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Linear Tetranickel String Complexes with Mixed Supported Ligands and Mixed-Valence Units $[Ni_2]^{3+}$: Synthesis, Crystal Structure, and Magnetic Studies

Che-Wei Yeh,[a] Isiah Po-Chun Liu,[a,b][‡] Rui-Ren Wang,[a] Chen-Yu Yeh,[c]
Gene-Hsiang Lee,[a] and Shie-Ming Peng*[a,b]

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The synthesis, crystal structures, and magnetic properties of linear tetranickel string complexes supported by mixed 2-(α-pyridylamino)-1,8-naphthyridine (Hpyany) and *N*-(*p*-tolylsulfonyl)dipyridyldiamine (H_2tsdpda) ligands are reported. In comparing the crystal structure of $[Ni_4(pyany)_2(tsdpda)_2Cl]$ (**1**) with that of $[Ni_4(pyany)_2(tsdpda)_2Cl(H_2O)](PF_6)$ (**2**), the one-electron-reduced compound **1** displays shorter Ni(3)–Ni(4) (ca. 2.28 Å) and longer Ni(3)–N (ca. 2.02 Å) bond lengths. Similar trends have also been observed for axial NCS^--substituted derivatives $[Ni_4(pyany)_2(tsdpda)_2(NCS)]$ (**3**) and $[Ni_4(pyany)_2(tsdpda)_2(NCS)_2]$ (**4**). These structural variations indicate the formation of a mixed-valence $[Ni_2]^{3+}$ unit and a three-electron, two-center Ni(4)–Ni(3) σ bond. Magnetic measurements of **2** and **4** show that both terminal Ni(1) and Ni(4) ions are in the high-spin states (*S* = 1) and are antiferromagnetically coupled. The one-electron-reduced complexes **1** and **3**, however, exhibit a delocalized mixed-valence $[Ni_2]^{3+}$ unit ($S = {}^3/_2$), which is antiferromagnetically coupled with the terminal high-spin Ni^{II} ion.

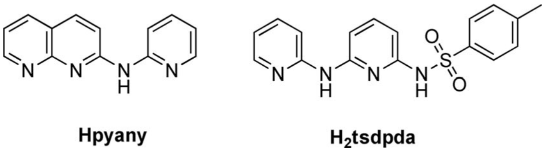
Introduction

Metal string complexes mimic the electric wires in our macroscopic world down to the atomic scale, and are expected to serve as molecular wires in the fabrication of future nanoelectronic devices.[1] Because of this potential application, numerous metal string complexes have been synthesized and characterized in the past two decades.[2] The general approach to synthesize the metal string complexes is to utilize oligo-α-pyridylamido ligands. These ligands contain numerous amido and pyridino groups, which can stabilize the cationic 1D linear transition-metal backbone.

Recently, oligo-(α-pyridylamido) ligands have been modified by insertion of naphthyridino and anilino groups. Interestingly, the resulting metal string complexes exhibit novel physical properties. For instance, the bis(naphthyridylamido) (bna^-) ligand is less anionic than the tripyridyldiamido ($tpda^{2-}$) ligand. The resulting pentanickel string complex $[Ni_5(bna)_4(NCS)_2]\cdot(NCS)_2$ has a reduced metal framework and greater electronic mobility, which shows about 40 % conductance enhancement relative to that of the $[Ni_5(tpda)_4(NCS)_2]$ complex.[3] This result suggests that the modification of supporting organic ligands is a suitable method to fine-tune the properties of metal string complexes.[2d]

In addition to the crystal structures, the physical properties of metal string complexes may also be modulated by utilizing mixed ligands. In our previous report, trinickel string complexes with various mixed ligands exhibited various spin states because of the different interactions between the axial ligands and metal ions.[4] It suggested that a novel metal string complex may be synthesized by carefully designing its surrounding ligands, since the coordinated ability and steric hindrance of these ligands are quite different, and these can modulate the physical properties of the linear metal framework.

Based on the above ideas, new tetranickel string complexes with mixed 2-(α-pyridylamino)-1,8-naphthyridine (Hpyany) and *N*-(*p*-tolylsulfonyl)dipyridyldiamine (H_2tsdpda) ligands (Scheme 1) have been synthesized and isolated. The crystal structures, and magnetic properties of these tetranickel string complexes are reported and discussed in this work.



Scheme 1. Hpyany and H_2tsdpda ligands.

For clarity, the tetranickel string complexes presented in this paper are as follows: $[Ni_4(pyany)_2(tsdpda)_2Cl]$ (**1**), $[Ni_4(pyany)_2(tsdpda)_2Cl(H_2O)](PF_6)$ (**2**), $[Ni_4(pyany)_2(tsdpda)_2(NCS)]$ (**3**), and $[Ni_4(pyany)_2(tsdpda)_2(NCS)_2]$ (**4**).

