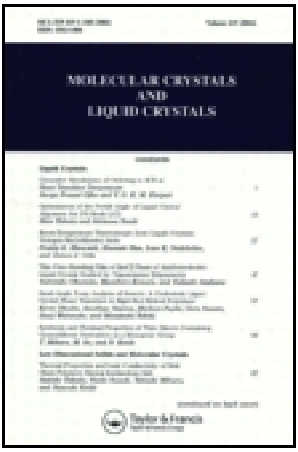

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

# Pressure Effect on Ferromagnetic Transition and Charge-Transfer Phase Transition in a Mixed-Valence Iron Complex (n-C 3 H 7 ) 4 N[Fe II Fe III (dto) 3 ](dto=C 2 O 2 S 2 )

Miho Itoi [a] , Norimichi Kojima [a] , Yoshihiko Kobayashi [b] & Kichizou Asai [b]

[a] Graduate School of Arts and Sciences, The University of Tokyo, Komaba 3-8-1, Megro-ku, Tokyo, 153-8902

[b] The University of Electro-Communications, Chofugaoka 1-5-1, Choufu-shi, Tokyo, 182-8585

To cite this article: Miho Itoi, Norimichi Kojima, Yoshihiko Kobayashi & Kichizou Asai (2003): Pressure Effect on Ferromagnetic Transition and Charge-Transfer Phase Transition in a Mixed-Valence Iron Complex (n-C 3 H 7 ) 4 N[Fe II Fe III (dto) 3 ](dto=C 2 O 2 S 2 ), Molecular Crystals and Liquid Crystals, 379:1, 377-382

To link to this article: http://dx.doi.org/10.1080/713738653

*Mol. Cryst. Liq. Cryst.*, Vol. 379, pp. 377-382

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290090750

# Pressure Effect on Ferromagnetic Transition and Charge-Transfer Phase Transition in a Mixed-Valence Iron Complex $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3](dto = C_2O_2S_2)$

MIHO ITOI[a], NORIMICHI KOJIMA[a],
YOSHIHIKO KOBAYASHI[b] and KICHIZOU ASAI[b]

[a]*Graduate School of Arts and Sciences, The University of Tokyo, Komaba 3-8-1, Megro-ku, Tokyo, 153-8902 and*
[b]*The University of Electro-Communications, Chofugaoka 1-5-1, Choufu-shi, Tokyo, 182-8585*

Iron mixed-valence complex $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ $(dto=C_2O_2S_2)$ exhibits not only the ferromagnetic transition at 6.5 K but also the charge-transfer phase transition between $Fe^{II}$ and $Fe^{III}$ around 120 K. In order to elucidate the mechanism of the charge-transfer phase transition, we measured the magnetic susceptibility under external pressure. Under hydrostatic pressure up to 0.9 Gpa, the critical temperature of the charge-transfer transition strongly depends on external pressure, while the Curie temperature remains unchanged. Under uniaxial stress of 0.6 GPa, on the other hands, the Curie temperature increases up to 15 K, while the charge-transfer temperature remains unchanged. After releasing uniaxial stress, the zero field magnetization at ambient pressure has two peaks at 7 K and 15 K, which implies two kinds of ferromagnetic spin configuration coexist, i.e. $Fe^{III}$ (S=5/2), $Fe^{II}$(S=0) and $Fe^{III}$ (S=1/2), $Fe^{II}$ (S=2). The coexistence of two kinds of ferromagnetic spin configuration was also observed for $(n\text{-}C_4H_9)_4N[Fe^{II}Fe^{III}(dto)_3]$ at ambient pressure.

