

Axial Extension of Metal String Complexes: Crystal Structure of $\{\text{Ni}_3(\text{dpa})_4[\text{Ag}(\text{CN})_2]_2\}$

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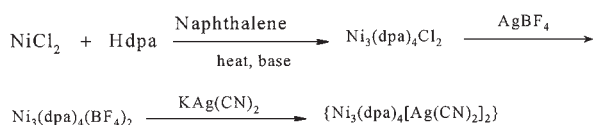
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A novel complex, $\text{Ni}_3(\text{dpa})_4[\text{Ag}(\text{CN})_2]_2$ (**1**), was synthesized and structurally characterized. The first example of metal string complex with axial metallic ligand shows length of 20.5 Å. Axial $[\text{Ag}(\text{CN})_2]^-$ ligands still remain two vacant sites, which potential possibly form longer string complex.

Polynuclear transition metal complexes have become an interesting field of molecule-based magnetic and electronic materials.¹ The first linear trinuclear complex with the di(2-pyridyl)amine (Hdpa) ligand, $\text{Cu}_3(\text{dpa})_4\text{Cl}_2$, was structurally characterized in 1990.² Since then, five similar compounds containing Ni, Co, Cr, Ru, and Rh atoms have been reported.³ To investigate the interesting topic of long linear metal string complexes for potential application as molecular wires, two strategies have been proposed. One strategy, which is to make long polypyridylamido ligands, has led to the synthesis of the nonanickel complex.⁴ Another strategy is to modify or use long axial ligands. In recent years considerable research has been done to replace the axial ligands, by such ligands as NCS^- , BF_4^- , $\text{N}(\text{CN})_2^-$, N_3^- , and PF_6^- among others.^{1b,5} Such replacement shows us that the axial ligands can tune metal-metal distances. But so far these axial ligands are all organic ligands. Our interest is to introduce metallic ligands to extend metal string complexes. The versatile $[\text{Ag}(\text{CN})_2]^-$ ligand is a linear rigid-rod bridge ligand⁶ and is widely used as a building block to form a variety of multi-dimensional coordination polymers. But very few monomer compounds containing $[\text{Ag}(\text{CN})_2]^-$ ligand have been prepared. Here we report a new linear metal string complex extended by the $[\text{Ag}(\text{CN})_2]^-$ ligand.

The title compound, $\{\text{Ni}_3(\text{dpa})_4[\text{Ag}(\text{CN})_2]_2\}$, was synthesized using a step by step (SBS) strategy,⁷ shown in Scheme 1, which, in recent years, has proved to be a good pathway to synthesize new heterometal complexes. Crystals were isolated from three solutions layered with water and acetone. The new compound is difficult to dissolve in organic solvents other than DMF and DMSO, which is in contrast to the good solubility of $\text{Ni}_3(\text{dpa})_4\text{X}_2$ ($\text{X} = \text{Cl}^-$, NCS^- , BF_4^-) with organic axial ligands in organic solvents. IR (KBr pellet, cm^{-1}): 2164(w), 1607(s), 1597(m), 1471(s), 1462(sh, s), 1431(s), 1368(m), 1358(sh, m), 1315(m), 1285(w), 1157(m), 1018(m), 765(m), 742(w), 642(w), 518(w), 433(w). MS (FAB): 1149, $[\text{NC-Ag-CN-Ni}_3(\text{dpa})_4-\text{NC-Ag}]^+$; 1017, $[\text{NC-Ag-CN-Ni}_3(\text{dpa})_4]^+$.



Scheme 1. SBS synthetic strategy of the title complex.

The crystal structure of the title compound is shown in Figure 1.⁸ In the crystal, the central fragment, $[\text{Ni}_3(\text{dpa})_4]^{2+}$, is a linear trimetallic unit with a spiral arrangement of four dipyridylamido ligands. The spiral arrangement results from steric crowding of the hydrogen atoms on the pyridyl rings, but there are no unusual bond lengths or angles in the four dpa ligands. The $[\text{Ag}(\text{CN})_2]^-$ anions in the $[\text{Ni}_3(\text{dpa})_4]^{2+}$ chromophore occupy the axial coordination sites of the two terminal nickel atoms, and the nickel-N distances differ remarkably for the terminal and central nickel atoms. Ignoring the Ni–Ni separations the central Ni atom is four-coordinate with a rhombohedral geometry and involves the four independent deprotonated nitrogen atoms of the dpa anions. Usually in low-spin square co-planar nickel systems, the Ni–N distance is about 1.90 Å,⁹ which is consistent with the mean Ni–N distance of 1.896(4) Å in the title complex. The terminal nickel atoms are five-coordinate, square pyramidal, giving a slight rhombohedral component, $\text{NiN}_4\text{N}_{(\text{CN})}$ chromophore. The mean Ni–N distance, 2.089(5) Å, is significantly longer than those of the central NiN_4 environment but is consistent with equatorial Ni–N distances of 2.0–2.1 Å¹⁰ usually found in square-based pyramidal nickel(II) compounds. Although the axial Ni– $\text{N}_{(\text{CN})}$ distance, 2.014(5) Å, is slightly shorter than those of other terminal Ni–N distances, the axial ligand, $[\text{Ag}(\text{CN})_2]^-$, can be replaced by transition metal salts via precipitation. From the structural information it is obvious that the terminal nickel atoms are high spin and the central nickel atom is low spin, which is consistent with other nickel string complexes.^{4,5b,11}