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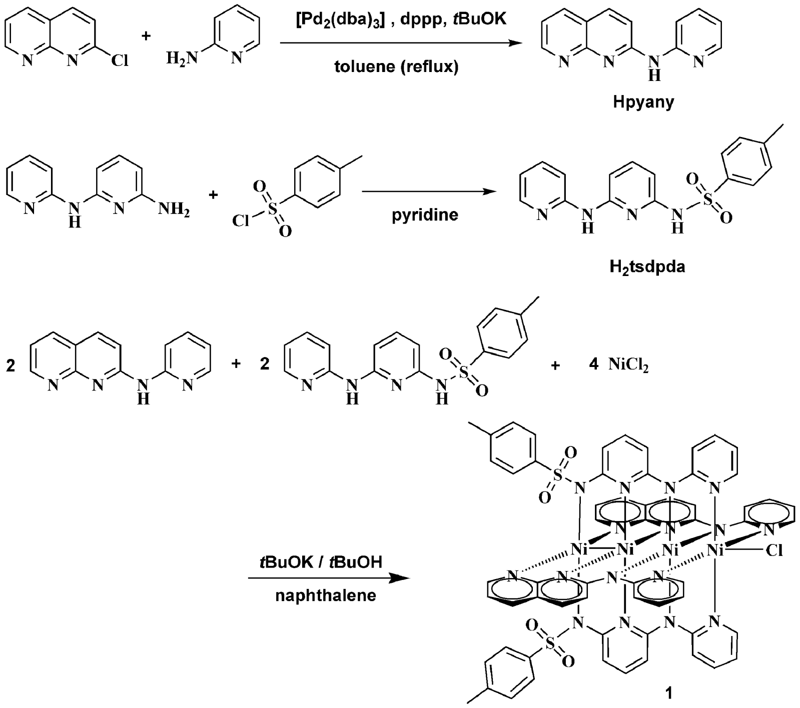
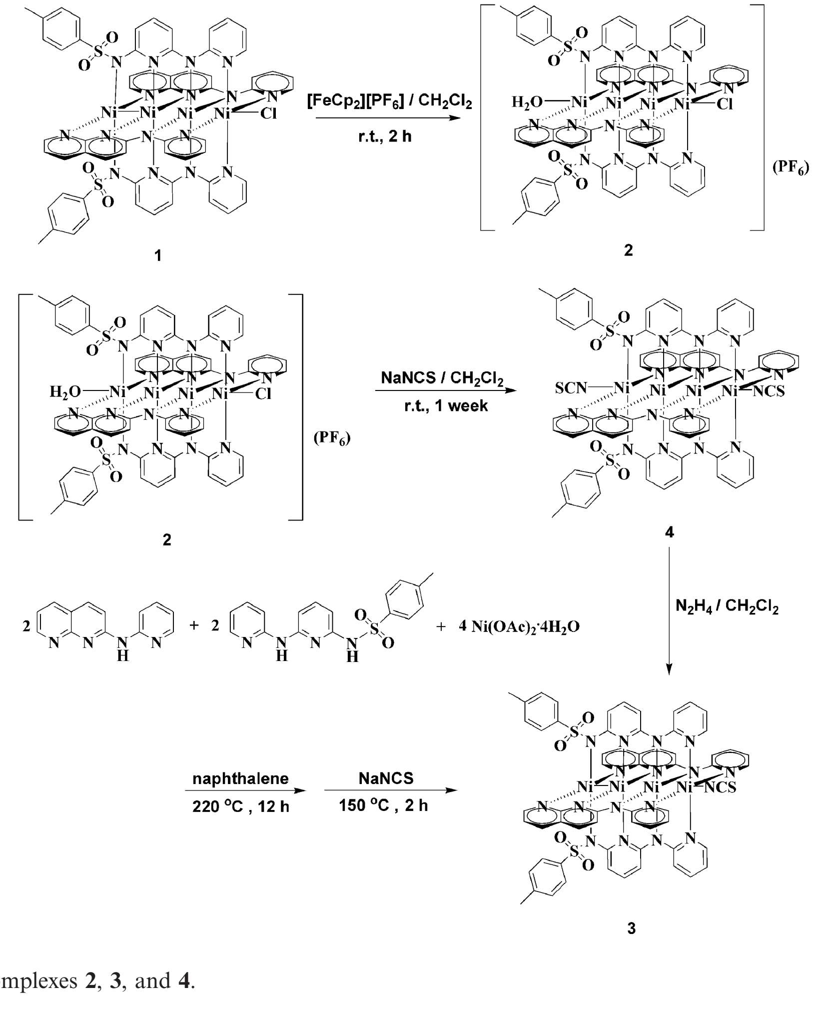
[a] Department of Chemistry, National Taiwan University,
Taipei, Taiwan
[b] Institute of Chemistry, Academia Sinica,
Taipei, Taiwan
[c] Department of Chemistry, National Chung Hsing University,
Taichung, Taiwan
[‡] Current address: Institut für Anorganische Chemie,
Universität Bonn, Bonn, Germany



Scheme 2. Synthesis of complex **1** [dba = dibenzylideneaceton; dppp = 1,3-bis(diphenylphosphanyl)propane].



