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MS24-O5 Synthesis and Characterization of Asymmetric Tetranuclear Nickel Chains without Disordered Ligand Phenomenon in Crystallography

Lien-Hung Tsou¹, Marc Sigrist², Ming-Hsi Chiang², Er-Chien Horng¹, Chun-hsien Chen¹, Gene-Hsiang Lee¹, Shie-Ming Peng^{1,2}

1. Department of Chemistry, National Taiwan University, No. 1, Sec. 4, Roosevelt Rd., Taipei, Taiwan (R.O.C.)

2. Institute of Chemistry, Academia Sinica, 128 Academia Road, Section 2, Nankang, Taipei, Taiwan (R.O.C.)

email: d01223123@ntu.edu.tw

The new ligand, 2-(2-(5-phenylpyridyl)amino)-1,8-naphthyridine (Hphpyany), was synthesized by the reaction of 2-chloro-1,8-naphthyridine with 2-amino-5-phenylpyridine in the presence of potassium *tert*-butoxide under palladium(0)-catalyzed condition. The linear tetranickel metal complexes, $[\text{Ni}_4(\text{phpyany})_4(\text{Cl})_2](\text{CF}_3\text{SO}_3)_2$ **1**, $[\text{Ni}_4(\text{phpyany})_4(\text{Cl})_2](\text{BF}_4)_2$ **2**, $[\text{Ni}_4(\text{phpyany})_4(\text{NCS})_2](\text{ClO}_4)_2$ **3** and $[\text{Ni}_4(\text{phpyany})_4(\text{NCS})_2](\text{CF}_3\text{SO}_3)_2$ **4** were synthesized and have been crystallographically characterized. All of the complexes consist of four phpyany ligands, wrapped around a linear tetranickel core, in the same orientation. The remarkably short Ni-Ni distances (ca. 2.33 Å) for **1** and **3** indicate partial metal-metal bonding, which can be viewed as both complexes containing one mixed-valence Ni_2^{3+} unit. Magnetic susceptibility measurements reveal that the Ni_4^{7+} complexes exhibit antiferromagnetic interactions ($J = -42 \text{ cm}^{-1}$ for **1** and -46 cm^{-1} for **3**) between the Ni^{2+} and the Ni_2^{3+} units, while the Ni_4^{8+} complexes **2** and **4** exhibit antiferromagnetic interactions ($J = -33 \text{ cm}^{-1}$ for **2** and -35 cm^{-1} for **4**) between the two terminal Ni^{2+} ions. The results of the cyclic voltammetry indicate the presence two reversible redox couples at $E_{1/2}^{(1)} = 0.07 \text{ V}$, $E_{1/2}^{(2)} = -0.80 \text{ V}$ for **1**, and at $E_{1/2}^{(1)} = 0.12 \text{ V}$, $E_{1/2}^{(2)} = -0.74 \text{ V}$ for **3**. The products of the oxidation process $E_{1/2}^{(1)}$ of **1** and **3** are the corresponding oxidized species **2** and **4**, respectively. The value of conductance is $9.39 (\pm 0.301) \times 10^{-4} G_0$ and the value of resistance is $13.7 (\pm 4.4) \text{ M}\Omega$ for **4** were measured by means of the STM break-junction. This represents the first conductance measurement of a linear tetranickel chain.

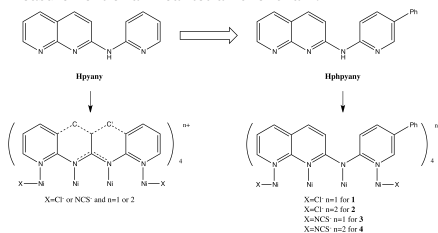


Figure 1. Crystallographic disordered ligand on C and C' (left bottom) and schematic diagram for complexes 1, 2, 3 and 4 (right bottom).

Keywords: Metal-metal interactions, Nitrogen ligands, Electrochemistry, Magnetic properties, Single molecular conductance