A Combined Structural, Spectroscopic, Electrochemical, And Magnetic Study Of Nickel(II) Pyrazolates: Dinuclear $[Ni_2]$, Linear $[Ni_3]$, And Triangular $[Ni_3]$ Incorporating five-/Six-Coordinate Ni^{2+} Ions.

Zhichun Shi[1], Dr Indranil Chakraborty[1], Prof Yiannis Sanakis[2], Prof Raphael G Raptis[1]
[1]Florida International University, Chemistry Department, [2]Institute of Nanoscience and Nanotechnolgy
zshi008@fiu.edu

Single crystals of four nickel(II) polynuclear clusters based on four differently substituted pyrazole ligands, including a dinuclear [Ni2(4-Br-pz)3]+[ClO4]- (1), two linear trinuclear [Ni3(4-NO2-pz)6(py)2] (2) and Ni3(4-NO2-pz)6(4,4’-azp)2] (3), and two triangular trinuclear clusters [Ni3(μ3-OH)(4-Cl-pz)4]+[ClO4]- (4) and [Ni3(μ3-OH)(4-I-pz)4]+[ClO4]- (5), have been prepared and studied. All five complexes have been fully characterized by SCXRD, FTIR, UV-Vis-NIR, NMR, Raman, Cyclic Voltammetry, and elemental analysis. Their magnetic properties are currently under investigation in order to probe their relationship to the topological structure. For instance, the linear [Ni3] cluster is a paramagnetic species with an S = 1 ground state.

The dinickel cluster [Ni2] consists of two Ni2+ metal ions, three bridging 4-bromo-pyrazolates, four pyridines and two water molecules as terminal ligands, and one perchlorate (ClO4-) counterion (Figure 1a).

Figures 1b and 1c show two neutral linear trinuclear nickel complexes [Ni3]. These compounds incorporate pyridine (1b) or 4,4’-azopyridine (1c) as terminal ligands, resulting in different electrochemical properties. Similar linear motifs have been well studied by others as extended metal atom chains (EMACs).

Two similar triangular trinuclear cationic nickel complexes, [Ni3], (Figures 1d and 1e), are constructed by three Ni2+ centers, one μ3-OH bridging group, six pyridines (each Ni2+ ion coordinating to two pyridines in the axial and equatorial direction), one perchlorate (ClO4-) anion as the counterion, and four bridging pyrazolates (4-choloro-pyrazolate or 4-iodine-pyrazolate). Two types of coordination modes of nickel ion are displayed in the crystal structure, i.e., two six-coordinate and one five-coordinate Ni2+ centers.

Figure 1. The crystal structures of the complex (a) [Ni2(μ-4-Br-pz)3](ClO4), (b) [Ni3(μ-4-NO2-pz)6(py)2(H2O)4], (c) [Ni3(μ-4-NO2-pz)6(4,4’-azp)2(H2O)4] (d) [Ni3(μ3-OH)(μ-4-Cl-pz)4](ClO4) (side-view), and (e) [Ni3(μ3-OH)(μ-4-I-pz)4](ClO4) (top-view). H atoms and C atoms of pyridines (in 1c and 1d) are omitted for clarity.

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