Structure, XAS and magnetism of copper(II) and nickel(II) heterometallic complexes based on the $[Cr(NCS)_6]^{3-}$ and $[Cr(NCS)_4(NH_3)_2]^-$ units

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The new heterometallic compounds, $\{[Ni(tren)(H_2O)]_2(\mu_{1,3}\text{-}NCS)\}[Cr(NCS)_6]$ (**1**), $\{[Cu(tren)(H_2O)]_2(\mu_{1,3}\text{-}NCS)\}[Cr(NCS)_6]$ (**2**) and $[Ni(tren)(H_2O)(NCS)][Cr(NCS)_4(NH_3)_2]$ (**3**) (tren = tris(2-aminoethylo)amine), were obtained and characterized by X-ray analysis, IR spectra, XAS and magnetic measurements. The compounds **1** and **2** were isomorphous and crystallized in the monoclinic $P2_1/c$ space group. These compounds consisted of a homometallic NiNi and CuCu dimers in **1** and **2**, respectively, in which metal ions were coordinated by a single thiocyanate $\mu_{1,3}\text{-}NCS^-$ bridge, and the $[Cr(NCS)_6]^{3-}$ unit as the counterion. Crystal lattice of compound **3** had an orthorhombic Pbca symmetry. Single monomeric nickel ions and $[Cr(NCS)_4(NH_3)_2]^-$ ions were arranged in the form of columns composed of alternately arranged complex cations and anions stabilised by hydrogen bonding. The XAS spectra on the selected 3d metals (Ni, Cu, Cr) L-edge and the N and O K-edge were intended to enable the determination of the spin state and configuration of Ni, Cu, Cr and to relate this information to other properties of materials, such as local symmetry of central atoms, charge state, covalency of unoccupied valence orbitals. The K-edge and L-edge XAS spectra confirmed the elemental composition and local geometry of transition metals occurring in newly synthesized molecular materials. Similarities in topology, local symmetry and structure enabled significant simplification of the magnetic properties modelling by assuming magnetic coupling inside $\{Ni^{II}Ni^{II}\}$ or $\{Cu^{II}Cu^{II}\}$ binuclear units separated by paramagnetic $[Cr(NCS)_6]^{3-}$ units in **1** and **2**. The obtained results indicated dominant antiferromagnetic interactions between metal ions in the dimers, which was confirmed by theoretical DFT and *ab initio* CASSCF/NEVPT2 calculations.

Słowa kluczowe

Copper(II), Nickel(II), Chromium(III), Coordination chemistry, Magnetism

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