

UC Davis

UC Davis Previously Published Works

Title

Rapid cooling and magnetic field-induced cooperative effect for the metastable quintet state in a spin crossover complex

Permalink

<https://escholarship.org/uc/item/7fb4k5pr>

Journal

Applied Physics Letters, 74(26)

ISSN

0003-6951

Authors

Yu, Z
Liu, K
Tao, JQ
[et al.](#)

Publication Date

1999-06-28

DOI

10.1063/1.123250

Peer reviewed

Rapid cooling and magnetic field-induced cooperative effect for the metastable quintet state in a spin crossover complex

Z. Yu^{a)}

State Key Laboratory of Coordination Chemistry, Department of Chemistry, Nanjing University, Nanjing, 210093, People's Republic of China

K. Liu

Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218

J. Q. Tao, Z. J. Zhong, and X. Z. You

State Key Laboratory of Coordination Chemistry, Department of Chemistry, Nanjing University, Nanjing, 210093, People's Republic of China

G. G. Siu

Department of Physics and Materials Science, City University of Hong Kong, Hong Kong

(Received 5 February 1999; accepted for publication 28 April 1999)

Our study shows that metastable quintet state of spin crossover complex $[\text{Fe}(\text{dpp})_2(\text{NCS})_2] \cdot \text{py}$ (dpp=dipyrido[3,2-a:2',3'-c] phenazine, py=pyridine) at low temperatures may be realized by a rapid cooling. The relaxation from quintet state to singlet spin at low temperatures depends on the both of time and previous history of the sample. The U-shaped dents of the magnetic effective moment depending on the temperature after initial rapid zero-field cooling indicate an obvious affection of magnetic field to the realization of singlet state in the transition range. The observations for this sample are indeed consistent with the fact that cooperative effects play a very important role in the spin transition. © 1999 American Institute of Physics. [S0003-6951(99)00426-X]

The phenomenon of electron spin crossover, also known as spin transition, spin equilibrium, or spin trapping, has developed into an important area of contemporary coordination chemistry as well as of applied physics over the last several decades since these materials have significant potential applications in molecular switching, memory storage, and display devices.¹ The feature of spin crossover occurs in some complexes of six-coordinate first-row transition metal as the result of the electron spin instability. For certain complexes, the spin crossover can be induced by thermal energy, pressure,² light irradiation³ [known as light induced excited spin state trapping (LIESST), and Reverse-LIESST] and soft x-ray irradiation⁴ [soft x-ray induced excited spin state trapping (SOXIESST)]. For an iron (II) complex, the singlet state of Fe^{2+} is a low spin (LS) state with spin $S=0$, which is the stable state at low temperatures. It also exists as a metastable quintet state with a high spin (HS) of $S=2$. The transition from the LS state to HS can be realized by LIESST or SOXIESST. Although it is in principle, possible to induce such a HS metastable state at low temperatures by rapid cooling, the phenomenon has only been successfully demonstrated in a few systems.⁵

Recently, a new kind of iron (II) spin crossover complex $[\text{Fe}(\text{dpp})_2(\text{NCS})_2] \cdot \text{py}$ has been fabricated.⁶ The structure has been determined by x-ray diffraction to be cis-dithiocyanatobiscis-dithiocyanatobis (dipyrido[3,2a:2',3'-c] phenazine), where the more extended aromatic ring is expected to show strong intermolecular $\pi-\pi$ interactions to enhance the cooperativity. The complex belongs to the family of spin crossover complex $[\text{Fe}(\text{phen})_2(\text{NCS})_2](\text{phen}$

=1,10-phenanthroline). The behavior of spin crossover shows an abrupt temperature dependence with a very wide thermal hysteresis (about 60 K), almost several hundred times larger than $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ does.⁷ The existence of hysteresis, as proven in the previous works,^{1,8,9} establishes that spin transition proceeds as first-order phase transition and present of cooperative effects. In this work, we showed the realization of HS metastable state at low temperatures by rapid cooling; the study of spin transition by controlling speed of cooling or warming; and the influence from magnetic field in the spin transition.