Keywords: mixed-valence; spin crossover; charge transfer; pressure effect

## INTRODUCTION

Transition metal complexes with $d^4$-$d^7$ have a possibility of spin transitions between the low-spin (LS) and the high-spin (HS) states. In particular there are various kinds of Fe (II) complexes exhibiting spin crossover transition. In the case of mixed-valence transition metal complexes whose spin states lie in the spin-crossover region, new types of conjugated phenomena coupled with spin and charge are expected. From the viewpoint, we have synthesized the mixed-valence complex $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ ($dto=C_2O_2S_2$). This complex exhibits the charge transfer phase transition where spin-crossover and charge transfer phenomena take place simultaneously[1,2]. In order to elucidate the origin of the charge transfer transition, we investigated the uniaxial stress effect as well as hydrostatic pressure effect on the charge transfer phase transition in $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$. In this paper, we report the behavior of the magnetic susceptibility for the title complex under the external pressure.

## EXPERIMENTAL PROCEDURE

$(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ was synthesized in a similar way to prepare $(n\text{-}C_3H_7)_4N[M^{II}Cr^{III}(dto)_3]$ (M = Fe, Co, Ni, Zn)[3]. A solution of $KBa[Fe(dto)_3]\cdot 3H_2O$ in a methanol-water mixture was stirred. To this, a solution of $FeCl_2\cdot 4H_2O$ and $(n\text{-}C_3H_7)_4NBr$ in a methanol-water mixture was added. In this way, $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ was obtained as black colored precipitate. In the case of the application of hydrostatic pressure, the high-pressure apparatus is a pencil type champ-cell made of CuBe alloy (C1720B-H)[4]. We used a mixture of two kinds of Fluorinart as a fluid pressure medium. Wrapped powdered sample in polyethylene film was placed in the champ-cell and compressed up to 0.9 Gpa. The pressure was determined by measuring the superconducting temperature of Sn placed in the champ-cell. In the case of the application of the uniaxial stress, the pressure apparatus is a piston cylinder type and wrapped powdered sample was compressed up to 0.6 Gpa. The static magnetic susceptibility was measured by a Quantum Design MPMS5 SQUID susceptmeter.

## RESULT AND DISCUSSTION

$(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ is presumed to have a honeycomb network with an alternating array of $Fe^{II}$ and $Fe^{III}$ atoms through dto bridges, which is estimated by the single crystal analysis of $(n\text{-}C_3H_7)_4N[Co^{II}Fe^{III}(dto)_3]$[5]. This iron polynuclear complex exhibits

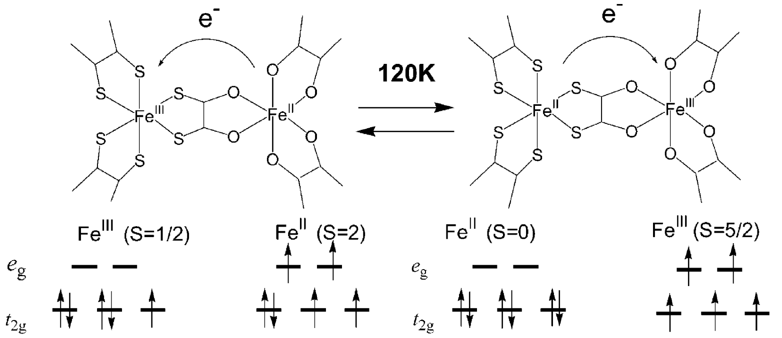

FIGURE 1 Schematic representation of the charge transfer phase transition at 120 K for $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$. The left side denotes the high temperature phase, and the right side denotes the low temperature phase.

