Metal String Complexes: Synthesis and Crystal Structure of [Ni₇(µ₄-phdpda)₄] and [Ni₄(µ₄-teptra)Cl₂] (H₂phdpda = N-Phenyldipipyridyldiamine and H₄teptra = Tetrapyridyltriamine)

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

In previous reports, the extension of dinuclear metal complexes to metal string complexes supported by oligo-α-ligand ligands was focused on the trinuclear [M(M₃-tpda)₃] (M = Cr,² Co,³ Ni,⁴ Cu,⁵ Rh,⁶ Ru,⁷ dpa = dipyridyl-2,2'-diamino amion) and pentanickel(II) 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 [Ni₄(µ₄-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 II [Ni₇(µ₄-teptra)Cl₂].

Ligand I was synthesized by the palladium-catalyzed cross-coupling of (6-bromo-2-pyridyl)(6-amino-2-pyridyl)amine and (6-amino-2-pyridyl)(2-pyridyl)amine. The nickel string complex of [Ni₇(µ₄-teptra)Cl₂] was synthesized in a manner similar to the tri- and pentanickel metal complexes. It was identified by mass spectrometry (FAB) and X-ray diffraction. The structure of [Ni₇(µ₄-teptra)Cl₂] is shown in Figure 2. As with the [Ni₄(µ₄-pda)Cl₄] and [Ni₄(µ₄-pda)Cl₄] complexes, the heptanickel chain is helically wrapped by four syn-syn-syn-syn-syn-type teppa⁺ligands. The complex exhibits approximate D₃₅ 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 2.383(1)

(14) The H₂phdpda 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(dba)₃ (0.84 g, 0.8 mmol), dppp (0.66 g, 0.16 mmol), BuOK (15.44 g, 0.12 mol), and 18-crown-6 ether (28.41 g, 0.12 mmol) re 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 MgSO₄ powder was added to remove the water. The solution was concentrated. 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, [(6-Bromo-2-pyridyl)(2-pyridyl)amine and (6-amino-2-pyridyl)(2-pyridyl)amine)], was obtained by X-ray single-crystal diffraction study, [Ni₇(µ₄-teptra)Cl₂], obtained by X-ray single-crystal diffraction study, shows several features as shown in Figure 1. First, the tetranickel chain is helically wrapped by four syn-syn-syn-type phosphoryl 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 Npyridine and two cis Namine atoms. This arrangement may be the contributing factor to the stronger trans influence by Npyridine than by Namine. Second, the four N(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 (2.20 Å) in [Ni₄(µ₄-pda)Cl₂] complexes. ⁶⁻³ The average Ni–Ni bonds are 1.924(4) Å for Ni(1)–Ni, 1.913(3) Å for Ni(2)–Ni, 1.913(3) Å for Ni(3)–Ni, and 1.927(4) Å for Ni(4)–Ni, comparable to the Ni–Ni distance found in the low-spin square-planar Ni(II) coordination and consistent with the diamagnetic behaviour.

The Ib ligand was synthesized as described in the literature.¹³ 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 [Ni₇(µ₄-teptra)Cl₂] was synthesized in a manner similar to the tri- and pentanickel metal complexes.¹² It was identified by mass spectrometry (FAB) and X-ray diffraction. The structure of [Ni₇(µ₄-teptra)Cl₂] is shown in Figure 2. As with the [Ni₄(µ₄-pda)Cl₄] and [Ni₄(µ₄-pda)Cl₄] complexes, the heptanickel chain is helically wrapped by four syn-syn-syn-syn-syn-type teppa⁺ ligands. The complex exhibits approximate D₃₅ 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 2.383(1).
Figure 1. (a) Crystal structure of [Ni(μ₅-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(μ₅-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 1.887(8), (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.

2.374(2) Å. These are shorter than the Ni–Ni distance of 2.443(1) Å in [Ni(μ₅-dpa)Cl₂]₄ but are comparable to the outer Ni–Ni distance of 2.385(2) Å in the [Ni(μ₅-tpdpa)Cl₂] complex. 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(μ₅-tpdpa)Cl₂] complex. 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(1.887(8) Å) are short, consistent with a square-planar, diamagnetic arrangement of nickel(II) ions. The terminal NiⅢ 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–N bonds. Their average distances, 2.112(8) and 2.104(8) Å, are consistent with high-spin nickel(II) ions (S = 1, μ = 2.82 μB; μM = 4.0 μB). 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 = −83 cm⁻¹).

Attempts to isolate other metal string complexes with 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(μ₅-phdpda)]₄ and [Ni(μ₅-teptra)Cl₂]₄ (22 pages, print/PDF). See any current masthead page for Web access instructions.

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