All magnetic measurements were performed in a superconducting quantum interference device (SQUID). The measuring procedure is as follows. The sample at room temperature was first loaded directly into the sample chamber at 5 K within zero magnetic field. Twenty minutes was allowed for the sample to reach thermal equilibrium before a 0.1 T field was turned on. The temperature dependence of the susceptibility was measured in three sequences; where (a) warming up from 5 to 300 K in about 3 h; (b) cooling down from 300 to 5 K in about 7 h; (c) warming up again from 5 to 300 K in about 3 h. The warming and cooling rates are essentially constant in each sequence. Figure 1 shows the result of such temperature cycling for both susceptibility and calculated effective moment per Fe ion for the three sequences of measurements. After the initial rapid zero field cooling (ZFC), below 100 K a metastable HS state, instead of the normal LS state, was realized. Increasing temperature in sequence (a) leads to an abrupt spin transition from HS to LS at about 100 K, followed by another sharp transition from LS back to HS at about 165 K. The susceptibility curve in the sequence (a) therefore has a U-shaped dent, indicating the trapping be-

^{a)}Electronic mail: zhiyu@public1.ptt.js.cn

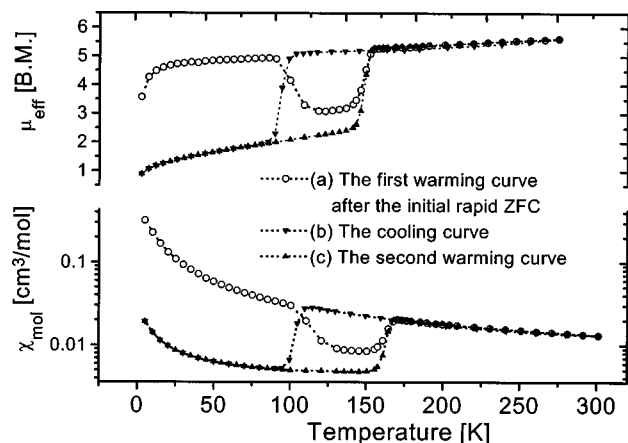


FIG. 1. Dependence of the molar susceptibility (bottom) and effective moment per Fe ion (top) on temperature cycling in complex $[\text{Fe}(\text{dpp})_2(\text{NCS})_2] \cdot \text{py}$. The three sets of symbols represent different steps in the cycle.

tween HS and LS states. The presence of HS metastable state at low temperatures indicates that the lattice structure in HS state at room temperature is probably frozen by the rapid cooling, and that the rate of spin state conversion is relatively slower than that of the structure change.⁵ Low temperature HS metastable state induced by the rapid ZFC is reproducible. Scans in sequences (b) and (c) confirm the two spin trappings seen in (a). In sequence (b), cooling down the sample does not induce the spin transition from HS to LS until around 100 K, and the LS state is maintained at lower temperatures. In sequence (c), warming up induces a single LS to HS transition at about 165 K. Note that the transitions in (b) and (c) are both single processes, and they essentially overlap with the U shape of curve (a), establishing a strong thermal hysteresis.

Close examination shows that in scan (a), the spin transitions are not as sharp as those in (b) and (c), also the values of susceptibility are higher than that in the LS state. The apparent gradual and incomplete trapping to the LS state in scan (a) is a manifestation of dynamic nature of the spin transition. The melting of the HS metastable lattice into the LS lattice is not only temperature dependent, but also time dependent. For example, at 100 K, the transition of HS to LS needs about 1 h to reach equilibrium (*vide post*). But in scan (a), the total measuring duration from 100 to 165 K is less than 40 min, and is too short to reflect a complete conversion of the HS state to LS state. In the subsequent cooling scan (b), the same temperature range took about 2 h to complete, therefore the LS state was much better established.

Figure 2 shows two examples of such spin relaxation at 100 K, achieved by different processes. In the first measurement, the sample was zero field cooled to 5 K, turning on a 0.1 T field, then warming up to 100 K. The measurements (solid symbols) were made at 100 K after the temperature has been stabilized. In the second measurement, the sample was cooled in the 0.1 T field from 300 K directly to 100 K and measured again at 100 K (open symbols). There is an appreciable difference between the two curves as the relaxation from the warming process takes about 20 min longer than the cooling one. Both of these measurements show significant deviation from the first-order kinetics. This is indeed

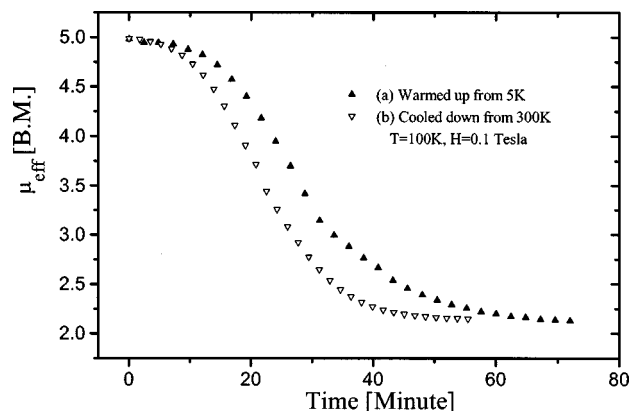


FIG. 2. The relaxation of HS state to LS state at 100 K for complex $[\text{Fe}(\text{dpp})_2(\text{NCS})_2] \cdot \text{py}$ in two processes: (a) warmed up from 5 K after a rapid zero field cooling and (b) cooled down directly from 300 K.

