Metal String Complexes: Synthesis and Crystal Structure of $[Ni_4(\mu_4\text{-phdpda})_4]$ and $[Ni_7(\mu_7\text{-teptra})_4Cl_2]$ (H_2phdpda = *N*-Phenyldipyridyldiamine and H_3teptra = Tetrapyridyltriamine)

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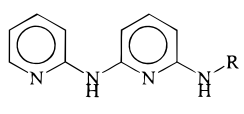
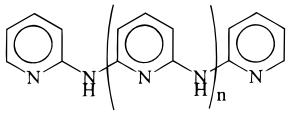
Metal string complexes are highly interesting in the fundamental study of metal−metal interactions[1−9] and in their potential application as molecular metal wires. We are interested in developing a new type of ligand, namely, oligo-α-pyridylamino ligands, **I** and **II**, which might bind metal ions in a string.[1,8,9]



I. R = ph, N-phenyldipyridyldiamine (**H_2phdpda**)



IIa. n=1, tripyridyldiamine (**H_2tpda**)
IIb. n=2, tetrapyridyltriamine (**H_3teptra**)

In previous reports, the extension of dinuclear metal complexes[10−12] to metal string complexes supported by oligo-α-pyridylamino ligands was focused on the trinuclear $[M_3(\mu_3\text{-dpa})_4X_2]$ (M = Cr,[2] Co,[3,4] Ni,[5] Cu,[6] Rh,[7] Ru;[7] dpa$^-$ = dipyridylamido anion) and pentanuclear $[M_5(\mu_5\text{-tpda})_4X_2]$ (M = Co, Ni)[8,9] complexes. Here we report two new types of metal string complexes; one contains an even number of the metal in a string of ligand **I** $[Ni_4(\mu_4\text{-phdpda})_4]$, and the other is an extension of the tri- and pentanickel(II) complexes to at this time the longest metal string of ligand **IIb** $[Ni_7(\mu_7\text{-teptra})_4Cl_2]$.

Ligand **I** was synthesized by the palladium-catalyzed cross-coupling[1,13] of (6-bromo-2-pyridyl)(2′-pyridyl)amine and aniline with high yield.[14] **I** was characterized on the basis of ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.

The nickel string complex of ligand **I** was synthesized by treating equimolar amounts of $NiCl_2$ and **I** in refluxing naphthalene and adding ^{t}BuOK as a base. The crude product was obtained by extraction using acetone and characterized by mass spectrometry (FAB) and X-ray diffraction.[15] The structure of $[Ni_4(\mu_4\text{-phdpda})_4]$, obtained by X-ray single-crystal diffraction study, shows several features as shown in Figure 1. First, the tetranickel metal chain is helically wrapped by four syn-syn-syn type phdpda^{2-} ligands, with two phenyl groups positioned in cis conformation on one side and the other two cis phenyl groups positioned on the other side. Each of the four nickel(II) ions is bonded by two cis $N_{pyridine}$ and two cis N_{amido} atoms. This arrangement may be the contributing factor to the stronger trans influence by N_{amido} than that by $N_{pyridine}$. Second, the four Ni(II) ions are collinear. The angles of Ni−Ni−Ni are nearly 180°. The Ni−Ni distances are 2.3269(6), 2.3010(6), and 2.3280(6) Å, which are comparable with the inner Ni−Ni distance (∼2.30 Å) in $[Ni_5(\mu_5\text{-tpda})_4X_2]$ complexes.[8,9] Third, the average Ni−N bonds are 1.924(4) Å for Ni(1)−N, 1.915(3) Å for Ni(2)−N, 1.913(3) Å for Ni(3)−N, and 1.927(4) Å for Ni(4)−N, comparable to the Ni−N distance found in the low-spin square-planar Ni(II) configuration and consistent with the diamagnetic behavior.[16]

The **IIb** ligand was synthesized as described in the literature[1,13] by the palladium-catalyzed cross-coupling of (6-bromo-2-pyridyl)-(2′-pyridyl)amine and (6-amino-2-pyridyl)(2′-pyridyl)amine. The nickel string complex of $[Ni_7(\mu_7\text{-teptra})_4Cl_2]$ was synthesized in a manner similar to the tri- and pentanuclear metal complexes.[17] It was identified by mass spectrometry (FAB) and X-ray diffraction. The structure of $[Ni_7(\mu_7\text{-teptra})_4Cl_2]$ is shown in Figure 2. As with the $[Ni_3(\mu_3\text{-dpa})_4Cl_2]$[5] and $[Ni_5(\mu_5\text{-tpda})_4Cl_2]$[8,9] complexes, the heptanickel chain is helically wrapped by four syn-syn-syn-syn-syn-syn type teptra^{3-} ligands. The complex exhibits approximate D_4 symmetry. The seven Ni(II) ions and the two chloride ions are collinear. Three values of Ni−Ni distances are found in this complex. The longest ones which correspond to a Ni ion connected with an axial ligand Cl$^-$ are 2.383(1) and