Scheme 3. Synthesis of complexes **2**, **3**, and **4**.

Results and Discussion

Synthesis and Characterization

The overall synthetic routes to the Hpyany and H_2tsdpda ligands, and then to complexes **1**–**4** are summarized in Schemes 2 and 3. The Hpyany ligand was prepared by reaction of 2-chloro-1,8-naphthyridine and 2-aminopyridine with palladium catalyst. The H_2tsdpda ligand was prepared by reaction of dipyridyldiamine (H_3dpda) with *p*-toluenesulfonyl chloride (*p*TsCl) in pyridine. Treatment of Hpyany and H_2tsdpda with $NiCl_2$ in the presence of *t*BuOK generated compound **1**. The one-electron-oxidized compound **2** was obtained by treating **1** with $[FeCp_2][PF_6]$ (Cp = cyclopentadienyl) in CH_2Cl_2. The axial ligand exchange of compound **2** to generate compound **4** was achieved by stirring **2** with an excess amount of NaNCS in CH_2Cl_2. The one-electron-reduced compound **3** was obtained by treatment of **4** with N_2H_4 in CH_2Cl_2 or by reaction of Hpyany and H_2tsdpda with $Ni(OAc)_2$ in naphthalene heated at reflux followed by ligand exchange.

X-ray Analysis

The crystallographic data for **1**–**4** are listed in Table 1. The labeled ORTEP plots excluding solvent molecules and selected bond lengths for all complexes are reported in Figures 1, 2<yigr2 pos="x11">, 3, 4, and 5. The core structures of **1**–**4** reveal a tetranickel framework, which are helically wrapped by two pyany$^-$ and two tsdpda^{2-} ligands. These ligands adopt a (2,2)-*trans* arrangement, which causes these compounds to exhibit an approximate C_2 symmetry. Crystallographically, compounds **1**–**4** all exhibit one independent metal string in an asymmetric unit.

The tetranickel cores of **2** and **4** are $[Ni_4]^{8+}$, in which the coordination environment of the terminal Ni(1) and Ni(4) atoms is square pyramidal, whereas that of Ni(2) and Ni(3) is square planar. The outmost Ni(1)–N and Ni(4)–N bond lengths are around 2.10 Å, thereby suggesting a high-spin nickel(II) ($S = 1$) character.[5] The inner Ni(2) and Ni(3) are of a low-spin nickel(II) electronic configuration ($S = 0$) judging by their short Ni–N bond lengths (ca. 1.90 Å).[6] The axial ligands at the terminal Ni^{II} ions of **2** and **4** are different. The large PF_6^- ion of **2** does not bond to the Ni(4) ion due to the steric interaction with the two tolylsulfonyl groups. Instead of the PF_6^- ion, a neutral H_2O molecule occupies the axial position. Hydrogen bonds were observed between the hydrogen atoms of H_2O and oxygen atom of two tolylsulfonyl groups. The small NCS^- ligand, however, does not show steric interaction with the tolylsulfonyl groups. Compound **4** has two axial NCS^- ligands and is suitable for conductivity measurement.[3]

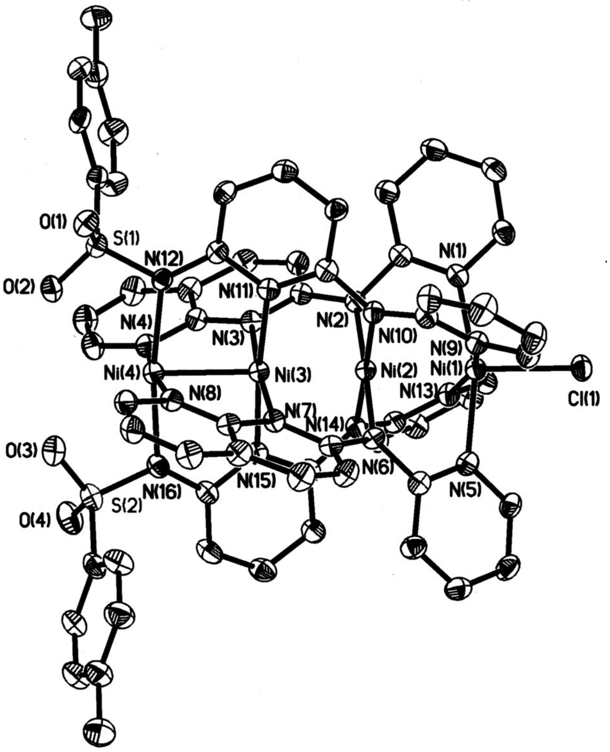


Figure 1. Molecular structure of complex **1**. Ellipsoids are drawn at 30% probability levels. Hydrogen atoms and interstitial solvent molecules have been omitted for clarity.

