# Structural Diversity, XAS and Magnetism of Copper(II)-Nickel(II) Heterometallic Complexes Based on the $[Ni(NCS)_6]^{4-}$ Unit

Autorzy

Natalia Tereba

Tadeusz M. Muzioł

Joanna Wiśniewska

Robert Podgajny

Alina Bieńko

Grzegorz Wrzeszcz

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The new heterometallic compounds, $[\{Cu(pn)_2\}_2Ni(NCS)_6]_n \cdot 2nH_2O$ (**1**), $[\{Cu^{II}(trien)\}_2Ni(NCS)_6Cu^{I}(NCS)]_n$ (**2**) and $[Cu(tren)(NCS)]_4[Ni(NCS)_6]$ (**3**) (pn = 1,2-diaminopropane, trien = triethylenetetramine and tren = tris(2-aminoethylo)amine), were obtained and characterized by X-ray analysis, IR spectra, XAS and magnetic measurements. Compounds **1**, **2** and **3** show the structural diversity of 2D, 1D and 0D compounds, respectively. Depending on the polyamine used, different coordination polyhedron for Cu(II) was found, i.e., distorted octahedral (**1**), square pyramidal (**2**) and trigonal bipyramidal (**3**), whereas coordination polyhedron for nickel(II) was always octahedral. It provides an approach for tailoring magnetic properties by proper selection of auxiliary ligands determining the topology. In **1**, thiocyanate ligands form bridges between the copper and nickel ions, creating 2D layers of **sql** topology with weak ferromagnetic interactions. Compound **2** is a mixed-valence copper coordination polymer and shows the rare ladder topology of 1D chains decorated with $[Cu^{II}(tren)]^{2+}$ antennas as the side chains attached to nickel(II). The ladder rails are formed by alternately arranged Ni(II) and Cu(I) ions connected by N2 thiocyanate anions and rungs made by N3 thiocyanate. For the Cu(I) ions, the tetrahedral thiocyanate environment mixed N/S donor atoms was found, confirming significant coordination spheres rearrangement occurring at the copper precursor together with the reduction in some Cu(II) to Cu(I). Such topology enables significant simplification of the magnetic properties modeling by assuming magnetic coupling inside $\{Ni^{II}Cu^{II}_2\}$ trinuclear units separated by diamagnetic $[Cu(NCS)(SCN)_3]^{3-}$ linkers. Compound **3** shows three discrete mononuclear units connected by N-H…N and N-H…S hydrogen bonds. Analysis of XAS proves that the average ligand character and the covalency of the unoccupied metal d-based orbitals for copper(II) and nickel(II) increase in the following order: **1** ® **2** ® **3**. In **1** and **2**, a weak ferromagnetic coupling between copper(II) and nickel(II) was found, but in **2**, additional and stronger antiferromagnetic interaction between copper(II) ions prevailed. Compound **3**, as an ionic pair, shows, as expected, a spin-only magnetic moment.

Słowa kluczowe

hexaisothiocyanatonickelate(II) complexes, thiocyanato bridges, single crystal XRD, XAS, magnetic properties, spin density



Adres publiczny

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