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(14) The H_2phdpda was synthesized by the palladium-catalyzed cross-coupling of aryl bromide and primary amine: (6-Bromo-2-pyridyl)(2′-pyridyl)-amine (10.0 g, 0.04 mol) and aniline (3.72 g, 0.04 mol) with catalyst $Pd_2(dba)_3$ (0.84 g, 0.8 mmol), dppp (0.66 g, 0.16 mmol), ^{t}BuOK (13.44 g, 0.12 mol), and 18-crown-6 ether (28.41 g, 0.12 mol) were refluxed in 200 mL of benzene for 48 h under argon. Water (150 mL) was added to remove the salt. Then, the solution was extracted by 50 mL of dichloromethane three times. A 30-g aliquot of anhydrous $MgSO_4$ powder was added to remove the water. The color of the solution was dark brown. The crude product, a dark brown powder, can be obtained by filtering and removing the solvent. The powder was recrystallized with 15 mL of dichloromethane. A pale yellow powder, H_2phdpda, was then obtained (yield 76.5%). The H_2phdpda ligand is characterized on the basis of its ^{1}H and ^{13}C NMR and mass spectrometry data. The ^{1}H in DMSO-d_6 clearly shows two singlets (9.30, 8.81 ppm), five doublets (8.19, 7.69, 7.63, 7.05, 6.32 ppm), and five triplets (7.56, 7.42, 7.24, 6.87, 6.82 ppm), which are consistent with the structural assignment. IR (KBr): ν 3258, 3172 (NH), 1606, 1589 cm^{-1} (C═C). MS (FAB): *m*/*z* (%) 263.1 (60) $[M + 1]^+$.

(15) $NiCl_2$ (0.5 g, 3.8 mmol) and H_2phdpda (1.0 g, 3.8 mmol) were placed in a Erlemyer flask, to which naphthalene (15 g) was added. The mixture was heated (∼160−180 °C) for 2 h to remove water. Then a solution of potassium *tert*-butoxide (0.8 g) in *tert*-butyl alcohol (5 mL) was added dropwise. Heating was continued until the volume of the naphthalene solution was reduced to less than 10 mL. After the mixture had cooled, *n*-hexane was added to wash out the naphthalene. The remaining solid was extracted by acetone and recrystallized from acetone/*n*-hexane. A black crystal was then obtained (yield 30%). IR (KBr): ν 1600, 1589, 1553 cm^{-1} (C═C). MS (FAB): *m*/*z* (%) 1274.3 (5) $[M]^+$. Crystal data for $[Ni_4(\mu_4\text{-phdpda})_4]\cdot C_5H_{12}$: dimensions 0.5 × 0.45 × 0.2 mm, monoclinic, space group $P2_1/n$, a = 15.2024(2) Å, b = 24.4219(1) Å, c = 17.1093(2) Å, β = 96.844(1)°, V = 6306.9(1) Å^3, Z = 4; CCD SMART diffractometer with graphite monochromated Mo Kα radiation, and Sadabs absorption correction (T_{min} = 0.54, T_{max} = 0.72). A total of 30 356 reflections were measured and 11 134 unique reflections (2θ < 55°, R_{int} = 0.057) were used in the refinement. Full-matrix least-squares refinement on F^2 converged to R_F = 0.088 (all data), 0.046 ($I > 2\sigma(I)$); R_{wF^2} = 0.134 (all data), 0.114 ($I > 2\sigma(I)$). The pentane molecule is disordered and has large thermal parameters. (U ranging from 0.352(10) to 0.483(19), $U_{av} \cong$ 0.40.)

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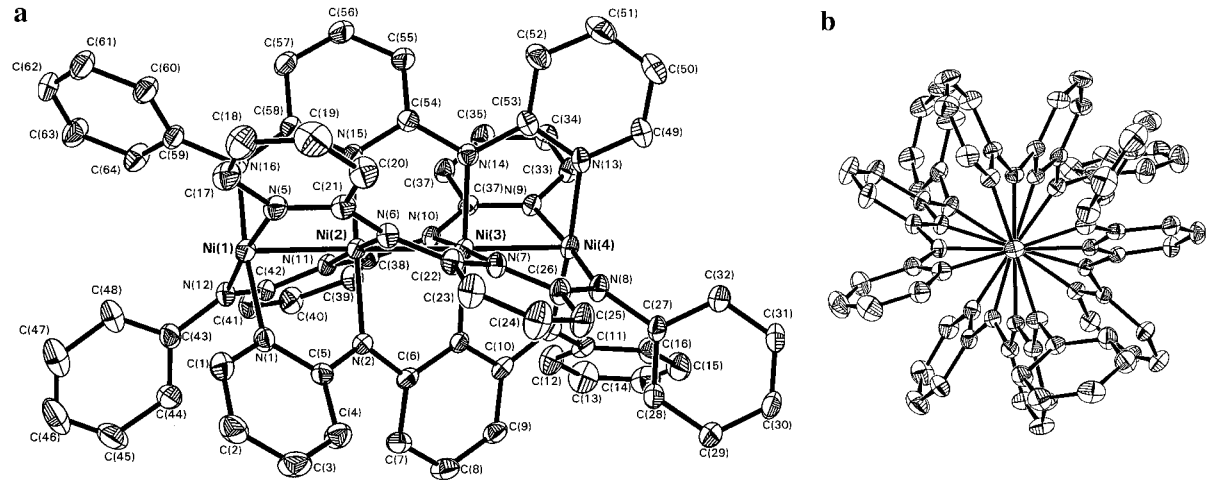