Table 1. X-ray crystallographic data for **1**, **2**, **3**, and **4**.

	1·$3.5CH_2Cl_2·C_6H_{14}$	**2**·$2CH_2Cl_2·Et_2O$	**3**·$4CH_2Cl_2·0.5EtOH$	**4**·$3.5CH_2Cl_2$
Formula	$C_{69.5}H_{67}Cl_8N_{16}Ni_4O_4S_2$	$C_{66}H_{62}Cl_5F_6N_{16}Ni_4O_6PS_2$	$C_{66}H_{57}Cl_8N_{17}Ni_4O_{4.5}S_3$	$C_{65.5}H_{53}Cl_7N_{18}Ni_4O_4S_4$
M_r	1815.41	1796.5	1806.95	1783.51
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a [Å]	15.0592(5)	14.3336(2)	14.9080(4)	39.7482(9)
b [Å]	15.9191(6)	14.8998(2)	15.6760(4)	16.0945(5)
c [Å]	17.8018(6)	18.7954(3)	17.6095(5)	25.8662(6)
α [°]	81.483(2)	75.8719(8)	81.8419(17)	90
β [°]	74.805(2)	87.4940(7)	75.5677(18)	118.1843(14)
γ [°]	68.839(2)	68.2975(9)	70.4780(18)	90
V [Å^3]	3833.9(2)	3611.92(9)	3748.57(17)	14585.3(7)
Z	2	2	2	8
T [K]	150(2)	150(2)	150(2)	293(2)
$\rho_{calcd.}$ [g cm^{-3}]	1.573	1.652	1.601	1.624
$R1$[a]/$wR2$[b] [$I > 2\sigma(I)$]	0.0755/0.2061	0.0759/0.2297	0.0738/0.1981	0.0711/0.1936
$R1$[a]/$wR2$[b] (all data)	0.1039/0.2331	0.1179/0.2614	0.1141/0.2330	0.1380/0.2300

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, in which $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, $P = (F_o^2 + 2F_c^2)/3$.

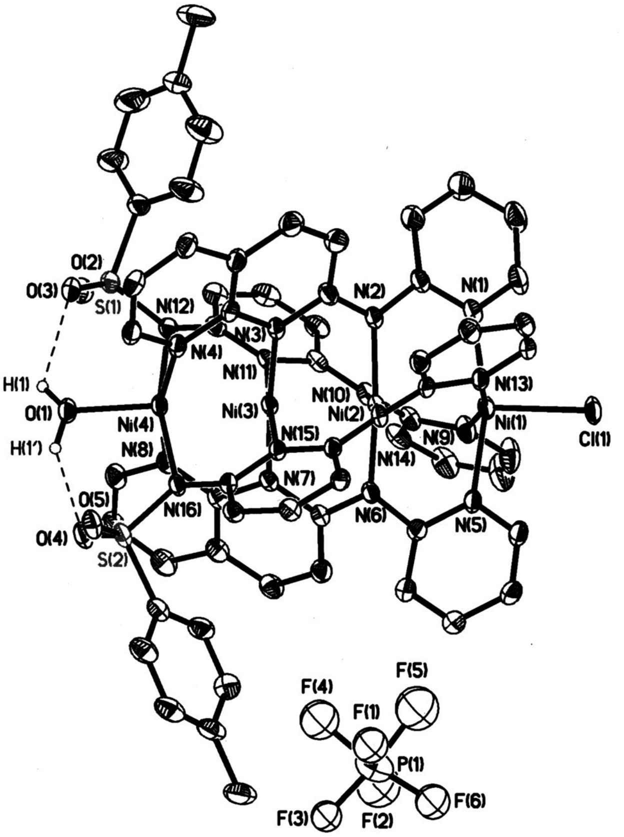


Figure 2. Molecular structure of complex **2**. Ellipsoids are drawn at 30% probability levels. Hydrogen atoms and interstitial solvent molecules have been omitted for clarity.

