.²² Assuming the negative charges only resonate on the nitrogen atoms then the negative charges on nitrogen atoms, and C–C and C–N bond orders are as depicted in the chemical structure drawing in Table 2. The charge distributions from outer to inner nitrogens are $-15/67$, $-30/67$ and $-22/67$, respectively. The amido positions have larger negative charge than the other nitrogen atoms. Therefore, the $Ni(2)-N(2)_{av}$ distances (1.907–1.920 Å) are the shortest among the $Ni(k)-Ni(k)$ bond distances ($k = 1, 2$ or 3). In general, the bond orders of C–C and C–N bonds are inversely proportional to the bond distances. It should be noted that the torsion angles $\varphi(3)$ for both compounds are of 13.68–15.86° smaller than the outer $\varphi(2)$ and $\varphi(1)$ of 16.25–17.57 and 18.05–19.85°, respectively, because the naphthyridyl unit is more rigid than the pyridine unit. The dication of compound **1b**, comprised by a Ni_6^{12+} core, four $bpyany(2-)$, and two thiocyanate axial ligands, is depicted in Fig. 1. The average bond distance of $Ni(1)-N(1)_{av}$ is of 2.117(8) Å, which is longer than those of Ni–N distances for the internal Ni ions, suggesting that the terminal Ni ions are in a high spin state of $S = 1$. As depicted in Fig. 2, the ORTEP drawing of compound **4** shows that the molecule consists of a Ni_6^{11+} core supported by four $bpyany(2-)$ ligands in a helical arrangement, two Cl^- axial ligands and one counter anion PF_6^- . The bond distance of $Ni(3)-Ni(4)$ is of 2.202(3) Å, which is shorter by 0.094(3) Å as compared to that of the compound **1b**. The $Ni(3)-N(3)_{av}$ bond distances are of 1.903(13) Å for **1b** and 2.009(6) Å for **4**. Based on our previous studies of multinuclear nickel and

Table 1 Crystal data for compounds **1b** and **4**

Compound	1b ·2CH ₂ Cl ₂ ·4CH ₃ CN	4 ·8CH ₂ Cl ₂ ·2H ₂ O
Formula	C ₁₃₂ H ₁₀₄ B ₂ Cl ₄ N ₃₀ Ni ₆ S ₂	C ₈₀ H ₆₈ Cl ₁₈ F ₆ N ₂₄ Ni ₆ O ₂ P
<i>M_r</i>	2690.25	2532.91
<i>T</i> /K	150(1)	150(1)
<i>λ</i> /Å	0.71073	0.71073
Crystal system	Orthorhombic	Tetragonal
Space group	<i>Pbca</i>	<i>P4/ncc</i>
<i>a</i> /Å	22.0967(2)	15.9683(7)
<i>b</i> /Å	18.7432(2)	15.9683(7)
<i>c</i> /Å	29.3512(2)	41.456(2)
<i>V</i> /Å ³ , <i>Z</i>	12156.18(19), 4	10570.7(8), 4
<i>μ</i> /mm ⁻¹	1.098	1.583
Crystal size/mm	0.33 × 0.20 × 0.03	0.32 × 0.32 × 0.30
<i>θ</i> Range for data collection/°	1.39–25.00	1.61–27.50
Reflections collected	67142	58084
Indep. reflections (<i>R_{int}</i>)	10695 (0.0918)	6028 (0.0742)
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0874, 0.2212	0.1106, 0.3232
<i>R</i> 1, <i>wR</i> 2 (all data) ^a	0.1277, 0.2479	0.1694, 0.3818
GOF	1.172	1.047

$$^a R1 = \sum \|F_o\| - |F_c| / \sum \|F_o\|; wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}; w = 1/\sigma^2(F_o^2) + (aP)^2 + bP, \text{ where } P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3.$$

Table 2 Average bond distances (Å) and torsion angles (°) for compounds **1b** and **4**^{a,b}