consistent with the fact that cooperative effects are known to play an important role for spin transition processes in the solid.^{5,8,9} Fitting the curves to typical phase transition kinetics, such as nucleation and phase propagation, turns out to be very difficult, because it involves complicated functions of the HS phase concentration in the sample. In the present case, the cooperative effects are demonstrated by the difference between the U-shape curve in temperature scan (a) and the thermal hysteresis loop formed in scans (b) and (c), as well as the different relaxation behavior just shown. The long-range order of predominantly like spins⁸ is probably broken into domain-like structures by rapid cooling, though the Fe ion remains on high spin state. The domain formation may be affected or perturbed by external conditions. Therefore the cooperative effects might be observed in stabilization of the spin state by external conditions such as magnetic field.

There have been both experimental and theoretical works on the influence of a magnetic field to the spin transition.^{10,11} In the $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ complex, the transition temperature was found to be lowered by 0.1 K by applying a 5 T field, and a more significant shift¹¹ was expected in much higher fields. In the present system, the magnetic field dependence of the spin trapping had also been studied. Figure 3 shows the U-shaped temperature scans of the sus-

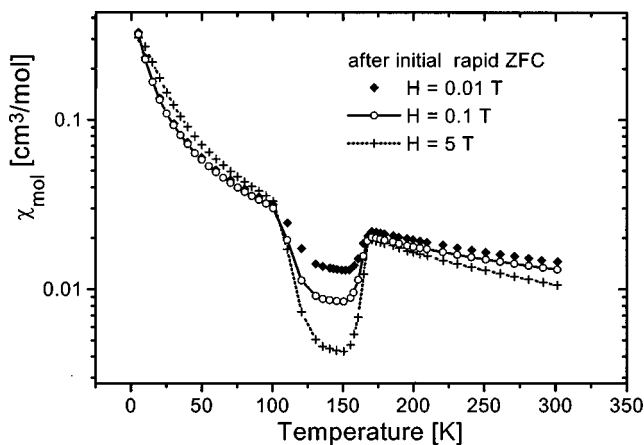


FIG. 3. Temperature dependence of the molar susceptibility for complex $[\text{Fe}(\text{dpp})_2(\text{NCS})_2] \cdot \text{py}$ measured in different magnetic fields after the initial rapid zero-field cooling.

ceptibility at various magnetic fields after the initial ZFC. In all cases, there is a U-shaped dent in the transition range (100–165 K). However a stronger field induces more LS states in the temperature range. Our experimental results agree to the predication of Sasaki,¹¹ exhibiting spin state stabilization on the influence of magnetic field. Note that even in a 5 T field, the susceptibility of the compound from the ZFC still has a higher value than that from the consequent field cooling (FC) in scan (b). The reason may be claimed in two points, (1) as the discussion of relaxation at 100 K (*vide ante*), the rate of spin conversion of the sequence (b) is faster than that of sequence (a); (2) but on the contrary, the measuring rate of the sequence (b) is slower than that of sequence (a). In fact, the time factor outweighs the field factor absolutely since a complete LS state was observed by Mössbauer effect⁶ for the sample at 80 K without magnetic field.

In order to see the effect of cooling speed and cooling field on the spin transition, we have performed the following experiments. In addition to the initial rapid ZFC (time $t = 20$ min, field $H = 0$), we have performed rapid FC ($t = 20$ min, $H = 0.1$ T), slow ZFC ($t = 2$ h, $H = 0$), and slow FC ($t = 2$ h, $H = 0.1$ T) individually before measuring the spin transition. Here the “slow cooling” refers to cooling the sample gradually down to 5 K over a 2 h span, in contrast to the rapid quenching previously mentioned. The temperature dependence of the magnetic susceptibility was then measured in the same way as in scan (a). Interestingly, the first three processes all led to a low temperature metastable HS state, whereas only the slow FC process led to a low temperature LS. The observation of the low temperature HS states in both slow and rapid ZFC processes also indicates that the presence of magnetic field perturbs to the stabilization of metastable HS state. However, the magnetic field alone, as in the rapid FC case, is not sufficient to remove the metastable HS state. Only in the slow field cooling process can the magnetic field convert HS into the LS state before the structure is frozen at low temperatures.

