Correlation between Cooperative Spin Crossover Phenomena and Intermolecular Interactions in Fe(III) Complexes

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Spin crossover complexes show a spin state conversion induced by external stimuli such as temperature, pressure, and light. In the cooperative spin crossover phenomena, interactions between spin crossover molecules play an important role [1,2]. In order to investigate the relation between spin crossover phenomena and intermolecular interactions systematically, the preparations, crystal structure analyses, magnetic susceptibility measurements under pressures of $[Fe(qsal)_2]X$ (Fig.1, X = linear anions), which are expected to possess strong π-π interactions in the crystal packing, were carried out.

$Fe(qsal)_2$ complexes with linear anions were prepared by metathesis method. A newly prepared $[Fe(qsal)_2]I_3$ is clarified to be the novel spin crossover complex with T_{SCO} (spin crossover temperature) ~ 250 K. The crystal structure analysis reveals that $Fe(qsal)_2$ cations construct a one-dimensional chain with π-π interactions, and that the two-dimensional sheets composed of one-dimensional chains are separated by I_3 anions. As the pressure was applied, T_{SCO} shifts to higher temperatures by 7 K/kbar (Fig.2). On the other hand, $[Fe(qsal)_2]NCS$ containing smaller SCN linear anion has the three-dimensional π–π interactions between one-dimensional chains and T_{SCO} shifts higher temperatures by 21 K/kbar with narrowing thermal hysteresis loop. These results indicate the correlation between cooperative spin crossover behaviors and dimensionality of intermolecular interactions in $[Fe(qsal)_2]X$.

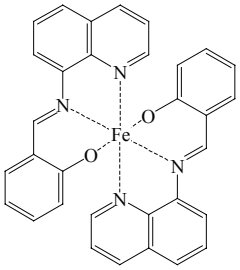

Fig.1 Molecular structure of $[Fe(qsal)_2]X$

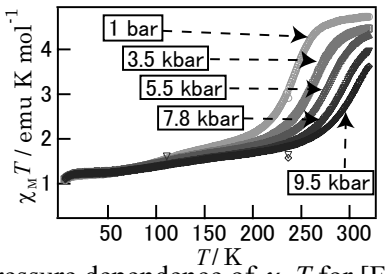

Fig.2 Pressure dependence of $\chi_M T$ for $[Fe(qsal)_2]I_3$

[1] K. Takahashi *et al.*, J. Am. Chem. Soc., 130 (2008) 6688.

[2] K. Takahashi et al., Polyhedron (2009), doi:10.1016/j.poly.2008.11.047.