Compound	1b	4
Ni(1)–Ni(2)	2.403(1)	2.411(3)
Ni(2)–Ni(3)	2.314(1)	2.285(3)
Ni(3)–Ni(4)	2.296(2)	2.202(3)
Ni(1)–N(1)	2.105(2)	2.101(7)
Ni(2)–N(2)	1.907(10)	1.920(6)
Ni(3)–N(3)	1.903(13)	2.009(6)
N(1)–C(1)	1.36(3)	1.319(12)
N(1)–C(5)	1.337(20)	1.377(12)
N(2)–C(5)	1.398(17)	1.391(11)
N(2)–C(6)	1.361(17)	1.369(10)
N(3)–C(6)	1.365(18)	1.333(10)
N(3)–C(10)	1.373(14)	1.351(10)
C(1)–C(2)	1.36(3)	1.376(16)
C(2)–C(3)	1.40(3)	1.368(18)
C(3)–C(4)	1.39(3)	1.396(17)
C(4)–C(5)	1.392(20)	1.415(13)
C(6)–C(7)	1.419(19)	1.436(11)
C(7)–C(8)	1.346(20)	1.353(13)
C(8)–C(9)	1.417(20)	1.423(12)
C(9)–C(10)	1.390(9)	1.424(10)
<i>φ</i> p(1) ^c	18.05	19.85
<i>φ</i> p(2) ^c	16.25	17.57
<i>φ</i> p(3) ^c	13.68	15.86

^a *D*₄ symmetry is used to calculate average bond distances and torsion angles. ^b X = axial ligand; *n* = 2 for compound **1b**, *n* = 1 for compound **4**; charge distributions on nitrogen atoms and π bond orders of C–C and C–N bonds are also shown in the chemical drawing. ^c Torsion angle $\phi_p(k)$ (°) is defined as N(*k*)–Ni(*k*)–Ni(*k* + 1) – N(*k* + 1) for *k* = 1, 2 or 3.

cobalt string complexes,¹² the nature of axial ligands does not significantly affect the metal–metal bond distances. The structures of compound **1b** and **4** are compared although they have different axial ligands. The Ni(3)–N(3)_{av} bond shows a significant increase of 0.106(13) Å from Ni¹²⁺ to Ni¹¹⁺ compounds. Most likely, in the Ni¹¹⁺ compounds the extra electron occupies in δ bond, mainly constructed from Ni(3) and Ni(4) *d*_{x²-y² orbitals. This δ bond also has M–L σ^* bonding character. This is consistent with the shortened Ni(3)–Ni(4) distance and the elongated Ni(3)–N(3)_{av} distance. In the case of the Co₆ complexes with the bpyany(2–) ligands, the reduction occurs on the whole hexacobalt chain; that is, the extra electron is delocalized over the Co₆ unit.²² As mentioned above, the 1-e⁻ reduction of compound **1b** occurs at central Ni(3)–Ni(4) unit according to the structural analysis. In other multinuclear nickel complexes, the redox reactions may occur on the whole multinickel chain or at a specific nickel atom (*i.e.* delocalized vs. localized electronic structure). For example, the oxidized complex [Ni₃(dpa)₄](PF₆)₃ has a delocalized electronic structure on the trinickel core and the electron is removed from the trinickel chain upon one-electron oxidation of [Ni₃(dpa)₄](PF₆)₂, where dpa is the anion of dipyridylamine.^{16c} In contrast, the pentanuclear nickel complex [Ni₅(tpda)₄(OTf)₂](OTf), where tpda is dianion of tripyridylamine, has a localized electronic structure and the oxidation occurs at one of the terminal nickel ion upon oxidation of the neutral molecule [Ni₅(tpda)₄(OTf)₂].^{12c} From the X-ray structural analysis, Co₆^{11+/12+} compounds can be described as delocalized electronic structures²² whereas Ni₆^{11+/12+} compounds are predominantly regarded as localized ones.}

Electrochemistry

The electrochemical studies of compounds **1a** and **3** are performed in CH₂Cl₂ solutions with using TBAP as the electrolyte. Compound **1a** displays rich features in its cyclic voltammogram as shown in Fig. 3. Compound **1a** exhibits three reversible redox

