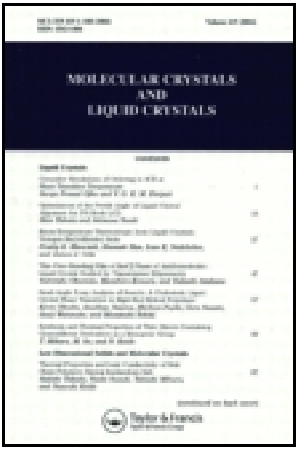

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Study on the Spin-Crossover System for $[Fe(4\text{-}NH_2trz)_3](p\text{-}CH_3C_6H_4SO_3)_2 \cdot nH_2O$

Shuji Toyazaki [a], Yuichi Murakami [a], Tokutaro Komatsu [a], Norimichi Kojima [a] & Toshihiko Yokoyama [b]

[a] Graduate School of Arts & Sciences, Univ. of Tokyo, Tokyo, 153-8902, Japan

[b] Graduate School of Science, Univ. of Tokyo, Tokyo, 113-0033, Japan

Version of record first published: 24 Sep 2006

To cite this article: Shuji Toyazaki, Yuichi Murakami, Tokutaro Komatsu, Norimichi Kojima & Toshihiko Yokoyama (2000): Study on the Spin-Crossover System for $[Fe(4\text{-}NH_2trz)_3](p\text{-}CH_3C_6H_4SO_3)_2 \cdot nH_2O$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 343:1, 175-180

To link to this article: http://dx.doi.org/10.1080/10587250008023522

Mol. Cryst. and Liq. Cryst., 2000, Vol. 343, pp. 175-180
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Study on the Spin-Crossover System for $[Fe(4\text{-}NH_2trz)_3](p\text{-}CH_3C_6H_4SO_3)_2{\bullet}nH_2O$

SHUJI TOYAZAKI[a], YUICHI MURAKAMI[a],
TOKUTARO KOMATSU[a], NORIMICHI KOJIMA[a] and
TOSHIHIKO YOKOYAMA[b]

[a]*Graduate School of Arts & Sciences, Univ. of Tokyo, Tokyo 153–8902, Japan and*
[b]*Graduate School of Science, Univ. of Tokyo, Tokyo 113–0033, Japan*

We have investigated the spin-crossover behavior for $[Fe(4\text{-}NH_2trz)_3](p\text{-}CH_3C_6H_4SO_3)_2{\bullet}nH_2O$. From the EXAFS measurement, it is confirmed that this complex has a linear chain polynuclear structure like the typical iron(II)-triazole complexes. In this complex, the number of crystal water, n, varies from 1.5 to 8 under the condition of water vapor pressure. The spin-crossover behavior in this complex strongly depends on the crystal water as well as the counter-anion. With increasing the number of crystal water from 1.5 to 8, the spin transition temperature decreases and the hysteresis width becomes narrower. In the case of n = 1.5, a stepped spin-crossover transition takes place and the intermediate spin state shows a unique thermal history.

Keywords: spin-crossover complex; thermal hysteresis; EXAFS; hydrogen bond

INTRODUCTION

Transition metal complexes with d^4~d^7 configuration have a possibility of the spin transition between the low-spin (LS) and the high-spin (HS) states. Iron(II) complexes coordinated by 1,2,4-triazole and its derivatives are known to form the Fe chain structure illustrated in Fig.1 and to show the spin transition between the diamagnetic state (S = 0) and the paramagnetic state (S = 2) with a large thermal hysteresis loop around room temperature.[1-6] Owing to this magnetic nature, the application to some molecular devices such as display and memory may be possible.

In order to search on the spin-crossover system having the bistability in the wide temperature range around room temperature, we have synthesized iron(II)-4-amino-triazole complexes with various kinds of sulfonate anion. In these systems, the spin transition temperature strongly depends on the amount of crystal water as well as the kind of counter-anion, e.g. while the color of $[Fe(4\text{-}NH_2trz)_3](p\text{-}CH_3C_6H_4SO_3)_2{\cdot}1.5H_2O$ is purple at room temperature, that of dehydrated $[Fe(4\text{-}NH_2trz)_3](p\text{-}CH_3C_6H_4SO_3)_2$ is white. The purple and white colors correspond to the low spin state and the high spin state of iron(II), respectively.

In this paper, we report and discuss the effect of crystal water on the spin-crossover behavior for $[Fe(4\text{-}NH_2trz)_3](p\text{-}CH_3C_6H_4SO_3)_2{\cdot}nH_2O$.

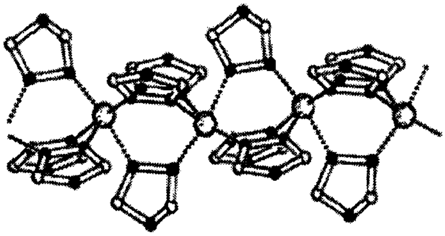

FIGURE 1 The Fe chain structure of the iron(II)-triazole complex. Large circle : Fe, small circle : C, black filled dot : N.