Figure 1. (a) Crystal structure of $[Ni_4(\mu_4\text{-phdpda})_4]$ (ORTEP view). Pertinent bond lengths (Å) and angles (deg): Ni(1)−Ni(2) 2.3269(6), Ni(2)−Ni(3) 2.3010(6), Ni(3)−Ni(4) 2.3280(6), $(Ni(1)-N)_{av}$ 1.924(4), $(Ni(2)-N)_{av}$ 1.915(3), $(Ni(3)-N)_{av}$ 1.913(3), $(Ni(4)-N)_{av}$ 1.927(4), Ni(1)−Ni(2)−Ni(3) 178.35(3), and Ni(2)−Ni(3)−Ni(4) 177.97(3). (b) Another illustration looking down the metal chain axis. Atoms are shown as 20% vibrational thermal ellipsoids.

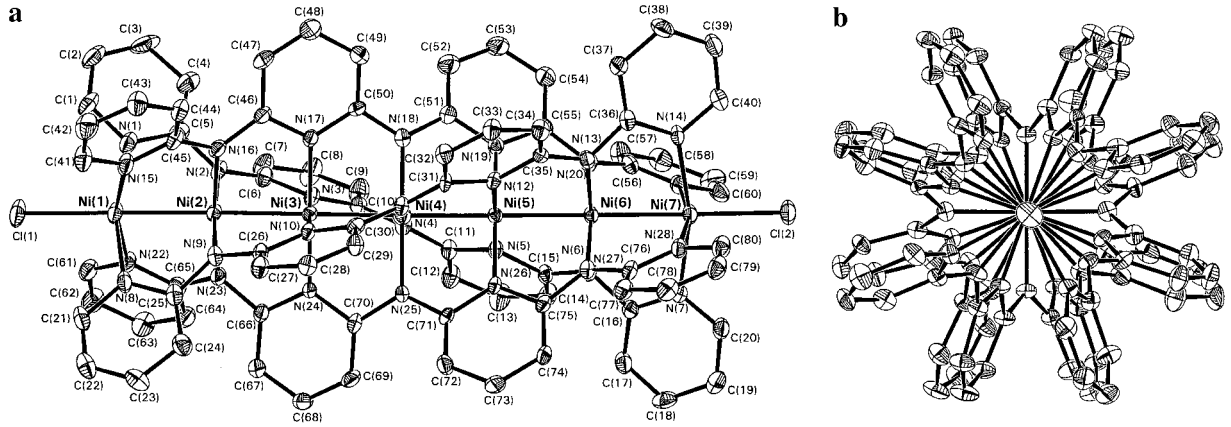

Figure 2. (a) Crystal structure of $[Ni_7(\mu_7\text{-teptra})_4]$ (ORTEP view). Pertinent bond lengths (Å) and angles (deg): Ni(1)−Ni(2) 2.383(1), Ni(2)−Ni(3) 2.310(1), Ni(3)−Ni(4) 2.225(2), Ni(4)−Ni(5) 2.215(2), Ni(5)−Ni(6) 2.304(1), Ni(6)−Ni(7) 2.374(2), Ni(1)−Cl(1) 2.370(3), $(Ni(1)-N)_{av}$ 2.112(8), $(Ni(2)-N)_{av}$ 1.903(7), $(Ni(3)-N)_{av}$ 1.917(7), $(Ni(4)-N)_{av}$ 1.922(7), $(Ni(5)-N)_{av}$ 1.910(7), $(Ni(6)-N)_{av}$ 1.888(7), $(Ni(7)-N)_{av}$ 2.104(8), Ni(7)−Cl(2) 2.357(3), Ni(1)−Ni(2)−Ni(3) 179.29(7), Ni(2)−Ni(3)−Ni(4) 179.73(7), Ni(3)−Ni(4)−Ni(5) 178.85(7), Ni(4)−Ni(5)−Ni(6) 179.75(6), Ni(5)−Ni(6)−Ni(7) 179.15(7), Cl(1)−Ni(1)−Ni(2) 179.0(1), and Cl(2)−Ni(7)−Ni(6) 179.0(1). (b) Another illustration looking down the metal chain axis. Atoms are shown as 20% vibrational thermal ellipsoids.