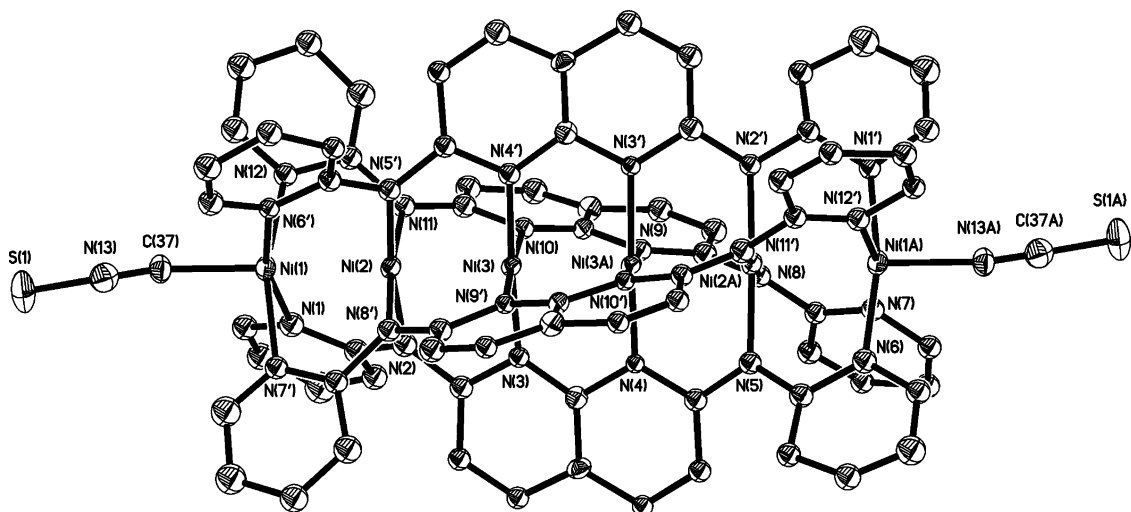


Fig. 1 ORTEP drawing of dication of complex **1b**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted and only one orientation of the four disordered bipyridine(2⁻) ligands is shown for clarity.

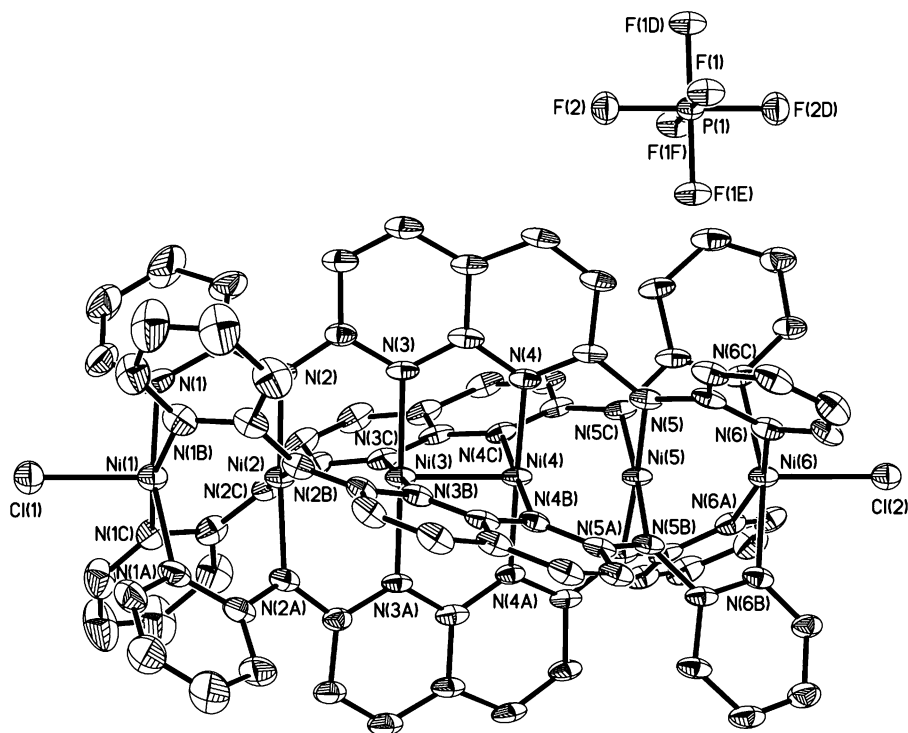


Fig. 2 ORTEP drawing of complex **4**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms and solvents are omitted for clarity. Atom labels A = (3/2 - x, 3/2 - y, z), B = (3/2 - y, x, z), C = (y, 3/2 - x, z), D = (1/2 + y, 1 - x, 1 - z), E = (1 - y, -1/2 + x, 1 - z), F = (3/2 - x, 1/2 - y, z).

couples at $E_{1/2} = -0.70$, -0.22 and $+1.08$ V (vs. Ag/AgCl). All electrochemical reactions undergo one-electron transfer, which was conformed by spectroelectrochemistry.²³ The redox reaction at $E_{1/2} = +1.08$ V corresponds to the first electron abstraction from the Ni₆¹²⁺ core. The redox couples at $E_{1/2} = -0.22$ and -0.70 V can be assigned to the first and second electron addition to the Ni₆¹²⁺ core to generate the corresponding Ni₆¹¹⁺ and Ni₆¹⁰⁺ complexes. The assignment was confirmed by the fact that the reaction of **1a** and **3** with hydrazine afforded **2** and **4**, respectively.

