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Unsymmetrical Linear Pentanuclear Nickel String Complexes: $[Ni_5(tpda)_4(H_2O)(BF_4)](BF_4)_2$ and $[Ni_5(tpda)_4(SO_3CF_3)_2](SO_3CF_3)$

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The one-electron oxidized linear pentanuclear nickel complexes $[Ni_5(tpda)_4(H_2O)(BF_4)](BF_4)_2$ (**1**) and $[Ni_5(tpda)_4(SO_3CF_3)_2](SO_3CF_3)$ (**2**) have been synthesized by reacting the neutral compound $[Ni_5(tpda)_4Cl_2]$ with the corresponding silver salts. These compounds have been characterized by various spectroscopic techniques. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 15.3022(1)$ Å, $b = 31.0705(3)$ Å, $c = 15.8109(2)$ Å, $\beta = 92.2425(4)°$, $V = 7511.49(13)$ Å^3, $Z = 4$, and compound **2** crystallizes in the monoclinic space group $C2/c$ with $a = 42.1894(7)$ Å, $b = 17.0770(3)$ Å, $c = 21.2117(4)$ Å, $\beta = 102.5688(8)°$, $V = 14916.1(5)$ Å^3, $Z = 8$. X-ray structural studies reveal an unsymmetrical Ni_5 unit for both compounds **1** and **2**. Compounds **1** and **2** show stronger Ni–Ni interactions as compared to those of the neutral compounds.

Much attention has been paid to linear multinuclear metal string complexes because of their attractive properties such as strong metal−metal interactions in the molecules and their potential to be applied as molecular electronics.[1−13] A number of multinuclear metal string complexes have been prepared and structurally characterized since the first reports of the trinuclear copper and nickel complexes bridged by di-2-pyridylamido ligand (dpa) in 1990−1991.[1,2] Previous reports showed that there are no metal−metal bonds in the neutral form of tri-, penta-, hepta-, and nonanuclear nickel complexes.[3,4] In these multinuclear nickel complexes, all the internal nickel ions are in a low-spin state, whereas the two external nickel ions are in a high-spin state with $S = 1$. The antiferromagnetic coupling constants between the two terminal nickel ions are -99, -8.3, -3.8, and -1.7 cm^{-1} for the tri-, penta-, hepta-, and nonanickel dichloride complexes, respectively.[4] Recently, Cotton et al. reported significant results for oxidized trinickel complex $[Ni_3(dpa)_4(PF_6)_2](PF_6)$,[5] in which the Ni−Ni and Ni−N bond lengths are much shorter

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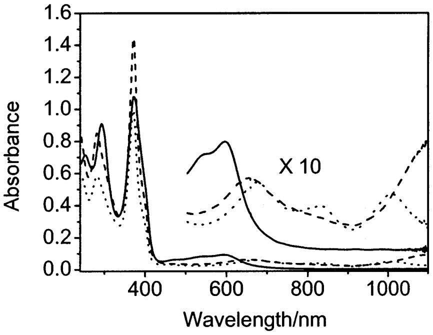

Figure 1. UV−vis spectra of (a) $[Ni_5(tpda)_4Cl_2]$ (—); (b) **1** (− −); (c) **2** (···) in CH_2Cl_2. Concentration: 1.0×10^{-5} M.

as compared to those of neutral analogue $[Ni_3(dpa)_4Cl_2]$. At the time their work was reported, we had synthesized the one-electron oxidation counterparts of the linear pentanuclear nickel string complexes. We report here the synthesis and the unusual unsymmetrical structures, including the unequal metal−metal bonds, of the linear one-electron oxidation pentanuclear string complexes, $[Ni_5(tpda)_4(H_2O)(BF_4)](BF_4)_2$ (**1**) and $[Ni_5(tpda)_4(SO_3CF_3)_2](SO_3CF_3)$ (**2**) ($tpdaH_2$ = tripyridyldiamine), along with their magnetic properties. To the best of our knowledge, compounds **1** and **2** are the first linear multinickel complexes with an unsymmetrical structure.