EXPERIMENTAL

Sample Preparation

Synthesis of $[Fe(4\text{-}NH_2trz)_3](p\text{-}CH_3C_6H_4SO_3)_2$ Iron powder was dissolved into the methanolic solution of p-toluenesulfonic acid. Ascorbic acid was used to prevent the partial oxidation of iron (II). After evaporating methanol $Fe(p\text{-}CH_3C_6H_4SO_3)_2$ precipitated as bluish powder. The crude product was recrystalized from methanol. Then the methanolic solution of $Fe(p\text{-}CH_3C_6H_4SO_3)_2$ was mixed with the methanolic solution of 4-amino-1,2,4-triazole. The desired complex precipitated immediately as white powder and was filtered off. Because of the hydration, the color of the complex turned to purple.

Although the number of crystal water, n, nearly equals to 1.5 under the ambient humidity, n increased from 1.5 under more humid condition. To keep n in the desired value more than 1.5, the hydrated compound was sealed into an aluminum capsule after the adjustment of n by means of thermogravimeter. In addition, the value less than 1.5 was acquired by drying in vacuum.

EXAFS Measurement

The Fe K-edge EXAFS spectra were taken in the conventional transmission mode at BL-10B in Photon Factory (operation energy of 2.5 GeV and stored current of 400-200 mA) in Institute of Materials Structure Science. A water-cooled Si(311) channel-cut crystal was employed as a monochromator. The sample was diluted with BN to give a pellet. In order to avoid the loss of crystal water in vacuum, the pellet was completely sealed with an adhesive substrate (Stycast No.1266).

Magnetic Measurement

The temperature dependence of magnetic susceptibility was measured with Quantum Design MPMS-5S SQUID susceptometer. The applied field was 5000 Gauss.

RESULTS AND DISCUSSION

Figure 2 represents the Fourier transforms of EXAFS for $[Fe(4\text{-}NH_2trz)_3](p\text{-}CH_3C_6H_4SO_3)_2 \cdot 1.5H_2O$ at 295K and 365K, which corresponds to the low spin state and the high spin state, respectively. The peaks of the Fourier transforms at 3.5Å and 3.8Å for 295K and 365K, respectively, are due to the Fe-Fe scattering and the peaks at 6.9Å and 7.3Å for 295K and 365K, respectively correspond to the Fe-Fe-Fe multiple scattering, which prove the straight one-dimensional Fe chain structure.

Figure 3 represents the spin-crossover behavior for $[Fe(4\text{-}NH_2trz)_3](p\text{-}CH_3C_6H_4SO_3)_2 \cdot nH_2O$ (n = 1.5, 3.5, 5.5, 8). As shown in Fig.1, with increasing the number of crystal water, n, the transition temperature lowers and the thermal hysteresis width becomes narrow. The samples of n = 1.5, 3.5 and 5.5 show a stepped low spin - high spin transition. The sample of n = 8 has no thermal hysteresis. In this system, the effect of crystal water on the spin transition

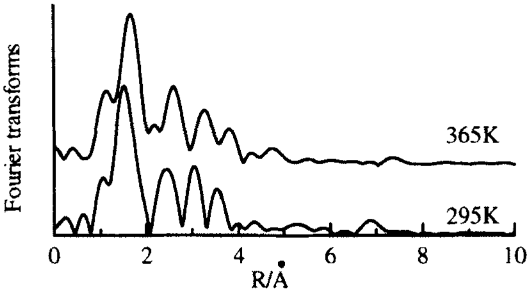

FIGURE2 Fourier transforms of EXAFS for $[Fe(4\text{-}NH_2trz)_3](p\text{-}CH_3C_6H_4SO_3)_2\bullet 1.5H_2O$ at 295K and 365K.

temperature is similar to the effect of counter-anion reported by J. J. A. Kolnaar et al.[7] The increment in the radius of counter-anion for $[Fe(4\text{-}NH_2trz)_3](anion)_2 \bullet nH_2O$ reduces the spin transition temperature,[5, 7, 8] which implies that the counter-anion performs as a spacer between Fe-chains and the increase of anion radius makes the lattice softer.

Figure 4 represents the spin-crossover behavior for n = 1.5 and n ~ 0. The spin transition for n = 1.5 is abrupt whereas that for n ~ 0 is gradual and the high-spin fraction remains even at 0K. This result contrasts with that shown in Fig.3. In this case, the crystal water is presumably supposed to form hydrogen bonds and make the lattice harder.