As expected, compounds **2** and **4** are air-sensitive and they are gradually oxidized back to **1a** and **3** in the air. The electronic spectra of **2** and **4** are identical to those obtained by electrolysis of **1a** and **3**, respectively, at an applied potential of -0.45 V. A similar electrochemical behavior for compound **3** was observed and the cyclic voltammogram reveals that there are three redox couples at $E_{1/2} = -0.73$, -0.23 and $+1.12$ V. These results indicate that the nature of the axial ligands does not significantly influence their electrochemical behavior.

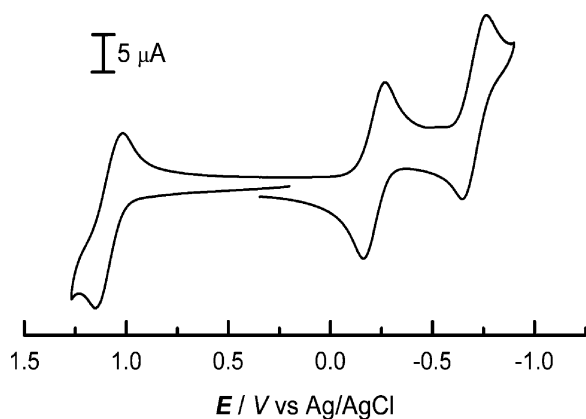


Fig. 3 The cyclic voltammogram of compound **1a** in CH_2Cl_2 containing 0.1 M TBAP with scan rate = 100 mV s^{-1} .

Magnetic properties

The plot of molar susceptibility (χ_M) and effective magnetic moments (μ_{eff}/μ_B) vs. absolute temperature (K) for compound **1a** are given in Fig. 4. The susceptibility (χ_M) curve shows antiferromagnetic coupling between the two terminal Ni(II) ions at temperatures lower than 14 K. Compound **1a** has an effective magnetic moment of $4.08 \mu_B$ at 300 K, being consistent with the fact that the two terminal nickel ions are in a high-spin state ($S = 1$) and the four internal nickel ions are in a low spin state ($S = 0$). The effective magnetic moment for compound **3** is $4.22 \mu_B$, which is comparable to that for compound **1a**. The dinuclear model of spin–spin exchange interaction is used in these hexanickel(II) compounds for data fitting¹¹ because the terminal Ni(II) are in a spin state of $S_1 = S_6 = 1$ whereas inner four Ni(II) ions in a spin state of $S_2 = S_3 = S_4 = S_5 = 0$, where S_k indicates the spin state for Ni(k) ions ($k = 1-6$). The Hamiltonian is expressed as $H = -2J_{16}S_1S_6$ where J_{16} represents the coupling constant between Ni(1) and Ni(6) ions. To obtain the coupling constant between two terminal Ni(II) ions, the χ_M is expressed by the following:¹¹

$$\chi_M = \frac{Ng^2\beta^2}{k(T - \theta)} \frac{2e^{2x} + 10e^{6x}}{1 + 3e^{2x} + 5e^{6x}} (1 - P) + \frac{2Ng^2\beta^2}{3kT} P$$

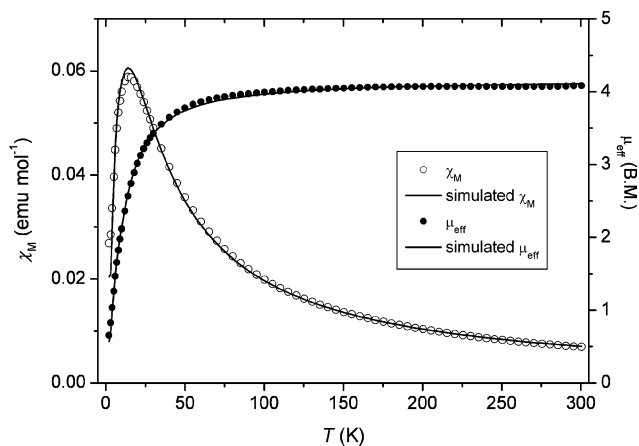


Fig. 4 The magnetic behavior for compound **1a**: molar magnetic susceptibility χ_M (\circ), temperature-dependent effective magnetic moments μ_{eff} (\bullet) and simulations (solid line, —).

where $N = 6.022 \times 10^{23}$, $\beta =$ Bohr magneton, $k =$ Boltzman constant ($0.695 \text{ cm}^{-1} \text{ K}^{-1}$), $T =$ absolute temperature (K), $\theta =$ Weiss temperature, $P =$ paramagnetic impurities where the spin state of $S = 1$ is assumed.