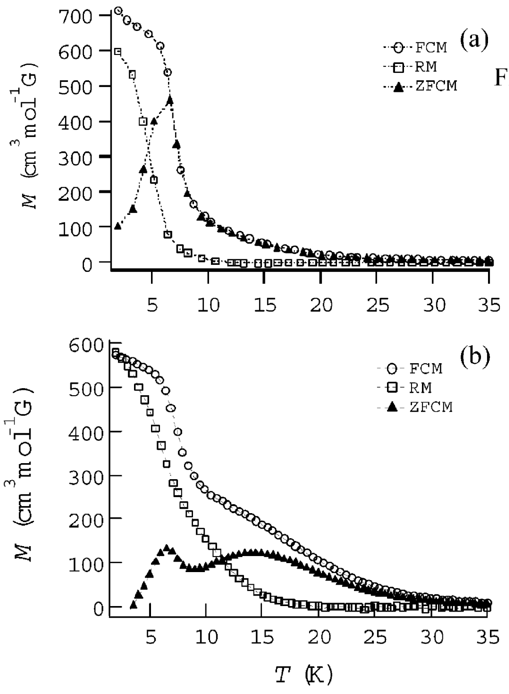

FIGURE 2 Field cooled magnetization (○), remnant magnetization (□) and zero field cooled magnetization (▲) for $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$. The external magnetic field is $H$= 30 G. (a) magnetization curves at ambient pressure, (b) magnetization curves at ambient pressure after applying uniaxial pressure up to 0.6 GPa.

the charge transfer phase transition around 120 K and the ferromagnetic transition at 6.5 K. The mechanism of charge-transfer transition is schematically shown in Figure 1.

At room temperature, $Fe^{II}$ (S=2) and $Fe^{III}$ (S=1/2) sites are coordinated by six O atoms and S atoms, respectively. Around 120 K, one electron of $Fe^{II}$ site transfers to $Fe^{III}$ site. Then, the $Fe^{III}$ (S=5/2) and $Fe^{II}$ (S=0) sites are coordinated by six O atoms and six S atoms respectively. The spin configuration of $Fe^{II}$ (S=0) and $Fe^{III}$ (S=5/2) brings the ferromagnetic order. In order to investigate the mechanism of the charge transfer phase transition around 120 K and the ferromagnetic order, we investigated the external pressure effect as well as the chemical pressure effect (i.e. cation size effect) on these phase transitions[6]. We found that the charge transfer phase transition occurs only for $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$ n = 3, 4 complexes. $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$(n=3,4) complexes show the low spin state of $Fe^{III}$ (S=1/2) and high spin state of $Fe^{II}$ (S=2) in high temperature and the low spin state of $Fe^{II}$ (S=0) and the high spin state of $Fe^{III}$ (S=5/2) below the critical temperature of the charge transfer phase transition. The Curie temperature (Tc) for n = 3, 4 is 6 K and 12 K, respectively. On the other hand, $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$(n=5,6) complexes show the high spin state of $Fe^{II}$ (S=2) and low spin state of $Fe^{III}$ (S=1/2) in all temperature region. The Curie temperature for n = 5, 6 is 18 K and 26 K, respectively. The Curie temperature for n = 3 and 4 is quite lower than that for n = 5 and 6, which is attributed to that the $Fe^{II}$ site in the lower temperature phase for n = 3 and 4 is diamagnetic low-spin state (S=0).

We applied hydrostatic pressure from 0.2 GPa to 0.9 GPa for $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ and measured the magnetic susceptibility. The critical temperature of the charge transfer transition increases by about 100 K under hydrostatic pressure up to 0.9 GPa, while the Curie temperature remains unchanged under hydrostatic pressure up to 0.6 GPa. [7].

Next, we applied uniaxial stress of 0.6 GPa for $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$. After releasing pressure, we measured the magnetic susceptibility at ambient pressure (Figure 2 (b)). The RM disappears at 15 K and ZFCM has two peaks at 7 K and 15 K, which implies that two spin configuration $Fe^{III}$ (S=5/2) - $Fe^{II}$ (S=0) and $Fe^{III}$ (S=1/2) - $Fe^{II}$ (S=2) coexist. On the other hand, the charge transfer phase transition temperature remains unchanged.

We discuss the pressure effect on the charge transfer phase transition and the ferromagnetic transition. The uniaxial stress application necessarily causes so-called Poisson's effect. If the uniaxial stress is applied, the two-dimensional honeycomb structure lies perpendicularly to *c* axis due to the preferred orientation. The stronger uniaxial stress is applied, each bulky cation is pressed onto honeycomb layer and then lattice parameter of the complex in the *ab* plane perpendicular to the stress application increases, while that along the uniaxial stress (*c* axis) decreases. On the other hand, in the case of hydrostatic pressure, a unit cell volume of crystal is isotoropically compressed as shown in Figure 3. We have confirmed from the powder X-ray diffraction on $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ complex that after applying uniaxial stress the diffraction peaks corresponding to the intra-layer distance shift to the lower angle side, while that corresponding to inter-layer distance shift to high angle side. Consequently, after applying uniaxial stress, the honeycomb ring is expanded and inter-layer distance is compressed. This phenomenon seems to occur for the $(n\text{-}C_4H_9)_4N[Fe^{II}Fe^{III}(dto)_3]$ compound at ambient pressure which is shown in Figure 4.