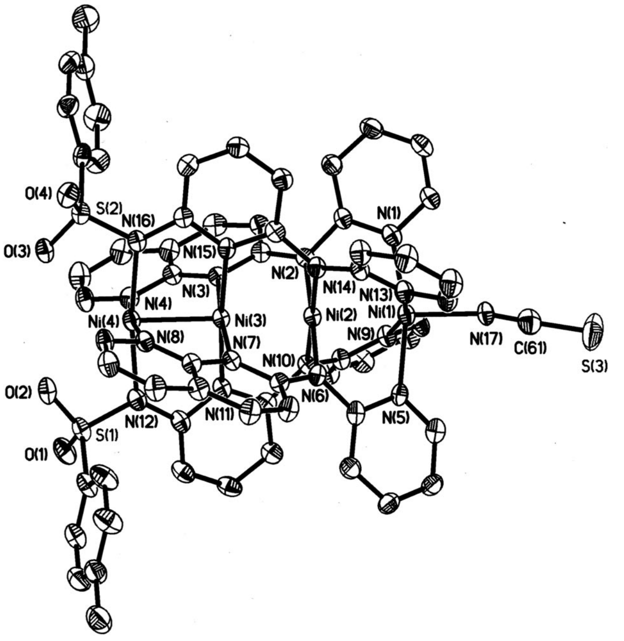


Figure 3. Molecular structure of complex **3**. Ellipsoids are drawn at 30% probability levels. Hydrogen atoms and interstitial solvent molecules have been omitted for clarity.

The one-electron-reduced compounds **1** and **3** possess a [Ni$_4$]$^{7+}$ core. Compounds **1** and **3** display a significantly shorter Ni(4)–Ni(3) bond length (ca. 2.28 Å) and a longer Ni(3)–N bond length (ca. 2.00 Å) than **2** and **4**. These structural variations indicate that an extra electron occupies the d$_{x^2-y^2}$ orbital of Ni(3), which results in the formation of a three-electron, two-center Ni(4)–Ni(3) σ bond and the $S = {}^3/_2$ mixed-valence [Ni$_2$]$^{3+}$ unit.[3,7] The Ni(1)–N and Ni(2)–N bond lengths of **1** and **3** are around 2.09 and around 1.90 Å, respectively. Considering these Ni–N bond lengths and the coordination spheres of Ni(1) (square pyramidal)

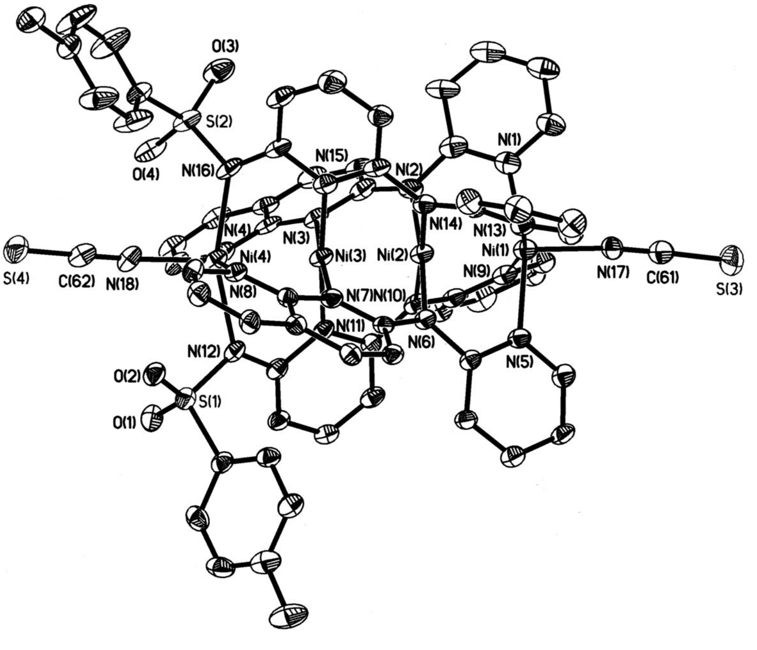


Figure 4. Molecular structure of complex **4**. Ellipsoids are drawn at 30% probability levels. Hydrogen atoms and interstitial solvent molecules have been omitted for clarity.