The simulated and experimental values for χ_M and μ_{eff} are matched well as depicted in Fig. 4. The simulated results for compound **1a** are as follows: $J_{16} = -5.1(6) \text{ cm}^{-1}$, $g = 2.1(1)$, $\theta = 0.00(2)$, $P = 0.034(13)$, $R = 1.5 \times 10^{-4}$ where R is defined as $\sum_i [(\chi_M T)_{\text{obs}}(i) - (\chi_M T)_{\text{calc}}(i)]^2 / \sum_i [(\chi_M T)_{\text{obs}}(i)]^2$. The results for compound **3** are as the following: $J_{16} = -5.0(4) \text{ cm}^{-1}$, $g = 2.19(1)$, $\theta = -0.74(1)$, $P = 0.037(5)$, $R = 4.7 \times 10^{-4}$. In our previous reports on tri-, penta-, hepta- and nonanickel string complexes, the two terminal nickel(II) ions in the complexes are in a high-spin state ($S = 1$) and the internal ones in a low-spin state ($S = 0$). The antiferromagnetic coupling constants between two terminal nickel(II) ions are calculated to be *ca.* -99 , -8.3 and -3.8 and -1.7 cm^{-1} for tri-, penta-, hepta- and nonanickel complexes, respectively.¹⁴ The coupling constant values (*ca.* -5 cm^{-1}) for compounds Ni_n^{2+} lie between those for the penta- and heptanickel complexes. These results suggest that the antiferromagnetic coupling is correlated well with the separation of the two terminal nickel ions in this series of multinickel compounds Ni_n^{2+} ($n = 3, 5, 6, 7$ or 9).

Fig. 5 shows the molar magnetic susceptibilities and effective magnetic moments with respect to absolute temperature (K) for compound **2**. The magnetic behavior is quite different from that of compounds **1a** and **3**. The effective magnetic moments for compound **2** are from $2.04 \mu_B$ at 2 K gradually increasing to $4.19 \mu_B$ at 300 K. The effective magnetic moments for compound **4** are from $1.66 \mu_B$ at 2 K gradually increasing to $4.30 \mu_B$ at 300 K. As mentioned earlier, we proposed that the 1- e^- reduction occurs in Ni(3) and Ni(4) unit and the two terminal nickel ions are in high-spin states of $S = 1$ on the basis of X-ray crystallographic studies. The theoretical magnetic moment for a spin-only system with three spin states of $S = 1, 1/2$ and 1 is calculated to be $4.36 \mu_B$. The magnetic values of 4.19 and $4.30 \mu_B$ (300 K) for compound **2** and **4** are in agreement with the calculated magnitude. Thus, a linear trinuclear model with Hamiltonian $H = -2J(S_1S_{34} + S_6S_{34}) - 2J'S_1S_6$ where J represents the coupling constant between Ni(1) (or Ni(6)) and Ni(3)–Ni(4) ions, J' between Ni(1) and Ni(6)

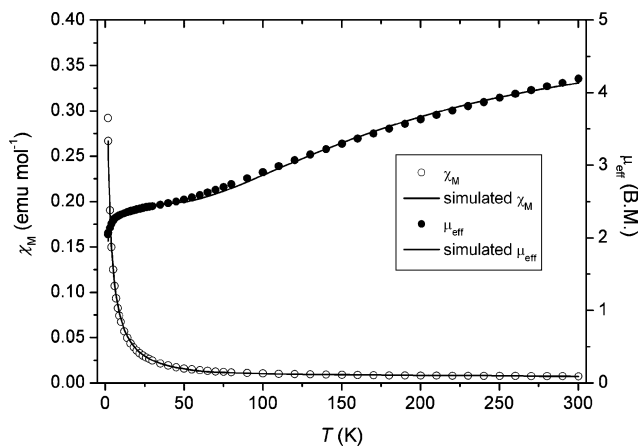


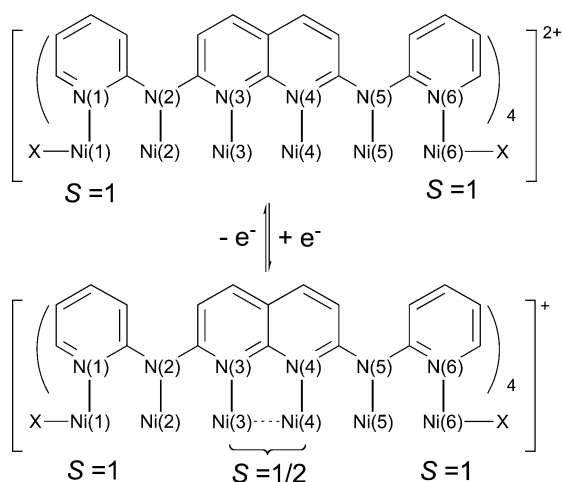
Fig. 5 The magnetic behavior for compound **2**: molar magnetic susceptibility χ_M (\circ), temperature-dependent effective magnetic moments μ_{eff} (\bullet), and simulations (solid line, —).