The one-electron oxidation of the pentanuclear nickel complexes were achieved by the reaction of excess silver salts and $[Ni_5(tpda)_4Cl_2]$ (**3**). Two one-electron oxidation products, **1** and **2**, were obtained and characterized by various spectroscopic methods such as mass spectrometry, UV−vis and IR spectroscopies, and X-ray diffraction. The UV−vis−NIR spectra of complexes **1** and **2** showed significant differences from that of the neutral compound, $[Ni_5(tpda)_4Cl_2]$. As shown in Figure 1, upon one-electron oxidation, the peaks for $[Ni_5(tpda)_4Cl_2]$ at 292, 373, 480, 548, and 594 nm shifted to 281, 372, 652, and 1150 nm for **1**, and 282, 372, 669, 832, and 1010 nm for **2**.

The most unambiguous confirmation for compounds **1** and **2** is from the X-ray crystal structures. Some selected bond distances for **1**, **2**, **3**, and $[Co_5(tpda)_4(NCS)_2]$ (**4**) are given in Table 1.[14] In compound **1**, five nickel ions are helically supported by four $tpda^{2-}$ ligands in a spiral configuration and essentially form a linear arrangement as shown in Figure 2. The axial ligands are provided by a BF_4^- anion and a H_2O molecule. The two positive charges in the Ni_5 core are compensated by two BF_4^- anions. The axial H_2O ligand forms a H-bond with one of the BF_4^- ions, in which the O(1)−F(10) distance is 2.707 Å. The nickel axial ligand bond distances are 2.252(6) and 2.475(4) Å for Ni(1)−O(1) and Ni(5)−F(1), respectively. The most striking feature in the crystal structure of **1** is that the Ni_5 chain of the molecule adopts an unsymmetrical structure with Ni−Ni distances of 2.337(1), 2.261(1), 2.245(1), and 2.300(1) Å for Ni(1)−Ni(2), Ni(2)−Ni(3), Ni(3)−Ni(4), Ni(4)−Ni(5), respectively. Compared to the Ni−Ni bond lengths in **3**, both the internal and external Ni−Ni bond distances in compounds **1** and **2** are shorter by 0.04−0.08 Å. Unlike the case of compound **3** where the Ni−N distances for the terminal Ni ions are considerably longer than those for the internal Ni ions, the average Ni−N distances in **1** are 2.022(6), 1.896(5), 1.911(5), 1.891(5), and 1.929(5) Å for Ni(1), Ni(2), Ni(3), Ni(4), and Ni(5), respectively. These results indicate that Ni(1) is in a high-spin state while the other four Ni ions are in a low-spin state, and the one-electron oxidation occurs at the terminal Ni(5) ion. However, we cannot rule out the possibility of the positive charge being delocalized in the four low-spin nickel ions simply by the crystal data.

Table 1. Selected Bond Distances for **1**, **2**, **3**, and **4**

	1	**2**	**3**	**4**
M(1)−X[a]	2.252(7)	2.059(7)	2.346(3)	2.07(1)
M(5)−Y[a]	2.475(4)	2.338(8)	2.346(3)	2.06(1)
M(1)−M(2)	2.337(1)	2.358(2)	2.385(2)	2.281(3)
M(2)−M(3)	2.261(1)	2.276(2)	2.306(1)	2.236(3)
M(3)−M(4)	2.245(1)	2.245(2)	2.306(1)	2.233(3)
M(4)−M(5)	2.300(1)	2.304(1)	2.385(2)	2.277(3)
M(1)−N	2.022(6)	2.081(10)	2.111(9)	1.96(1)
M(2)−N	1.896(5)	1.874(10)	1.90(2)	1.90(1)
M(3)−N	1.911(5)	1.904(9)	1.904(8)	1.93(1)
M(4)−N	1.891(5)	1.885(11)	1.90(2)	1.90(1)
M(5)−N	1.929(5)	1.948(9)	2.111(9)	1.96(1)

[a] X, Y = axial ligands: X = H_2O, Y = BF_4^- for **1**; X = Y = $CF_3SO_3^-$ for **2**; X = Y = Cl^- for **3**; X = Y = NCS^-, M = Co^{II} for **4**.

