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Structural, magnetic and dynamic characterization of liquid crystalline iron(III) Schiff base complexes with asymmetric ligands

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Abstract

The iron(III) complexes that were formed by coordination of the Fe III ion with the asymmetric tridentate liquid crystalline Schiff base ligand (L), the water molecules and the different counterions [PF 6 - (1), NO3 - (2), and Cl- (3)] were studied by electron paramagnetic resonance (EPR) spectroscopy. EPR spectroscopy demonstrated that each of the complexes investigated consists of two types of iron centers: S = 1/2 low-spin (LS) and S = 5/2 high-spin (HS). LS iron complexes 2, 3 and LS complex 1 in the temperature range 4.2-250 K have a (dxz,dyz)4(dxy)1 ground state. Interesting features werefound for the monocationic FeIII complex 1, [Fe(L)X(H2O)2]+X-, with X = PF6 - as the counterion. The LS and HS iron centers of 1 are coupled together antiferromagnetically and form a dimer structure by means of the water molecules and the PF6 - counterion. The second-type of LS and HS centers that are visible by means of EPR spectroscopy were best observed in the liquid crystalline (387-405 K) phase. The monitoring and the simulation of the EPR spectra enabled us to trace the dynamics of changing the number of the second-type of LS centers with respect to the first-type of LS centers. The observed dynamic process is characterized by the enthalpy value ΔH = 27.9 kJ/mol, which was caused by reorientation of the PF6 - counterion. Calculation of the observed g values for the second-type of LS complex 1 indicated that, in this case, the (d xy)2(dxz,dyz)3 ground state is stabilized. The conversion between the electron (dxz,d yz)4(dxy)1/(dxy) 2(dxz,dyz)3 configurations was found to be temperature dependent and was detected in the same material for the first time in iron complexes. We synthesized a novel compound, namely a liquid crystalline iron(III) Schiff base complex with the asymmetric ligand [Fe(L)X(H2O)2]+X-, where X = PF 6 - is the counterion. This compound has a labilelow-spin electron configuration that switches between the (dxz,d yz)4(dxy)1/(dxy) 2(dxz,dyz)3 ground states and is temperature-dependent. Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

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Keywords

Electronic structure, EPR spectroscopy, Iron, Magnetic properties, Metallomesogens, Molecular dynamics