FA4-MS33-P17

Spin transition in iron(III) complexes with pseudohalide terminal ligands. Ivan Nemec[a], Radovan Herchel[b], Zdeněk Trávníček[b], Ingrid Svoboda[c], Wolfgang Linert[d], [a]*Department of Inorganic Chemistry, Technical University Bratislava, Slovakia,* [b]*Department of Inorganic Chemistry, Palacky University, Olomouc, Czech Republic;* [c]*Materials Science, Technical University, Darmstadt, Germany;* [d]*Institute of Applied Synthetic Chemistry, Vienna University of Technology, Vienna, Austria*
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Spin transition (ST) is well documented for coordination compounds of the first transition row with the d^4-d^7 configuration of valence shell [1] and it is observed in the most cases for iron(II) and iron(III) complexes. Recently, we have reported about magnetic properties of the dinuclear cyanido-bridged Fe(III) complexes where ST is heavily influenced by strong antiferromagnetic exchange interaction through the cyanido linkage [2]. Despite the present cooperative interactions, spin-transition is of a very gradual character. In order to remove the strong exchange coupling, the dinuclear compounds were transformed into mononuclear ones by substitution of a cyanido linkage with the appropriate terminal ligand, which would maintain presence of ST. We decided to use pentadentate Schiff base ligands L^5 with {N_3O_2} donor set and as a substitution to a cyanido ligand the pseudohalide ligands were chosen. This also offers possibility to carry out very fine tuning of the overall ligand field by single substitution with respect to known spectrochemical row of ligands. The X-ray analysis and magnetic measurements confirmed the spin transition in some of the prepared compounds and ST is only secondarily influenced by clathrated solvent molecules. Different solvent molecules lead to different packing motives and those lead to different geometries of L^5. The molecules which do not undergo ST have different dihedral angle between the least square planes of aromatic rings of L^5 ligand from those that exhibit ST. This was also observed for compounds of iron(III) with hexadentate Schiff based ligands [3]. The compounds which show ST were structurally characterized at different temperatures and temperature dependence of their lattice parameters was evaluated.

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Mononuclear Co(II) complex with large zero-field splitting. Blažena Papánková[a], Roman Boča[a], Ľubor Dlháň[a], Ingrid Svoboda[b], Hartmut Fuess[b] , [a]*Institute of Inorganic Chemistry (FCHPT), Slovak University of Technology, 812 37 Bratislava, Slovakia.* [b]*Institut for Materials Science, Darmstadt University of Technology, 64289 Darmstadt, Germany*
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Zero-field splitting (ZFS) is measurable and used in many biological applications. However, its interpretation in terms of structure-property relations is still an open question. A mononuclear cobalt(II) complex, $[Co(Iz)_6(HCOO)_2]$, with homoleptic coordination sphere possessing the {CoN_6} chromophore has been prepared and structurally characterized with the aim to correlate the zero-field splitting parameter (D) with the structural tetragonality of cobalt complexes.

The structure of the $[Co(Iz)_6(HCOO)_2]$ is built up of $[Co(Iz)_6]$cations and formiato anions. The Co atom is in an octahedral environment formed by the tertiary N atom of the imidazole moieties. The bond distances involved in this octahedral geometry, (Co1-N1, Co1-N2 and Co1-N3) ranging from 2.143 to 2.211 Å. All the imidazole rings are individually planar. The counteranions are involved into the hydrogen bond network with the N-H moiety of the imidazole ligand.

A fit to the ZFS-model gave the following set of magnetic parameters: D/hc = +75.0 cm^{-1}, g_x = 2.695, χ_{TIP} = -8.80x10^{-9} m^3 mol^{-1}, (g_z = 2.0).

Far infrared spectroscopy is another technique which can be used to measure the energy gap – the zero- field splitting parameter D, directly [1].The absorption spectrum taken in the FAR-IR region exhibits manifold absorption peaks referring to the transitions between the crystal-field multiplets of the split $^4T_{1g}$ ground term ($^4A_{2g}$ + ^4E_g) [2, 3].
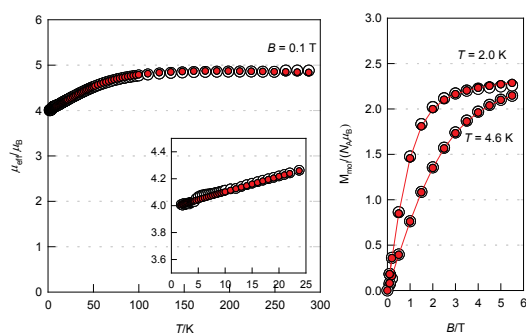

Fig. 1. Magnetic data: left temperature dependence of the effective magnetic moment; right – field dependence of the magnetization.

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Keywords: Magnetic properties of molecules-1, Cobalt compounds-2, Structural correlation-3