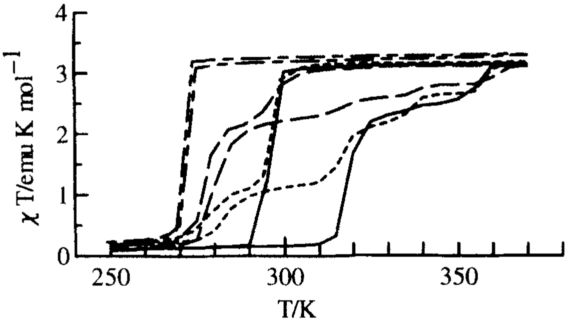

FIGURE 3 Temperature dependence of the magnetic susceptibility for $[Fe(4\text{-}NH_2trz)_3](p\text{-}CH_3C_6H_4SO_3)_2\bullet nH_2O$. n = 1.5 (solid), n = 3.5 (dot), n = 5.5(dash), n = 8 (dot-dash).

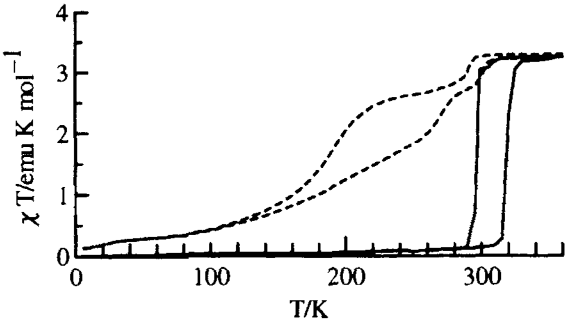

FIGURE 4 Temperature dependence of the magnetic susceptibility for $[Fe(4\text{-}NH_2trz)_3](p\text{-}CH_3C_6H_4SO_3)_2\cdot nH_2O$. n = 1.5 (solid), n ~ 0 (dot).

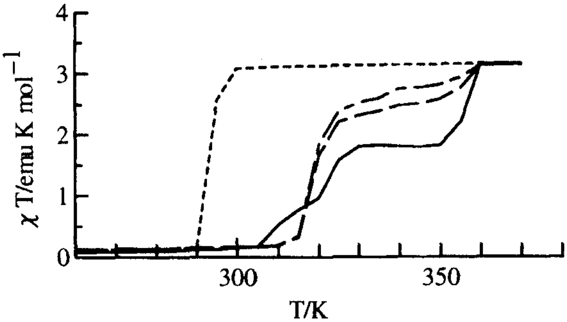

FIGURE 5 Temperature dependence of the magnetic susceptibility for $[Fe(4\text{-}NH_2trz)_3](p\text{-}CH_3C_6H_4SO_3)_2\cdot 1.5H_2O$.
First heating process (solid), cooling process(dot),
second heating process (dash), third heating process (dot-dash).

Figure 5 represents a curious spin-crossover behavior for n = 1.5. The intermediate state between 310 and 360 K gradually disappears by annealing and this change is not reversible. Similar irreversible thermal history of spin-crossover behavior was reported on a Langumuir film of an amphiphilic iron(II) complex.[9] The irreversible thermal history is assumed to arise from the rearrangement of inner structure by annealing.

As mentioned above, the effect of crystal water on the spin-crossover behavior is important as well as that of counter-anion. In particular, the two opposite functions of crystal water shown in Fig.3 and 4 are interesting. Additional study by means of IR Spectroscopy is in progress.

Acknowledgments

This work was supported in part by a grant-in-aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

References

[1] O. Kahn, J. Kröber and C. Jay, *Adv. Mater.* **4**, 718 (1992).
[2] J. Kröber, E. Codjovi, O. Kahn, F. Grolière and C. Jay, *J. Am. Chem Soc.* **115**, 9810(1993).
[3] C. Jay, F. Grolière, O. Kahn and J. Kröber, *Mol. Cryst. Liq. Cryst.* **234,** 255 (1993).
[4] J. Kröber, J. P. Audière, R, Claude, E. Codjovi, O. Kahn, J. G. Haasnoot, F. Grolière, C. Jay, A. Bousseksou, J. Linarès, F. Varret and A. Gontier-Vassal, *Chem. Mater.* **6**, 1404 (1994).
[5] L. G. Lavrenova, N. G. Yudina, V. N. Ikorskii, V. A. Varnek, I. M. Oglezneva, S. V. Larionov, *Polyhedron* **14**, 1333 (1995).
[6] Y. Garcia, P. J. Koningsbruggen, R. Lapouyade, L. Rabardel, O. Kahn, M. Wieczorek, R. Bronisz, Z. Ciunik, M. F. Rudolf, *Mol. Inorg. Chem.* 523–532 (1998).
[7] J. J. A. Kolnaar, Doctoral Thesis (Leiden Univ. 1998).
[8] V. G. Ksenofontov, D. Fuelber, M. Kaul, P. Gütlich, O. Kahn, Second Spin-Crossover family meeting, Gir sur Yvette-France 27–28 October 1995.
[9] H. Soyer, C. Mingotaud, M-L. Boillot, P. Delhaes, *Thin Solid Films* **327–329,** 435 (1998).