

Modeling Spin Crossover Complexes

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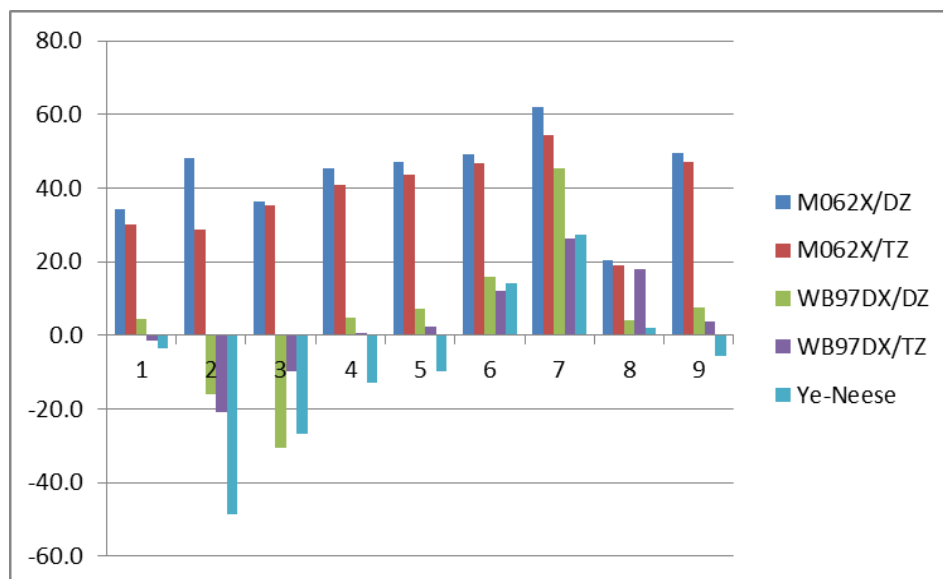
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A class of inorganic compounds called spin crossover systems have spin states so nearly degenerate that changes in temperature, pressure, and environment can change their relative stability and thus interconvert ground states [1]. We report computations complementing and extending the work of Ye and Neese [2] on the prototype $\text{Fe}(\text{phenanthroline})_2(\text{NCS})_2$ (**1** in the figure below) and related quasi-octahedral species, $[\text{Fe}(\text{L})(\text{NHS}_4)]$ with $\text{L} = \text{NO}^+$ (**2**), CO (**3**), PMe_3 (**4**), PH_3 (**5**), N_2H_4 (**6**), NH_3 (**7**) with $\text{NHS}_4^{2-} = 2,20\text{-bis}(2\text{-mercaptophenylthio})\text{diethylamine dianion}$. In addition we describe $\text{Fe}(\text{III})\text{PCL}$ ($\text{P} = \text{porphyrinate}$) (**8**) and $\text{Fe}(\text{phenanthroline})_2(\text{CN})_2$ (**9**).

The spin state preferences of set of reference compounds employed in [2] are well described by the ωB97XD functional with the cc-pVTZ basis, substantially smaller than the def2-QZVPP recommended for use with the B2PLYP functional. [2]



Spin state energies (kcal/mol, high spin state relative to low spin state) for Fe complexes.

We will present descriptions of the effect of relativistic (SO-ZORA) corrections and alternative choices of functional on the temperature response of crossover systems' state preferences and describes spin crossover in several four-coordinate systems.

[1] Halcrow, M. A., *Chem. Soc. Rev.*, 40: 4119-4142; Boussekson, A., Molnar, G., Salmon, L., Nicolazzi, W. *Chem. Soc. Rev.*, 40:3313-35, 2011;

[2] Ye, S., and Neese, F. *inorg. Chem.*, 49:772-4, 2010.