ions is used to simulate the magnetic data of compound **2** and **4**. Assuming $J' = 0$ and the impurities are taken into account, the χ_M with Weiss constant is expressed by the following:²⁴

$$\chi_M = \frac{Ng^2\beta^2}{k(T-\theta)} \frac{2e^{2x} + 10e^{6x}}{1 + 3e^{2x} + 5e^{6x}} (1-P) + \frac{2Ng^2\beta^2}{3kT} P$$

where $A = 1 + 10e^{3J/kT} + e^{AJ/kT} + e^{6J/kT} + 10e^{7J/kT} + 35e^{8J/kT}$, $B = 1 + 2e^{3J/kT} + e^{AJ/kT} + e^{6J/kT} + 2e^{7J/kT} + 3e^{8J/kT}$ and the other terms have their usual meanings as mentioned above. The best simulated results for compound **2** are as follows: $J = -63(1) \text{ cm}^{-1}$, $g = 2.43(2)$, $\theta = -1.1(1)$, $P = 0.026(1)$ and $R = 7.1 \times 10^{-4}$; for compound **4**: $J = -61(3) \text{ cm}^{-1}$, $g = 2.32(4)$, $\theta = -9.0(7)$, $P = 0.085(5)$ and $R = 1.7 \times 10^{-3}$, respectively, indicating relatively strong antiferromagnetic coupling between the terminal and the central dinickel ions. For compound **4**, the g value is consistent with the EPR result of 2.38, but for compound **2**, g is higher than the observed value of 2.32, suggesting the presence of zero-field splitting (zfs). As a matter of fact, a broad peak observed around 1.5 kG in EPR spectrum provides an evidence for zfs, so the average g value is increased (Fig. S3 and S4†).

The spin state changes of the nickel ions in the one-electron transfer process ($\text{Ni}_6^{12+/11+}$) can be proposed as shown in Scheme 3. For the Ni_6^{12+} complex **1** and **3**, the two terminal nickel ions are in high-spin states ($S = 1$) and the other four inner nickel ions are in low spin states ($S = 0$). Upon one-electron addition of Ni^{12+} compounds to produce Ni_6^{11+} ones, the extra electron is localized in the Ni(3)–Ni(4) unit with a spin state of $S = 1/2$ and the spin states on the other nickel ions do not change.



Scheme 3 The proposed nickel spin state representations for the respective Ni_6^{12+} and Ni_6^{11+} compounds. ($X = \text{NCS}^-$ or Cl^-).

Conclusion

We have synthesized a series of novel linear hexanuclear nickel(II) string complexes and the corresponding 1- e^- reduction products. This is the first report for linear hexanickel complexes. The Ni_6^{12+} complexes reveal weak antiferromagnetic coupling of *ca.* -5 cm^{-1} between two terminal nickel(II) ions of high-spin states ($S = 1$), consistent to our previous reports on the multinickel complexes. In electrochemical studies, the complexes exhibit three reversible redox reactions. X-Ray crystallographic determinations confirmed the identity and the structure of the 1- e^- reduction products.

Based on the crystallographic analysis of compound **4**, there is a partial metal–metal bond between Ni(3) and Ni(4) ions. The Ni(3)–Ni(4) bond distance of 2.202 Å is among the shortest nickel–nickel distances reported. The magnetic results demonstrate that the Ni_6^{11+} compounds show relatively strong antiferromagnetic coupling of about 60 cm^{-1} between the terminal and the central dinickel ions. Attempts to synthesize novel naphthyridyl-modified ligands and their corresponding metal string complexes are underway in our laboratory.

