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Inorganica Chimica Acta 459 (2017) 131–142

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Research paper

Counterion effect on the spin-transition properties of the second generation iron(III) dendrimeric complexes

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ARTICLE INFO

Article history:
Received 16 November 2016
Received in revised form 6 February 2017
Accepted 7 February 2017
Available online 9 February 2017

Keywords:
Iron(III) complex
EPR spectroscopy
Spin-crossover
Magnetic susceptibility
Dendrimers

ABSTRACT

The magnetic properties and the influence of counterions on the spin crossover properties of two novel Fe(III) dendrimeric complexes of the second generation, namely $[Fe(L)_2]^+X^-$, where L = 3,5-di(3,4,5-tris(tetradecyloxy)benzoyloxy)benzoyl-4-oxy-salicylidene-N'-ethyl-*N*-ethylenediamine X = Cl^- (**1**), ClO_4^- (**2**), have been studied for the first time by magnetic susceptibility measurements and electron paramagnetic resonance (EPR) method in a wide (4.2–300 K) temperature range. EPR results showed that compound **1** contains about 98% of high-spin (HS, $S = 5/2$) and ~2% of low-spin (LS, $S = 1/2$) Fe(III) centers, and undergoes an antiferromagnetic ordering below 7 K. The EPR integrated intensity of a broad line ($g \approx 2$), corresponding to the HS iron(III) centers, passes through a broad maximum at $T_{max} \approx 100$ K, which is indicative of short-range correlation effects. The anomalous broadening of this EPR line at low temperatures with the critical exponent $\beta = 1.5$ upon approaching the long-range ordering transition ($T_N^{EPR} = 7$ K) from above indicates the quasi-two-dimensional antiferromagnetic nature of magnetism in complex **1**. The spin-crossover effect is completely suppressed in compound **1**. The complex with ClO_4^- counterion demonstrates a different magnetic behavior. EPR data showed that compound **2** contains about 77% of LS and ~23% of HS Fe(III) centers at $T_N^{EPR} = 10.2$ K. It displays a partial spin crossover ($S = 5/2 \leftrightarrow 1/2$) above 150 K and undergoes the antiferromagnetic ordering below 10.2 K. The obtained results and the results of DFT calculations allowed us to conclude that a bilayered packing with a chain structure of Fe(III) centers in ionic bilayers is formed in compound **1**, whereas a dimeric structure of Fe(III) centers is formed in compound **2**. Thus, the ability of the counterion to form an effective network of hydrogen bonds and its size define the packing motif of the $[Fe(L)_2]^+$ complexes. Therefore, the replacing of the counterion has a significant impact on the magnetic properties of the compound.

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1. Introduction

The spin-crossover (SCO) phenomenon, where spin states may be switched reversibly between low-spin (LS) and high-spin (HS) configurations by external stimuli such as temperature, pressure and more rarely light irradiation, termed the LIESST effect [1–7], can occur in transition metal complexes with a d^4–d^7 electron configuration [1–4]. In particular, the light-induced excited spin-state trapping (LIESST effect), which induces conversion of a LS state to a HS state by means of light irradiation, has attracted considerable interest. Among the most extensively studied SCO materials are complexes of iron(II) (d^6) [8–10] and iron(III) (d^5) [11], which have caused the interest of many researchers as potential multifunctional materials in fields such as molecular electronics, memory storage, sensors and photoelectric devices [12–15]. However, such applications require that the spin transition occurs abruptly at ambient temperature (ideally room temperature) and with wide thermal hysteresis (for the memory effect) [16,17].

In the case of iron(III), which has a d^5 electron configuration, the transition occurs from a high spin state ($^6A_1$, $S = 5/2$) to a low spin state ($^2T_2$, $S = 1/2$) [18,19]. Iron(III) compounds, compared to the iron(II) systems, have the advantage of generally being air stable and thus would be expected to be more amenable to processing

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http://dx.doi.org/10.1016/j.ica.2017.02.008
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