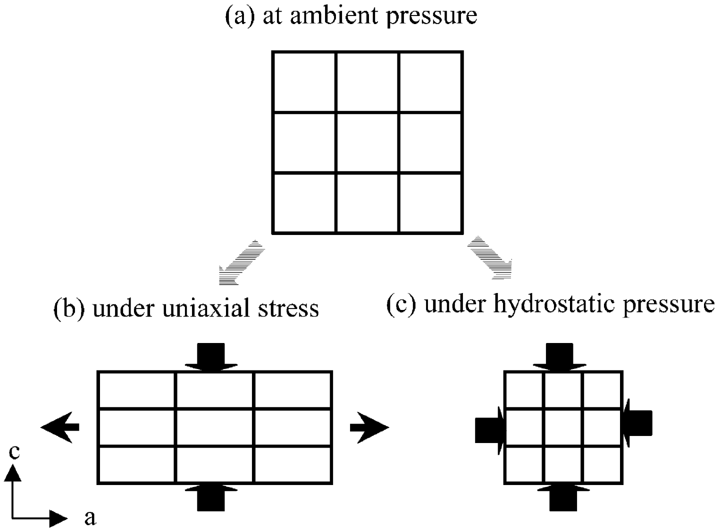

FIGURE 3 Schematic representation of pressure effect. (a), (b) and (c) denote the unit-cell volume of crystal at ambient pressure, under the uniaxial stress and under hydrostatic pressure, respectively. In $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$, the two-dimensional honeycomb network structure lies in *ab* plane. The uniaxial stress application causes Poisson's effect which increases the lattice parameter of *ab* plane and decreases that of *c* direction.

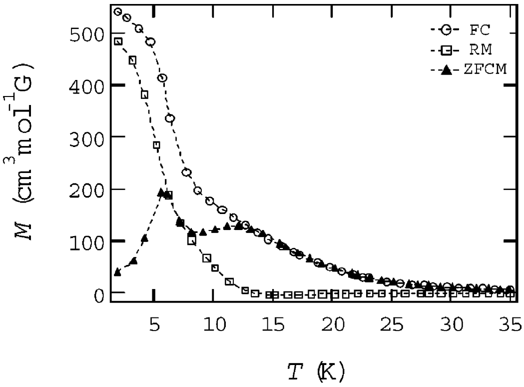

FIGURE 4 Field cooled magnetization (○ ), remnant magnetization ( □ ) and zero field cooled magnetization ( ▲ ) for $(C_4H_9)_4N[Fe^{II}Fe^{III}(dto)_3]$. The external magnetic field $H$=30G.

The Curie temperature for the n = 4 compound is 12 K. We confirmed that ZFCM has two peaks at 7 K and 12 K. It is supposed that since bulkier cation $(C_4H_9)_4N^+$ leads to lattice deformation, all $Fe^{II}$ (S=2) and $Fe^{III}$ (S=1/2) spin pairs would not take the charge transfer transition. For that reason, $Fe^{II}$ (S=2) -$Fe^{III}$ (S=1/2) pairs and $Fe^{II}$ (S=0) - $Fe^{III}$ (S=5/2) pairs coexist in low temperature region. In order to prove the coexistence of $Fe^{II}$ (S=2) - $Fe^{III}$ (S=1/2) pairs and $Fe^{II}$ (S=0) - $Fe^{III}$ (S=5/2) pairs, the measurement of the $^{57}$Fe Mössbaure spectrum is indispensable, and in progress.

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