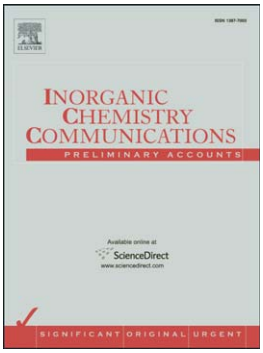

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Synthesis, Structures, and Magnetic Properties of Tetranuclear Nickel and Cobalt Complexes with 2-Mercaptobenzoxazole

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Abstract: The synthesis and magnetic properties of two tetranuclear Ni complex $Ni_4(L)_4(CH_3CN)_4(OCH_3)_4$ **1** and Co complexes $Co_4(L)_4(CH_3CN)_4(OCH_3)_4$ **2** (HL = 2-mercaptobenzoxazole) are reported. The X-ray structures reveal that **1** and **2** are isostructural with $[Ni_4O_4]$ **1** and $[Co_4O_4]$ **2** cubane-like cores. Analysis of the temperature dependent magnetic measurements data shows that both complexes are paramagnetic with weak antiferromagnetic coupling. One-*J* model and two-*J* model are both applied to fit the experimental magnetic data of **1** and the results indicate the exchange coupling between the type A Ni(II) ions affected by NCS three atoms bridge in 2-Mercaptobenzoxazole ligand.

Keywords: Tetranuclear Ni(II), Tetranuclear Co(II), Crystal structure, Magnetic properties, Cubane core

Polynuclear complexes of paramagnetic metal ions are intriguing because of their roles as model complexes for bioinorganic enzymes [1], potential application as catalysts [2], and candidacy as single-molecule magnets [3]. In several copper-, manganese-, and iron-containing proteins, the coordination environments of the active metal centers always contain nitrogen and sulfur atoms [4]. Inspired by these natural prototypes, the construction of such coordination spheres for metal clusters to mimic metalloenzyme active sites is of importance to extend the scope and function of coordination complexes. Although sulfur ligands are well known to coordinate with metal ions as soft donors, the ability of thiolate chelators, in particular, to tune the electronic states and reactivity of metal ions still remains unexplored. Magnetic studies of metallic clusters can provide useful information toward understanding the role of S donors on the electron spin states of metal ions. The first sulfur-bridged single molecule magnets (SMM) $[(\eta^5\text{-Cp})_2Dy(\mu\text{-SSiPh}_3)]_2$ with a large anisotropy barrier of U_{eff} = 133 cm^{-1} demonstrated the potential application as SMM. This work motivated the synthesis of polymetallic thiolate-bridged SMM [5]. However, the effects of soft donors such as sulfur species on the magnetic interactions and connections of paramagnetic metal centers are not fully understood. Thus, constructing polynuclear complexes or coordination polymers bridged by thiolates ligands to assemble paramagnetic ions would be of importance to improve the understanding of their magnetic behavior. In our previous work, 2-mercaptopyrimidine (PymSH) was used to form weak ferromagnets with MCl_2 (M = Mn^{2+} or Co^{2+}) under solvothermal conditions [6]. Structural analyses and magnetic studies revealed that the thiol groups in $Co(PymS)_2$ contributed to the magnetic interaction between the cobalt ions and resulted in a higher ordering temperature than $Co(PymO)_2$. With our continued interest in the effects of N and S heteroatom ligands on intermolecular magnetic exchange coupling, we chose, in this work, 2-mercaptobenzoxazole (HL) to serve as bridging ligand forming tetranuclear complexes with acetonitrile as terminal ligands and μ_3-methoxido ions to form metal clusters.

We herein report tetranuclear $Ni_4(L)_4(CH_3CN)_4(OCH_3)_4$ **1** and $Co_4(L)_4(CH_3CN)_4(OCH_3)_4$ **2** compounds with 2-mercaptobenzoxazole (HL) coordinating ligands. Complex **1** was synthesized by the reaction of $NiCl_2{\cdot}6H_2O$ (1 mmol) and HL (1 mmol) in methanol (4 mL) under Ar atmosphere, followed by the addition of NaOH (1 mmol) in methanol (4 mL). After 30 min, the solution was transferred to a 20 mL tube and subjected to diffusion with acetonitrile for 1 week. Green crystals appeared which were collected by filtration, washed with methanol, and dried in air. Complex **2** was prepared in a similar