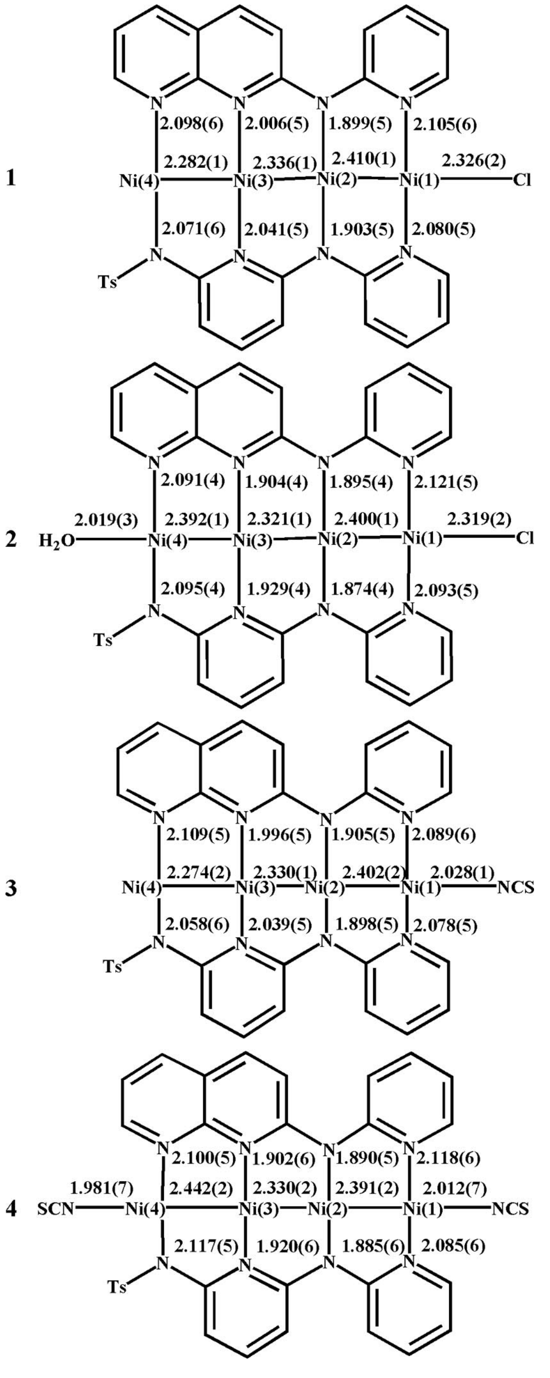
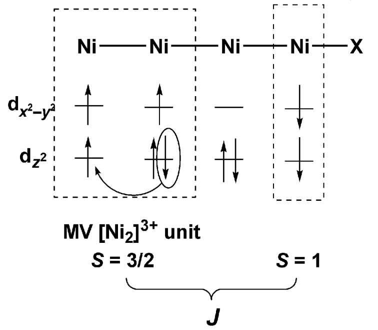


Figure 5. Selected interatomic distances [Å] observed for complexes **1**–**4**.

and Ni(2) (square planar), the Ni(1) and Ni(2) ions were assigned to high-spin ($S = 1$) and low-spin ($S = 0$) nickel(II) ions, respectively.[5,6]

In our previous reports, the mixed-valence (MV) $[Ni_2]^{3+}$ unit (Scheme 4) was found to be stabilized by four less anionic naphthyridyl groups.[3,7] The crystal structural analysis of **1** and **3**, however, suggests that the $[Ni_2]^{3+}$ unit can be stabilized by only two instead of four naphthyridyl groups, which might allow us to modulate the physical properties of metal string complexes by modifying the other two ligands.



Scheme 4. Coupling scheme for complexes **1** (X = Cl) and **3** (X = NCS).

Magnetism

Magnetic susceptibility measurements for compounds **1**–**4** were made on polycrystalline samples in the temperature range of 4–300 K (Figure 6). The $\chi_M T$ product values ($cm^3 mol^{-1} K$) of compounds **2** and **4** at 300 K are 2.03 and 1.81, respectively. These values are similar to that obtained from complexes with two uncoupled high-spin Ni^{II} ($S = 1$) ions (ca. 2).[3,6] The $\chi_M T$ values of **2** and **4** decrease gradually with decreasing temperature, which clearly indicates that an antiferromagnetic coupling is operating. To study the coupling constant of **2** and **4**, an isotropic Heisenberg–Dirac–van Vleck (HDvV) Hamiltonian – see Equation (1) – with $S_1 = S_2 = 1$ was used.[8]

$$H = -JS_1S_2 + g\beta SH \qquad (1)$$

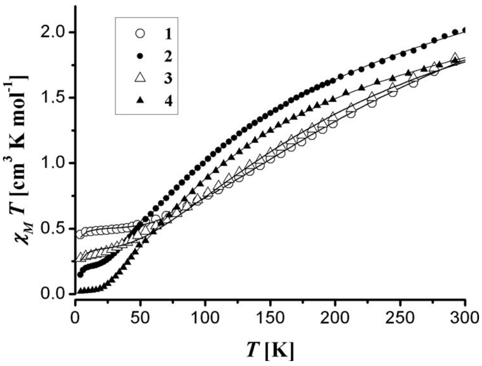


Figure 6. Plot of $\chi_M T$ versus T for complexes **1**–**4**. The solid line represents the best theoretical fit.