All the above observations indicate that cooperative effects play an important role in the spin transition since the cooperativity is associated with the fact that the equilibrium geometries in the LS and HS states are different. The nature of the cooperative mechanism may be clarified by both intra- and intermolecular interactions. The evidence of intermolecular interactions can be found in the structure determination of this compound $[\text{Fe}(\text{dpp})_2(\text{NCS})_2] \cdot \text{py}$.⁶ The crystal structure shows that ligand rings of molecules are stacked parallel to each other (interplanar distance is 3.5 Å), forming a column structure with strong $\pi-\pi$ interactions. The solvent pyridine molecule inserts between these columns and may cause the intercolumn van der Waals interactions. To compare to other spin crossover complexes in the family of $\text{Fe}(\text{phen})_2(\text{NCS})_2$, the ligand dpp has larger aromatic rings

to have stronger conductive ability of π electrons. This ability will enhance the inter-molecular interactions and cooperative effects. It is also possible that intramolecular coupling of the Fe ion with the molecular distortion occurred, as predicated for $\text{Fe}(\text{phen})_2(\text{NCS})_2$ by Sasaki.¹¹

In summary, we have studied the cooling speed and cooling field dependence of the spin crossover in complex $[\text{Fe}(\text{dpp})_2(\text{NCS})_2] \cdot \text{py}$. A low temperature metastable HS state is realized by zero field cooling or rapid field cooling, however, it can be destroyed by slow field cooling. The spin transition from HS to LS state is a dynamic process. The completion of the transition depends on both temperature and time, but on the other side, the completion is also perturbed by the applied magnetic field. The effect of cooling field and cooling speed showed a new light onto the understanding the cooperative effect associated with structure changing in spin crossover, although it is difficult to define the relationship between the spin conversion and cooperative effects.

This work was supported by the National Science Foundation of Jiangsu Province and by the National Science Foundation of the People's Republic of China. Work at The Johns Hopkins University has been supported by NSF Grant No. INT9600472.

¹P. Gülich, A. Hauser, and H. Spiering, *Angew. Chem. Int. Ed. Engl.* **33**, 2024 (1994); O. Kahn and E. Codjovi, *Philos. Trans. R. Soc. London Ser. A* **354**, 359 (1996); O. Kahn and C. J. Martinez, *Science* **279**, 44 (1998); E. König, *Struct. Bonding (Berlin)* **76**, 51 (1991); H. Toftlund, *Coord. Chem. Rev.* **94**, 67 (1989).

²H. G. Drickamer and C. W. Frank, *Electronic Transitions and the High Pressure Chemistry and Physics of Solids* (Chapman and Hall, London, 1973); E. Meissner, H. Köppen, C. P. Köhler, H. Spiering, and P. Gülich, *Hyperfine Interact.* **36**, 1 (1987); M. Konno and M. Kido, *Bull. Chem. Soc. Jpn.* **64**, 339 (1991).

³S. Decurtins, P. Gülich, C. P. Köhler, H. Spiering, and A. Hauser, *Chem. Phys. Lett.* **105**, 1 (1984); S. Decurtins, P. Gülich, K. M. Hasselbach, H. Spiering, and A. Hauser, *Inorg. Chem.* **24**, 2174 (1985); S. Decurtins, P. Gülich, C. P. Köhler, and H. Spiering, *J. Chem. Soc. Chem. Commun.* 430 (1985); A. Hauser, *J. Chem. Phys.* **94**, 2741 (1991).

⁴D. Collison, C. D. Garner, C. M. McGrath, J. F. W. Mosselmans, M. D. Roper, J. M. W. Seddon, E. Sinn, and N. A. Young, *J. Chem. Soc., Dalton Trans.* 4371 (1997).

⁵G. Ritter, E. König, W. Irlner, and H. A. Goodwin, *Inorg. Chem.* **17**, 224 (1978); H. A. Goodwin and K. H. Sugiyarto, *Chem. Phys. Lett.* **139**, 470 (1987); T. Buchen, P. Gülich, and H. A. Goodwin, *Inorg. Chem.* **33**, 4573 (1994), and references therein.

⁶J. Z. Zhong, J. Q. Tao, Z. Yu, C. Y. Duan, and X. Z. You, *J. Chem. Soc., Dalton Trans.* 327 (1998).

⁷E. W. Müller, H. Spiering, and P. Gülich, *Chem. Phys. Lett.* **93**, 567 (1982).

⁸D. H. Everett, *Trans. Faraday Soc.* **50**, 1077 (1950); **50**, 187 (1954), and references therein.

⁹A. Hauser, P. Gülich, and H. Spiering, *Inorg. Chem.* **25**, 4245 (1986).

¹⁰Y. Qi, E. W. Müller, H. Spiering, and P. Gülich, *Chem. Phys. Lett.* **101**, 502 (1983).

¹¹N. Sasaki and T. Kambara, *J. Phys. C* **15**, 1035 (1982), and references therein.