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Vibrational contribution to entropy in spin-crossover complexes with Jahn-Teller effect

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Introduction. Spin-crossover (SCO) effect in transition metal complexes offer an opportunity to fabricate bistable magnetic switching systems in molecular scale, therefore great attention has been paid to understand the detailed mechanism of SCO. The SCO is generally considered to be entropy driven: the driving force of the spin transition is the vibrational entropy associated
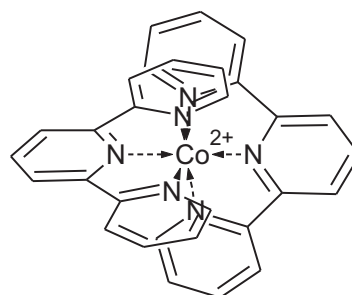

Fig. 1. Structure of Co(terpy)$_2$]$^{2+}$.

with the population of anti-bonding metal-ligand orbitals in the high-spin (HS) state. Recently characterized mononuclear cobalt(II) compounds with long alkyl chains, [Co(C$_n$-terpy)$_2$](BF$_4$)$_2$(n=0-22)(**1**, Fig.1.), put the question of driving force in a new perspective. Compounds **1** exhibit a unique reverse spin-transition behaviour [1], which cannot be explained on the basis of vibrational entropies. We considered the active Jahn-Teller (J-T) modes and distortions in **1** to find a possible mechanism of the cooperative interactions and to explain the observed unique thermal behaviour.

Method. DFT calculations were carried out at BP86/6-311G(d) and B3LYP*/6-311G(d) level on the [Co(terpy)$_2$]$^{2+}$ moiety in low-spin (LS) and high-spin (HS) states as a model for **1**, using Gaussian03 and ORCA programs. Vibrational levels of the calculated anharmonic potential surfaces were numerically estimated based on the Fourier Grid Hamiltonian method.

Results and Conclusion. The molecule in both spin states shows a distortion from an ideal D$_{2d}$ geometry due to the Jahn-Teller effect. In the high spin (HS) state, the operative J-T effect is of first order, however the geometric distortion is relatively small. In the low-spin (LS) state, the J-T effect is of second order, and it causes an elongated C$_{2v}$ geometry. The geometry distortion of metal-ligand bonding distances (~0.2 Å) is large
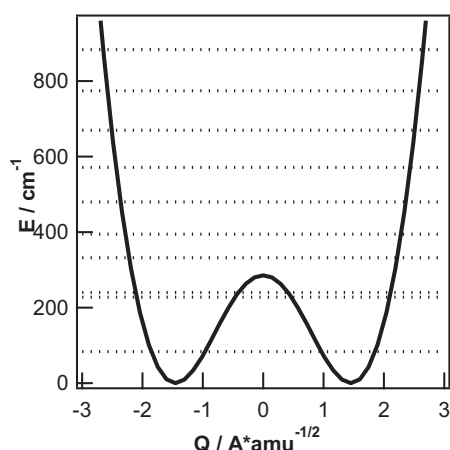
Fig. 2. Potential energy surface and vibrational levels along the Jahn-Teller mode in the low-spin (LS) state.

even compared to the geometry distortion associated with the spin-crossover (~ 0.1 Å). Potential energy scans show that there are two potential minima associated with the J-T effect, and the energy barrier between them is around 0.7-0.8 kcal/mol in free molecules in LS state (Fig. 2). In solid state, this barrier can be considerably higher due to intermolecular interactions. The high barrier between the two J-T minima and the associated large geometry distortion suggest that compound **1** can show an abrupt phase transition between static and dynamic J-T phases.

The EPR spectral parameters of **1** was simulated assuming statically distorted molecules, and also for molecules participating in the dynamic JT process. The results of the calculations compared with previous EPR experiments strongly support the presence of a static-dynamic J-T phase transition around 100-200 K in related cobalt (II) compounds.
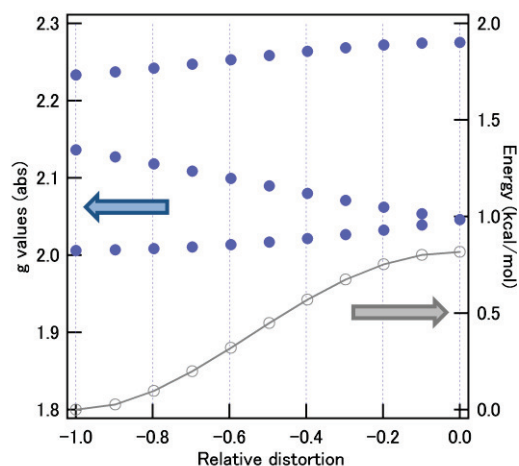
Based on these findings, we present a simple thermodynamic model that can explain the reverse spin-transition in **1** on single molecular basis. According to the model, the driving force of the reverse spin-transition is the vibrational entropy gain from the dynamic J-T mode. This entropy gain considerably shifts the transition temperature ($T_{1/2}$), hence the systems shows both regular and reverse spin-transition.

Reference:

[1] Hayami et al., Angew. Chem. Int. Ed. 2005, (44) 4899.

Fig. 3. *g* values (blue) and PES (gray) for the cobalt(II) along the Jahn-Teller mode.