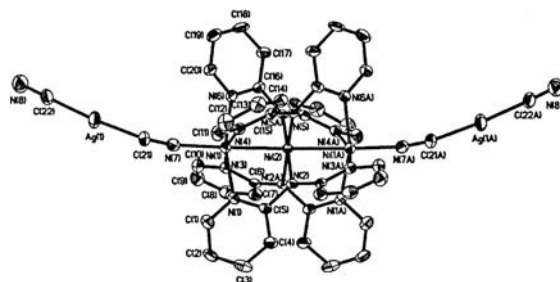


Figure 1. Perspective view of the title complex. Selected bond distances (Å) and angles (°): Ni(1)–Ni(2) 2.4030(7), Ni(1)–N(1) 2.069(5), Ni(1)–N(3) 2.109(5), Ni(1)–N(4) 2.089(5), Ni(1)–N(7) 2.014(5), Ni(2)–N(2) 1.898(4), Ni(2)–N(5) 1.895(4), Ag(1)–C(21) 2.062(6), Ag(1)–C(22) 2.053(7), C(21)–N(7) 1.130(7), Ni(1)–Ni(2)–Ni(1A) 179.02(6), Ni(1)–N(7)–C(21) 166.0(5), N(7)–C(21)–Ag(1) 170.5(6), C(21)–Ag(1)–C(22) 174.8(3).

In the title complex the Ni–Ni bonds are slightly shorter than that of $\text{Ni}_3(\text{dpa})_4\text{Cl}_2$, this situation is similar to those of $\text{Co}_3(\text{dpa})_4\text{Cl}_2$ and $\text{Co}_3(\text{dpa})[\text{N}(\text{CN})_2]_2$.¹²

The Ag–C distances are not unusual compared with other complexes containing the $[\text{Ag}(\text{CN})_2]^-$ ligand. The N(7)–C(21) distance is slightly longer than the N(8)–C(22) distance because of coordination to the nickel atom. The linear rigid-rod ligand, $[\text{Ag}(\text{CN})_2]^-$, and linear string component, $[\text{Ni}_3(\text{dpa})_4]^{2+}$, are near co-linear, which lengthens the string from 8.8 Å to 20.5 Å. The monomer structure is expected because of monodentate coordination of $[\text{Ag}(\text{CN})_2]^-$ ligand and there is no interaction between silver atoms.

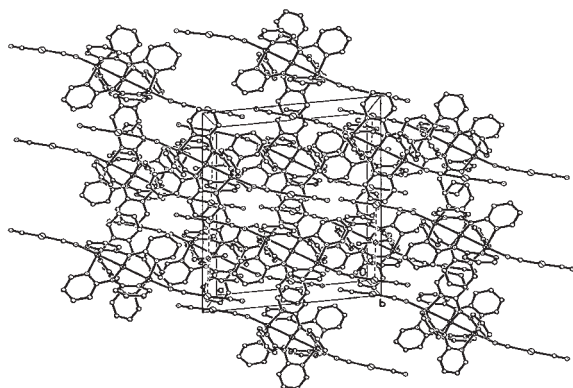


Figure 2. Packing view of the title complex.

In this work, we demonstrate the first example of a linear metal string complex with an axial metallic ligand. Because of the monodentate nature of the $[\text{Ag}(\text{CN})_2]^-$ anion in the title complex, two vacant sites are created, leaving the possibility of forming new longer string complexes. This work is currently underway in our lab.

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- Crystal data for $[\text{Ni}_3(\text{dpa})_4][\text{Ag}(\text{CN})_2]_2\text{CH}_3\text{COCH}_3$: $\text{C}_{47}\text{H}_{38}\text{Ag}_2\text{N}_{16}\text{Ni}_3\text{O}$, F.W. = 1234.80, monoclinic, space group $\text{C}2/c$, $a = 13.8618(7)$ Å, $b = 18.8781(7)$ Å, $c = 18.1690(9)$ Å, $\beta = 96.4070(10)^\circ$, $V = 4724.8$ Å³, $Z = 4$, $D_c = 1.736$ g·cm⁻³, $\mu = 2.044$ mm⁻¹, $\text{GOF} = 1.027$, $F(000) = 2472$, $T = 295$ K, crystal size 0.20 mm \times 0.07 mm \times 0.07 mm, 14998 reflections collected ($2\theta_{\text{max}} = 52.88^\circ$), 4856 independent, $R_{\text{int}} = 0.0575$, final residuals $R1 = 0.047$, $wR2 = 0.1107$ ($I \geq 2\sigma(I)$); $R = 0.1072$, $wR2 = 0.1258$ (all data). Intensity data were collected on a Bruker Smart CCD using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effect. Absorption corrections were applied with the program SADABS.
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