Experimental

Materials

All reagents and solvents were purchased from commercial sources and were used as received unless otherwise noted. CH_2Cl_2 was dried over CaH_2 and freshly distilled prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized twice from ethyl acetate and dried under vacuum. The 2,7-bis(*a*-pyridylamino)-1,8-naphthyridine (H_2bpyany) ligand was prepared from the reaction of 2,7-dichloro-1,8-naphthyridine with 2-aminopyridine.²²

Physical measurements

Absorption spectra were performed on a Hewlett Packard model 8453 spectrophotometer. IR spectra were obtained from a Nicolet Fourier-Transform with the range $500\text{--}4000 \text{ cm}^{-1}$. FAB mass spectra were taken on a JEOL HX-110 HF double-focusing spectrometer operating in the positive ion detection mode. Magnetic susceptibility were collected by a Quantum external magnetic field 10000 G. The diamagnetic contribution was calculated in terms of Pascal's constants. Electrochemistry was carried out on a CH Instruments, (Model 750A) using CH_2Cl_2 solvent with 0.1 M TBAP and 1 mM analytes. Cyclic voltammetry was recorded with a home-made three-electrode cell equipped with a BAS glassy carbon (0.07 cm^2) disk as the working electrode, a platinum wire as the auxiliary electrode, and a home-made Ag/AgCl (saturated) reference electrode. The reference electrode is 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 $E_{1/2} = +0.54 \text{ V vs. Ag/AgCl (saturated)}$. The working electrode was polished with $0.03 \mu\text{m}$ aluminium on Buehler felt pads and was subjected to ultrasound for 1 min prior to each experiment. The reproducibility of individual potential values was within $\approx 5 \text{ mV}$.

Syntheses

$[\text{Ni}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2](\text{PF}_6)_2$ (1a**).** Anhydrous NiCl_2 (181 mg, 1.4 mmol), H_2bpyany (251 mg, 0.80 mmol) and naphthalene (20 g) were placed in an Erlenmeyer flask. The mixture was heated (about $150\text{--}170 \text{ }^\circ\text{C}$) for 10 h with vigorous stirring, and at refluxing ($220 \text{ }^\circ\text{C}$) for 1 h. A solution of potassium *tert*-butoxide (224 mg, 2.0 mmol) in *tert*-butanol (10 mL) was added dropwise. The solution turned to dark brown. After 30 min, NaSCN (162 mg, 2.0 mmol) was added to the reacting flask. The mixture was heated for another 4 h, cooled to about $70 \text{ }^\circ\text{C}$, and 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 was extracted with CH_2Cl_2 , and treated with KPF_6 (184 mg, 1.0 mmol) in MeOH (10 mL). The solution was stirred for a day, and the solvent was removed under vacuum. The product was extracted with CH_2Cl_2 and crystallized by a CH_2Cl_2 solution layered with hexane. Deep brown crystals were obtained. Yield: 145 mg (36%). IR (KBr) ν/cm^{-1} : 2067 (C \equiv N), 1610, 1592, 1508, 1469, 1433, 1419, 1346 (py), 841 (P–F) UV/Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 286 (15.1), 415 (17.7), 566 (2.09); MS(FAB) m/z 1716 ($[\text{Ni}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2]^+$), 1658 ($[\text{Ni}_6(\mu_6\text{-bpyany})_4(\text{NCS})]^+$); EA (%): $[\text{Ni}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2](\text{PF}_6)_2$: calc.: C 44.27, H 2.41, N 18.14; found: C 44.46, H 2.55, N 18.34.

$[\text{Ni}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2](\text{BPh}_4)_2$ (1b). The procedure is similar to that for compound **1a**, except that NaBPh_4 (342 mg, 1.0 mmol) instead of KPF_6 was employed for counter anion exchange. The product was extracted with CH_2Cl_2 and recrystallized from the cosolvent CH_2Cl_2 – CH_3CN layered with hexane. Deep brown crystals were obtained. Yield: 151 mg (32%). IR (KBr) ν/cm^{-1} : 2068 (C \equiv N), 1638, 1593, 1560, 1527, 1504, 1472, 1433, 1362 (py); UV/Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 288 (12.1), 418 (17.7), 572 (1.47); MS(FAB) m/z 1716 ($[\text{Ni}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2]^+$), 1658 ($[\text{Ni}_6(\mu_6\text{-bpyany})_4(\text{NCS})]^+$); EA (%): $[\text{Ni}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2](\text{BPh}_4)_2 \cdot \text{CH}_2\text{Cl}_2 \cdot 4\text{CH}_3\text{CN}$: calc.: C 60.39, H 3.95, N 16.13; found: C 59.63, H 4.00, N 16.21.