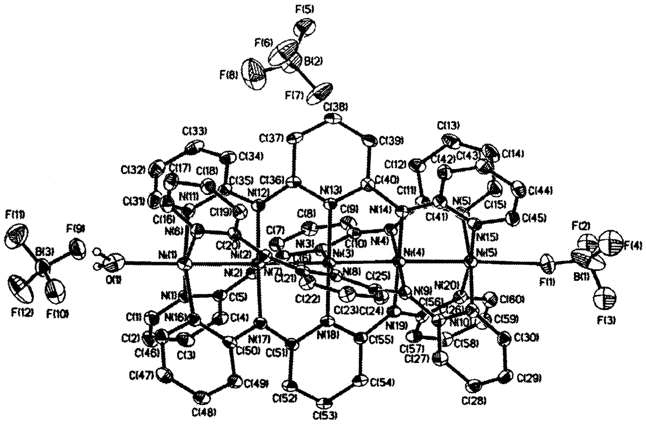

Figure 2. Crystal structure of compound **1**. Atoms are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

It has been found that trinuclear cobalt and chromium complexes exhibit both symmetrical and unsymmetrical structures depending on the nature of the axial ligands,[4] the crystal environment,[6,10] and the oxidation states.[4,11] The unsymmetrical structure of compound **1** might be induced by the different nature of the axial ligands, BF_4^- and H_2O, or by the different Ni−Ni interactions occurring in the molecule. However, the possibility of being induced by the different nature of the axial ligands should be ruled out, as evidenced by the crystal structure of **2**, in which the two

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(14) Crystal data for $[\mathbf{1}]\cdot 4CH_2Cl_2$, formula $C_{64}H_{54}B_3Cl_8F_{12}N_{20}Ni_5O$, M_w = 1956.85, monoclinic, space group $P2_1/n$, T = 150(1) K, a = 15.3022(1) Å, b = 31.0705(3) Å, c = 15.8109(2) Å, β = 92.2425(4)°, V = 7511.49(13) Å^3, Z = 4, μ = 1.603 mm^{-1}, D_c = 1.730 g cm^{-3}; 52924 reflections collected, 17219 independent, R_{int} = 0.0732, final residuals R1 = 0.0773, wR2 = 0.2052 [$I > 2\sigma(I)$]; R1 = 0.1322, wR2 = 0.2525 (all data). Crystal data for $[\mathbf{2}]\cdot CH_2Cl_2\cdot 3.5(H_2O)$, formula $C_{64}H_{53}Cl_2F_9N_{20}Ni_5O_{12.5}S_3$, M_w = 1933.89, monoclinic, space group $C2/c$, T = 150(1) K, a = 42.1894(7) Å, b = 17.0770(3) Å, c = 21.2117(4) Å, β = 102.5688(8)°, V = 14916.1(5) Å^3, Z = 8, μ = 1.493 mm^{-1}, D_c = 1.722 g cm^{-3}; 46772 reflections collected, 13104 independent, R_{int} = 0.0868, final residuals R1 = 0.1065, wR2 = 0.2781 [$I > 2\sigma(I)$]; R1 = 0.1605, wR2 = 0.3338 (all data).

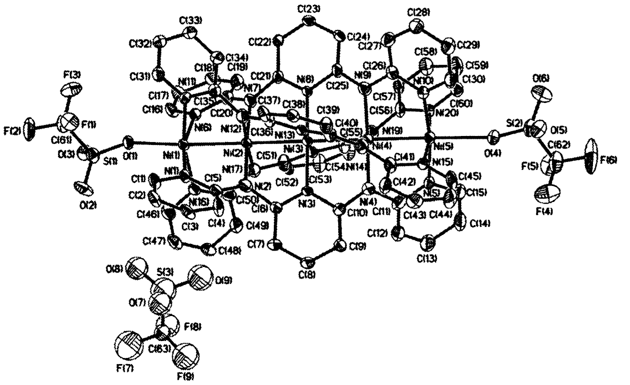

Figure 3. Crystal structure of compound **2**. Atoms are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

axial ligands are the same (Figure 3). Compared to **1**, the extent of asymmetry of compound **2** is even more pronounced, as judged from the unsymmetrical Ni−Ni bond distances of 2.358(2), 2.276(2), 2.245(2), and 2.304(2) Å. The significant differences between the two terminal nickel ions can also be viewed from the different metal−ligand bond distances of 2.059(7) and 2.338(8) Å for Ni(1)−O(1) and Ni(5)−O(4), respectively. The average Ni−N lengths are not significantly different from those in compound **1**, as shown in Table 1. According to the structural analyses, the electronic configuration of **2** can be considered identical with that of **1**.