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2.374(2) Å. These are shorter than the Ni−Ni distance of 2.443(1) Å in $[Ni_3(\mu_3\text{-dpa})_4Cl_2]$[5] but are comparable to the outer Ni−Ni distance of 2.385(2) Å in the $[Ni_5(\mu_5\text{-tpda})_4Cl_2]$ complex.[8,9] The intermediate ones are 2.310(1) and 2.304(1) Å, which are comparable to the inner Ni−Ni distance of 2.306(1) Å in the $[Ni_5(\mu_5\text{-tpda})_4Cl_2]$ complex.[8,9] The Ni−Ni distances of the innermost Ni ions are 2.225(2) and 2.215(2) Å, which are the shortest known Ni−Ni distances in any nickel complexes. The average Ni_{inner}−N bond distances, i.e., Ni(2)−N (1.903(7) Å), Ni(3)−N (1.917(7) Å), Ni(4)−N (1.922(7) Å), Ni(5)−N (1.910(7) Å), and Ni(6)−N (1.888(7) Å) are short, consistent with a square-planar, diamagnetic arrangement of nickel(II) ions.[9,14] The terminal Ni^{II} ions (Ni(1), Ni(7)) are in a square-pyramidal environment and exhibit long Ni−Cl bonds (2.370(3), 2.357(3) Å) and long Ni(1)−N and Ni(7)−N bonds. Their average distances, 2.112(8) and 2.104(8) Å, are consistent with high-spin nickel(II) ions ($S = 1$, $\mu = 2.82\ \mu_B$; $\mu_M = 4.0\ \mu_B$). A temperature-dependent magnetic study of this complex indicates that there is a weak antiferromagnetic interaction between the two terminal high-spin nickel(II) ions with $J = -3.8\ cm^{-1}$. This interaction is smaller than those of similar trinuclear ($J = -99\ cm^{-1}$) and pentanuclear nickel(II) complexes ($J = -8.3\ cm^{-1}$).

Attempts to isolate other metal string complexes with metal−metal bonding and demonstration of their potential application as molecular metal wire are underway.

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Supporting Information Available: Tables of crystal data, atomic coordinates, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for $[Ni_4(\mu_4\text{-phdpda})_4]$ and $[Ni_7(\mu_7\text{-teptra})_4Cl_2]$ (22 pages, print/PDF). See any current masthead page for Web access instructions.

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(17) $NiCl_2 \cdot 6H_2O$ (1.66 g, 7 mmol) and H_3teptra (1.02 g, 4 mmol) were placed in a Erlemyer flask, to which naphthalene (7.2 g) was added. The mixture was heated (∼160−180 °C) for 10 min to remove water. Then 1-butanol (3 mL) was added to the heated mixtures, and heating was continued until the 1-butanol had almost completely evaporated. A solution of potassium *tert*-butoxide (1.32 g, 12 mmol) in *tert*-butyl alcohol (20 mL) was added dropwise. Heating was continued until the remaining 1-butanol had evaporated completely. After the mixture had cooled, *n*-hexane was added to wash out the naphthalene. The remaining solid was extracted with CH_2Cl_2 and recrystallized from $CHCl_3$/*n*-hexane. A deep purple crystal was then obtained (yield 10%). IR (KBr): ν 1596, 1579, 1545 cm^{-1} (C═C). MS (FAB): *m*/*z* (%) 1890 (5) $[M]^+$. Crystal data for $[Ni_7(\mu_7\text{-teptra})_4Cl_2]\cdot 3CHCl_3$: dimensions 0.35 × 0.18 × 0.15 mm, monoclinic, space group $P2_1/n$, $a = 19.7542(7)$ Å, $b = 16.9432(5)$ Å, $c = 28.5946(9)$ Å, $\beta = 95.868(1)°$, $V = 9520.4(5)$ $Å^3$, $Z = 4$; CCD SMART diffractometer with graphite monochromated Mo Kα radiation, and Sadabs absorption correction ($T_{min} = 0.61$, $T_{max} = 0.80$). A total of 38 984 reflections were measured and 16 710 unique reflections ($2\theta < 55°$, $R_{int} = 0.063$) were used in the refinement. Full-matrix least-squares refinement on F^2 converged to $R_F = 0.153$ (all data), 0.085 ($I > 2\sigma(I)$); $R_{wF^2} = 0.309$ (all data), 0.254 ($I > 2\sigma(I)$). The chloroform molecules have large thermal parameters. (U ranging from 0.261(5) to 0.595(14), $U_{av} \cong 0.41$.)