The best-fit parameters obtained were $J = -70.7\ cm^{-1}$ and $g = 2.04$ for **2**; $J = -68.8\ cm^{-1}$ and $g = 1.98$ for **4**. The coupling constant J is in agreement with the moderate antiferromagnetic interaction.

According to the X-ray structural analysis and our previous studies, the spin centers of **1** and **3** can be assigned to $S = ^3/_2$ and $S = 1$ (Scheme 4). The $\chi_M T$ product values ($cm^3 mol^{-1} K$) of compounds **1** and **3** at 300 K are 1.81 and 1.83, respectively, which are significantly lower than the theoretical expected value for two uncoupled $S = ^3/_2$ and S

= 1 magnetic centers (ca. 2.88), thus indicating a relative strong antiferromagnetic interaction.[9] Upon cooling, the $\chi_M T$ product values of **1** and **3** decrease rapidly to reach a value of 0.46 and 0.28, respectively, at 4 K. This pattern suggests the presence of an antiferromagnetic coupling between $S = {}^{3}/_{2}$ and $S = 1$ centers and a S = ½ ground state. By means of the appropriate HDvV Hamiltonian [see Equation (1), $S_1 = {}^{3}/_{2}$, $S_2 = 1$], the experimental susceptibility curve could be well reproduced with the set of parameter $J = -121\ \text{cm}^{-1}$ and $g = 2.12$ for **1**; $J = -89.3\ \text{cm}^{-1}$ and $g = 1.97$ for **3**, which shows a relative stronger antiferromagnetic interaction.

Conclusion

Four linear tetranickel string complexes supported by mixed pyany$^-$ and tsdpda^{2-} ligands were synthesized and studied. An X-ray crystal structural analysis and the magnetic properties of compounds **1** and **3** indicate the formation of a mixed-valence $S = {}^{3}/_{2}$ $[Ni_2]^{3+}$ unit. It was found that the $[Ni_2]^{3+}$ unit can be stabilized by two naphthyridyl-containing ligands and the remaining two surrounding ligands can be modified. It is noteworthy that even-numbered metal strings exhibit structural and magnetic behavior that is different from odd-numbered ones.[10] The physical properties of even-numbered metal string complexes, could thus be tentatively fine-tuned by utilizing various sets of mixed ligands, which introduces a new approach to the development of future metal string complexes.

Experimental Section

Materials: All reagents and solvents were purchased from commercial sources and were used as received unless otherwise noted. The precursor 2-chloro-1,8-naphthyridine and the ligand *N*-(*p*-tolylsulfonyl)dipyridyldiamine (H_2tsdpda) were prepared according to the literature procedures.[3,10]

2-(α-Pyridylamino)-1,8-naphthyridine (Hpyany): 2-Chloro-1,8-naphthyridine (4.95 g, 30.2 mmol), *t*BuOK (4.37 g, 39.0 mmol), $[Pd_2(dba)_3]$ (0.820 mg, 0.895 mmol), and dppp (0.740 mg, 1.80 mmol) were placed in a flame-dried flask under argon. The mixture was stirred and heated at reflux in toluene (150 mL) for 72 h. The solvent was removed under reduced pressure. The mixture was purified by column chromatography over silica gel (Hpyany/silica gel = 0.9 wt.-%) with CH_2Cl_2/acetone (1:4), then the yellow powder of the Hpyany was obtained. Yield: 60%. ^{1}H NMR (400 MHz, [D]DMSO): δ = 10.3 (s, 1 H), 8.81 (dd, J = 4.0, 4.8 Hz, 1 H), 8.58 (d, J = 8.8 Hz, 1 H), 8.29 (dd, J = 3.6, 4.8 Hz, 1 H), 8.19 (t, J = 19.2 Hz, 1 H), 8.18 (t, J = 16.8 Hz, 1 H), 7.80 (tt, J = 15.6, 16.0 Hz, 1 H), 7.60 (d, J = 9.2 Hz, 1 H), 7.33 (dd, J = 7.6, 8 Hz, 1 H), 6.99 (tt, J = 12.0, 12.4 Hz, 1 H) ppm. MS (FAB): m/z = 223.1 $[C_{13}N_4H_{10} + H]^+$. $C_{13}H_{10}N_4$ (222.25): calcd. C 70.26, H 4.54, N 25.21; found C 70.27, H 4.66, N 25.55.