Theoretical calculations show that there are no metal−metal bonds in the neutral molecules of the pentanickel complexes, and the bond order for Co−Co in neutral pentacobalt complexes is estimated to be 0.5.[4b] Comparing compounds **1** and **2** to **3** and **4**, the Ni−Ni bond distances are between the corresponding metal−metal distances in **3** and **4**. We believe that considerable unsymmetrical Ni−Ni bonding interactions, especially, on the Ni(5) site exist in **1** and **2**.

The measured effective magnetic moments (μ_{eff}) and the molar magnetic susceptibilities (χ_M) of compounds **1** and **2** with respect to temperature are given in Figure 4. The experimental data obtained are close to the simulated values (solid lines).[15] At the temperatures measured, the effective magnetic moment (μ_{eff}) of 1.87 μ_B at 5 K increases gradually to a value of 2.86 μ_B for **2** at 300 K without reaching saturation. In the case of **1**, the magnetic moment increases even more slowly as compared to that of **2**. The effective magnetic moments for both **1** and **2** at room temperature are smaller than the estimated value of 3.32 μ_B (two independent spins of $S = 1$ and $S = {}^1/_2$). The magnetic data suggest that the terminal Ni(1) ion with $S = 1$ is antiferromagnetically coupled with the terminal Ni(5) ion with $S = {}^1/_2$. The coupling constants of the antiferromagnetic interactions in the pentanickel core are estimated to be −555 and −318 cm^{-1} for **1** and **2**, respectively, which are much higher than those for **3** (−8.3 cm^{-1}) and [$Ni_3(dpa)_4Cl_2$] (−99 cm^{-1}), indicating that there are strong metal−metal interactions in these oxidized complexes. The magnetic results are in agreement with the X-ray crystal structural analyses.

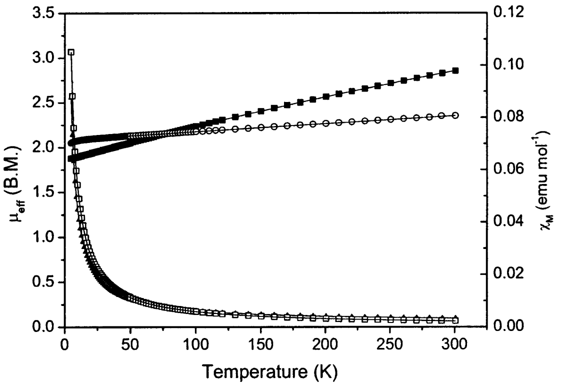

Figure 4. Temperature-dependent magnetic effective moments (μ_{eff}) and molar magnetic susceptibilities (χ_M). Compound **1** (○) and (□); compound **2** (■) and (▲). Solid lines represent fitting of the experimental data.

In summary, the one-electron oxidation products of the pentanuclear nickel string complexes have been successfully synthesized. The unusual unsymmetrical structures of these oxidized complexes are proven by X-ray crystal structure analysis. One of the terminal nickel ions (Ni(1)) can be regarded as being in a high-spin state with $S = 1$ while the other four nickel ions are in a low-spin state with an unpaired electron on Ni(5). The differences in the metal−metal interactions between the neutral and one-electron oxidation complexes might shed light on the application of these molecules as "molecular switches". The studies on the conductivity of both the neutral and one-electron oxidation complexes using SAM techniques are currently underway in our laboratory.

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Supporting Information Available: Synthetic procedure and characterization for compounds **1** and **2** and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The molar magnetic susceptibility (χ_M) was fitted with the following equation using $g = 2.41$: $\chi_M = C(1 + 10e^{3x})/4(1 + 2e^{3x}) + \chi_{\text{TIP}}$, where $C = Ng^2\beta^2/kT$, $x = J/kT$, and χ_{TIP} = temperature-independent paramagnetism ($\chi_{\text{TIP}} = 5.0 \times 10^{-4}$ and 1.0×10^{-4} cm^3 mol^{-1} for complexes **1** and **2**, respectively).