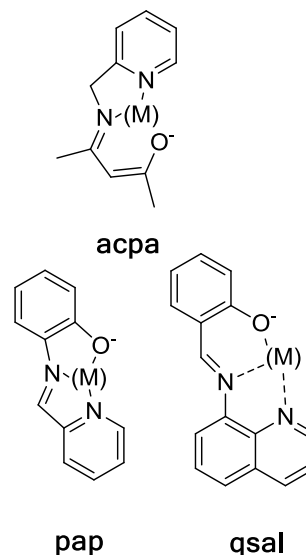


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### [Intro]

Thermal- and light induced spin-transition of transition metal complexes promises novel solutions in information technology. The key for the controlled use of such material is the better understanding how chemical structure can control the switching process between the low- (LS) and high-spin (HS) states. Fe(III) complexes with  $[\text{Fe}(\text{pap})_2]^+$  and  $[\text{Fe}(\text{qsal})_2]^+$  cations often shows anomalously slow HS  $\rightarrow$  LS relaxation, which cannot be explained on the basis of the regularly used multiphonon-relaxation model for a single coordinate<sup>1</sup>. We present an analysis comparing these ligand systems with the structurally closely related *acpa*, and determining the minimum-energy crossing points (MECPs) between the potential energy surfaces of the spin states.<sup>2,3</sup>



Scheme 1.

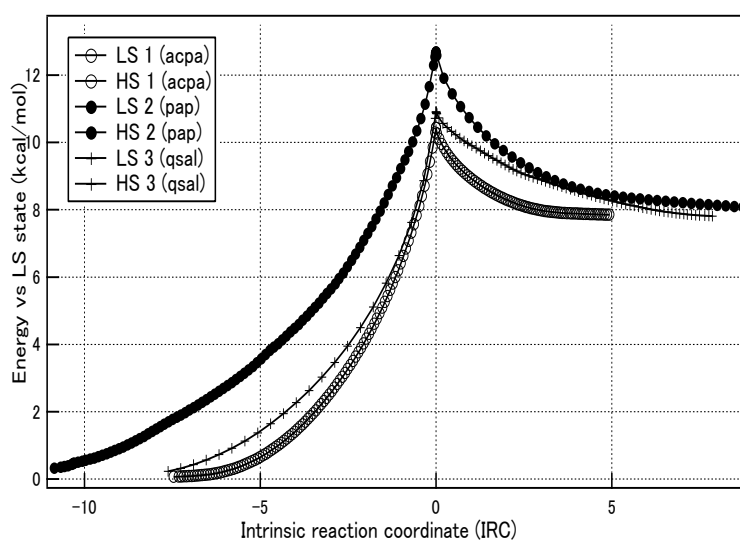
### [Method]

DFT calculation at B3LYP\*/6-311G(d) level was used to describe spin-crossover cations:  $[\text{Fe}(\text{acpa})_2]^+$  (**acpa**),  $[\text{Fe}(\text{pap})_2]^+$  (**pap**) and  $[\text{Fe}(\text{qsal})_2]^+$  (**qsal**). The equilibrium geometries were determined with Gaussian 09, the MECPs with the Orca software packages. The gradient pathway, the ideal relaxation path between the MECPs and optimal geometries were estimated with the Hessian-based predictor-corrector integrator IRC algorithm implemented in Gaussian'09.

### [Results]

The calculations reproduced well the geometry and spectroscopic properties and gave back almost the same HS-LS energy gap for all the three complexes (**acpa**: 7.80, **pap**: 7.91 and **qsal**: 7.88 kcal/mol). A careful analysis of the molecular geometry reveals a significant deviation of the bonding angles from the ideal octahedral around Fe(III) atoms, and that the spin-transition couples with these distortions. This distortion is the more pronounced in **pap**

and **qsal**, than in **acpa**. The energy of the MECPs are similar (**acpa**: 10.42, **pap**: 12.66 and **qsal**: 10.91 kcal/mol), in spite of the large differences if the crossing points are estimated assuming harmonic potential surfaces (**acpa**: 10.23, **pap**: 15.46 and **qsal**: 14.56 kcal/mol). Further investigation showed that the primary reason of these anomalies is the rigidity of the ligands, and that the pap and qsal ligands are largely confined in a planar geometry.



**Figure 1.** The potential energy surfaces of LS and HS state for **acpa**, **pap** and **qsal**.

This analysis is a significant improvement compared to the single coordinate approach that uses the total symmetric stretching of M–L bonds as the only coordinate to discuss the spin-energy surfaces. This method has been successfully tested for other complex systems before.<sup>2</sup> The main advantage is that it doesn't require a-priori knowledge about the normal modes that are involved, and also scales relatively well with the size of the studied system.

### [Reference]

1. E. Buhks, G. Navon, M. Bixon, and J. Jortner, *J. Am. Chem. Soc.* 102 (1980) 2918.
2. Y. Shiota, D. Sato, G. Juhász, and K. Yoshizawa, *J. Phys. Chem. A.* 114 (2010) 5862.
3. D. Sato, Y. Shiota, G. Juhász, and K. Yoshizawa, *J. Phys. Chem. A.* 114 (2010) 12928.