$[Ni_4(pyany)_2(tsdpda)_2Cl]$ (1): A mixture of Hpyany (150 mg, 0.675 mmol), H_2tsdpda (230 mg, 0.675 mmol), naphthalene (30 g), and $NiCl_2$ (230 mg, 1.77 mmol) was placed in an Erlenmeyer flask. After stirring the mixture at 200 °C for 12 h, *t*BuOK (240 mg, 2.14 mmol) in *t*BuOH (3 mL) was added dropwise. The solution then turned dark green and was stirred for an additional 8 h. After cooling the mixture to 70 °C, hexane was added and the resulting precipitate was filtered out. The solid (yield 314 mg, 67%) was extracted with CH_2Cl_2 and layered with hexane. After one week, deep green crystals were obtained; yield 23.4 mg, 5%. MS (MALDI): m/z = 1390 $[Ni_4(pyany)_2(tsdpda)_2Cl + H]^+$. $C_{125}H_{106}Cl_4N_{32}Ni_8O_{10}S_4$ (2956.01): calcd. C 50.79, H 3.61, N 15.16; found C 50.46, H 3.60, N 15.28.

$[Ni_4(pyany)_2(tsdpda)_2Cl(H_2O)](PF_6)$ (2): The complex **1** (20.0 mg, 0.0144 mmol) was dissolved in CH_2Cl_2 (50 mL) and treated with $[FeCp_2][PF_6]$ (5.30 mg, 0.0170 mmol). The resulting solution was stirred for 2 h and dried under vacuum. The powder was extracted with CH_2Cl_2/diethyl ether (1:1) to get rid of the $FeCp_2$. The solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2. Brown crystals were obtained by slow diffusion of diethyl ether into this solution; yield 16.2 mg, 70%. MS (FAB): m/z = 1389 $[Ni_4(pyany)_2(tsdpda)_2Cl]^+$. $C_{121}H_{98}Cl_4F_{12}N_{32}Ni_8O_{10}P_2S_4$ (3189.82): calcd. C 45.56, H 3.10, N 14.05; found C 45.67, H 3.15, N 13.98.

$[Ni_4(pyany)_2(tsdpda)_2(NCS)]$ (3): A mixture of Hpyany (150 mg, 0.675 mmol), H_2tsdpda (230 mg, 0.675 mmol), naphthalene (30 g), and $Ni(OAc)_2{\cdot}4H_2O$ (400 mg, 1.61 mmol) was placed in an Erlenmeyer flask. After stirring the mixture at 200 °C for 18 h, the mixture was cooled to 150 °C and NaNCS (270 mg, 3.33 mmol) was added. The solution then was stirred for an additional 2 h. After cooling the mixture to 70 °C, hexane was added and the resulting precipitate was filtered out. The solid (yield 353 mg, 74%) was extracted with CH_2Cl_2 and layered with hexane. After one week, deep green crystals were obtained; yield 47.7 mg, 10%. MS (FAB): m/z = 1413 $[Ni_4(pyany)_2(tsdpda)_2NCS + H]^+$. $C_{63}H_{50}Cl_4N_{17}Ni_4O_4S_3$ (1581.96): calcd. C 47.83, H 3.19, N 15.05; found C 47.52, H 3.35, N 15.96.

$[Ni_4(pyany)_2(tsdpda)_2(NCS)_2]$ (4): Complex **2** (20.0 mg, 0.0124 mmol) was dissolved in CH_2Cl_2 (50 mL) and treated with NaNCS (10.0 mg, 0.123 mmol). The resulting solution was stirred for a week and dried under vacuum. The solid was extracted with CH_2Cl_2 and layered with hexane. After one week, deep brown crystals were obtained; yield 12.8 mg, 70%. MS (FAB): m/z = 1413 $[Ni_4(pyany)_2(tsdpda)_2NCS + H]^+$. $C_{64}H_{50}Cl_4N_{18}Ni_4O_4S_3$ (1640.05): calcd. C 46.87, H 3.07, N 15.37; found C 46.51, H 3.41, N 15.70.

Physical Measurements: FAB mass spectra were recorded with a JEOL HX-110 HF double-focusing spectrometer operating in the positive-ion detection mode. The MALDI spectra were performed with a MALDI-TOF mass spectrometer Voyager DE-STR. ^{1}H NMR spectra were recorded in DMSO with a Bruker AMX 400 MHz spectrometer. Magnetic susceptibility data were collected with a Quantum external magnetic field 3000 G instrument.

X-ray Structure Determinations: Crystallographic data were collected at 150(1) K with a NONIUS Kappa CCD diffractometer with graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å). Cell parameters were retrieved and refined with DENZO-SMN software on all observed reflections. Data reduction was performed with the DENZO-SMN software.[11] An empirical absorption was based on the symmetry-equivalent reflection, and absorption corrections were applied with the SORTAV program.[12] All the structures were solved and refined with the SHELX-97 programs.[5] The hydrogen atoms were included in calculated positions and refined with a riding mode.

CCDC-763548 (for **1**), -763680 (for **2**), -763682 (for **3**), and -763681 (for **4**) contain the supplementary crystallographic data 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.

Acknowledgments

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