$[\text{Ni}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2](\text{PF}_6)_2$ (2). To a solution of compound **1a** (100 mg, 0.05 mmol) in CH_2Cl_2 (50 mL) was added excess of hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) under an Ar atmosphere. The resulting solution gradually turned to dark green. After the solution was stirred for 3 h, anhydrous $\text{MgSO}_4(\text{s})$ was added to the solution to remove H_2O . The mixture was filtered through Celite. Recrystallization from a CH_2Cl_2 solution layered with hexane gave deep greenish purple crystals. Yield: 57 mg, 57%. IR (KBr) ν/cm^{-1} : 2065 (C \equiv N), 1591, 1556, 1508, 1470, 1430, 1367, 1340 (py), 838 (P–F); UV/Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 410 (18.5), 663 (2.28); MS(FAB) m/z 1716 ($[\text{Ni}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2]^+$), 1658 ($[\text{Ni}_6(\mu_6\text{-bpyany})_4(\text{NCS})]^+$); EA (%): $[\text{Ni}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2](\text{PF}_6)_2 \cdot \text{CH}_2\text{Cl}_2$: calc.: C 46.25, H 2.59, N 18.70; found: C 46.79, H 2.88, N 18.64.

$[\text{Ni}_6(\mu_6\text{-bpyany})_4\text{Cl}_2](\text{PF}_6)_2$ (3). The procedure is similar to that for the compound **1a**, except that NaNCS salt was not used. Recrystallization from a 1,2-dichloroethane solution layered with hexane afforded deep brown crystals. Yield: 78.4 mg (20%). IR (KBr) ν/cm^{-1} : 1610, 1593, 1558, 1508, 1469, 1433, 1369, 1346 (py), 839 (P–F); UV/Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 286 (13.7), 416 (17.2), 566 (1.75); MS(FAB) m/z 1672 ($[\text{Ni}_6(\mu_6\text{-bpyany})_4\text{Cl}_2]^+$), 1635 ($[\text{Ni}_6(\mu_6\text{-bpyany})_4\text{Cl}]^+$); EA (%): $[\text{Ni}_6(\mu_6\text{-bpyany})_4\text{Cl}_2](\text{PF}_6)_2 \cdot \text{ClCH}_2\text{CH}_2\text{Cl}$: calc.: C 43.12, H 2.54, N 16.31; found: C 42.92, H 2.80, N 16.67.

$[\text{Ni}_6(\mu_6\text{-bpyany})_4\text{Cl}_2](\text{PF}_6)_2$ (4). The procedure is similar to that for compound **2**, except that compound **3** (98 mg, 0.05 mmol) instead of compound **1a** was employed. Recrystallization from a CH_2Cl_2 solution layered with hexane gave deep greenish purple crystals. Yield: 60 mg, 66%. IR (KBr) ν/cm^{-1} : 1610, 1593, 1558, 1508, 1469, 1433, 1369, 1346 (py), 842 (P–F); UV/Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 290 (11.4), 410 (18.0), 665 (2.59); MS(FAB) m/z 1672 ($[\text{Ni}_6(\mu_6\text{-bpyany})_4\text{Cl}_2]^+$), 1635 ($[\text{Ni}_6(\mu_6\text{-bpyany})_4\text{Cl}]^+$); EA (%): $[\text{Ni}_6(\mu_6\text{-bpyany})_4\text{Cl}_2](\text{PF}_6)_2 \cdot 2\text{CH}_2\text{Cl}_2$: calc.: C 44.73, H 2.64, N 16.92; found: C 45.52, H 2.83, N 16.64.

bpyany) $_4\text{Cl}]^+$); EA (%): $[\text{Ni}_6(\mu_6\text{-bpyany})_4\text{Cl}_2](\text{PF}_6)_2 \cdot 2\text{CH}_2\text{Cl}_2$: calc.: C 44.73, H 2.64, N 16.92; found: C 45.52, H 2.83, N 16.64.

X-Ray crystallographic determinations

The crystals were mounted on a glass fiber. Crystal data were collected on a NONIUS Kappa CCD diffractometer with monochromatized Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at $T = 150(1) \text{ K}$. Cell parameters were retrieved and refined using DENZO-SMN software²⁵ on all observed reflections. Data reduction was performed with the DENZO-SMN software.²⁶ An empirical absorption was based on the symmetry-equivalent reflections and absorption corrections were applied with the SORTAV program. All the structures were solved by using the SHELXS-97²⁷ and refined with SHELXL-97²⁸ by full-matrix least squares on F^2 values. Hydrogen atoms were fixed at calculated positions and refined using a riding mode.

CCDC reference numbers 227616 and 288123.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516749c

Acknowledgements

We thank the National Science Council of Taiwan and the Ministry of Education of Taiwan for financial support of this work.

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