SPIN STATES OF Mn(II) AND Fe(III) COMPLEXES WITH THIOSEMICARBAZONE

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Mn(II) and Fe(III) complexes with condensation product of thiosemicarbazide and 2-acetylthiazole have been synthesized and characterized by single-crystal X-ray diffraction [1]. Two complexes have the same ligand system – bis tridentate coordination of the thiosemicarbazone ligand through the NNS donor set of atoms. Furthermore, the central metal ions in both cases have the same d^5 electronic configuration. However, measured magnetism and analysis of the crystal geometries show that these two complexes have a different number of unpaired electrons. We rationalized the results by electronic structure calculations based on density functional theory. High-spin Mn(II) complex has trigonal-prismatic geometry with ionic metal-ligand bonding. Hund's rule of maximum multiplicity is responsible for its sextet spin-ground state. On the other hand, low-spin Fe(III) complex has octahedral coordination and strong metal-ligand covalency with delocalization of spin density toward ligands. Low-spin, doublet state is favored because of the nephelauxetic effect, i.e., smaller pairing energy in Fe(III) complex.

Our results show that the difference in the electronic structure of the two complexes, i.e., different spin-ground states, directly affects these molecules' structure, magnetism, reactivity, and biological activities.

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[1] Stojičkov, M., Zlatar, M., Mazzeo, P. P., Bacchi, A., Radanović, D., Stevanović, N., Jevtović, M., Novaković, I., Anđelković, K., Sladić, D., Čobeljić, B., Gruden, M. (2023). Polyhedron, 237, 116389.