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Study on the Rapid Spin Equilibrium in $Ph_4P[Zn^{II}Fe^{III}(mto)_3]$ (mto = Monothiooxalato)

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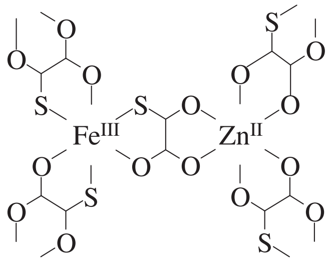
We synthesized a mto (= monothiooxalato)-bridged heterometal complex, $Ph_4P[Zn^{II}Fe^{III}(mto)_3]$ consisting of $Fe^{III}O_3S_3$ and $Zn^{II}O_6$ octahedra and investigated its physical properties. $Ph_4P[Zn^{II}Fe^{III}(mto)_3]$ has a two-dimensional honeycomb network structure. The ESR and ^{57}Fe Mössbauer spectra revealed that the rapid spin equilibrium in which the high-spin (HS) state and the low-spin (LS) state exchange in the time scale of $10^{-10} < \tau < 10^{-7}$ s occurs at the $Fe^{III}O_3S_3$ site, which is the first report for an assembled metal complex system.

One of the most important topics in recent research in the field of molecular solids is to produce various kinds of multifunctionalities coupled with transport, optical, or magnetic properties.[1–3] In the case of assembled heterometal complex systems whose spin state is situated in the spin-crossover region, novel types of conjugated phenomena coupled with spin and charge are expected. In fact, recently Kojima et al. discovered a new type of phase transition for a dithiooxalato-bridged iron mixed-valence complex, $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ (dto = dithiooxalato), where the thermally induced charge-transfer phase transition reversibly occurs around 120 K in order to minimize the free energy in the whole system.[4] $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ has a two-dimensional honeycomb network structure with an alternating array of Fe^{II} and Fe^{III} atoms through dto ligand, and the $(n\text{-}C_3H_7)_4N^+$ cation layers are intercalated between two $[Fe^{II}Fe^{III}(dto)_3]_\infty$ layers.[5] In the high-temperature phase, the Fe^{III} ($S = 1/2$) and Fe^{II} ($S = 2$) sites are coordinated by six S atoms and six O atoms, respectively. In the low-temperature phase, on the other hand, the Fe^{III} ($S = 5/2$) and Fe^{II} ($S = 0$) sites are coordinated by six O atoms and six S atoms, respectively. Moreover, $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ behaves as a ferromagnet with $T_C = 7$ K.[4]

In general, the Fe^{III} site coordinated by six S atoms is in the low-spin (LS) state, while the Fe^{III} site coordinated by six O atoms is in the high-spin (HS) state. Therefore, it is expected that the spin state of Fe^{III} coordinated by three S atoms and three O atoms is situated in the spin-crossover region. Actually, the spin equilibrium in which the high-spin (HS) state and the low-spin (LS) state exchange have been confirmed for mononuclear Fe^{III} complexes consisting of $Fe^{III}O_3S_3$.[6,7] However, the rapid spin equilibrium phenomenon has not yet been observed for assembled metal complex systems. From this viewpoint, in order to build an assembled metal complex system including $Fe^{III}O_3S_3$ site, we have synthesized $Ph_4P[Zn^{II}Fe^{III}(mto)_3]$ (mto = monothiooxalato) (**1**) consisting of $Fe^{III}O_3S_3$ and $Zn^{II}O_6$ octahedra and investigated the spin state of the $Fe^{III}O_3S_3$ site in **1**. The two-dimensional network structure of $[Zn^{II}Fe^{III}(mto)_3]$ is schematically shown in Scheme 1.



Scheme 1. Schematic representation of the 2-D network structure in $[Fe^{III}Zn^{II}(mto)_3]$ complex.

$K_2(mto)$ was prepared according to a previous paper.[8] A methanol solution of iron(III) nitrate (291 mg, 0.72 mmol) was added to a methanol solution of $K_2(mto)$ (393 mg, 2.16 mmol) and $(C_6H_5)_4PBr$ (453 mg, 1.08 mmol). After stirring for 1 h, $[Fe^{III}(mto)_3]^{3-}$ solution was given. This suspension was filtered to remove solid impurities. The filtrate was cooled at −10 °C, and methanol solution (25 mL) of zinc(II) chloride (65 mg, 0.48 mmol) was added to the filtrate. The mixture was stirred for 12 h. The red-brown colored product was collected by suction filtration and dried in vacuo. Elemental Analysis calculated for $C_{30}H_{20}O_9PS_3ZnFe$: C, 46.62; H, 2.60; S, 12.45%. Found: C, 45.82; H, 2.85; S, 12.54%.

Powder X-ray diffraction measurement was performed in order to determine the crystal system and space group. The static magnetic susceptibility was measured by a Quantum Design, MPMS-5 SQUID susceptometer between 2 and 300 K under 0.5 T. The X-band ESR measurement was performed between 10 and 300 K. The ^{57}Fe Mössbauer spectra were measured between 10 and 300 K. The spectra were calibrated by using the six lines of a body-centered cubic iron (α-Fe) foil, the center of which was taken as zero isomer shift. The spectra were fitted with a MossWinn 3.0 program.[9]

The powder X-ray diffraction pattern of **1** resembles clearly that of $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$, which implies that the crystal structure of **1** consists of two-dimensional honeycomb network structure.[5,10] The crystal system and space group of **1** were assigned to hexagonal and $P6_3$, respectively.

Figure 1 shows the molar magnetic susceptibility multiplied by temperature, $\chi_M T$, as a function of temperature for **1**. The $\chi_M T$ value decreases with lowering temperature. In $(n\text{-}C_4H_9)_4N[Zn^{II}Fe^{III}(ox)_3]$ (ox = oxalato) with similar structure of **1**, the $\chi_M T$ value (= 4.22 $cm^3\,K\,mol^{-1}$) is essentially constant in the whole temperature range of 4.2–300 K.[11] However, the $\chi_M T$ value for **1** decreases from 3.60 (at 300 K) to 2.66 $cm^3\,K\,mol^{-1}$ (at 4.2 K). In connection with this, it should be noted that the spin-only $\chi_M T$ value is 4.375 $cm^3\,K\,mol^{-1}$ for the HS state ($S = 5/2$) of Fe^{III}, while that is 0.375 $cm^3\,K\,mol^{-1}$ for the LS state ($S = 1/2$) of Fe^{III}. Therefore, the $\chi_M T$ value of **1** is situated in the middle value between the magnetic moments for the HS and LS states of Fe^{III}. The $\chi_M T$ curve steeply decreases below

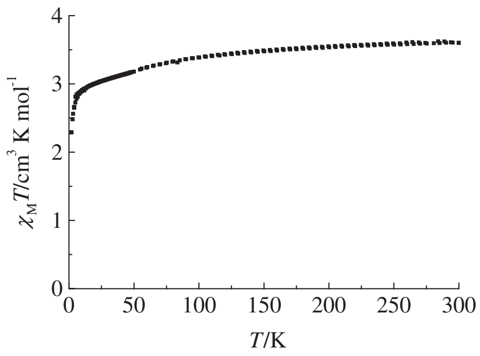


Figure 1. Molar magnetic susceptibility multiplied by temperature, $\chi_M T$, as a fuction of temperature for **1**.

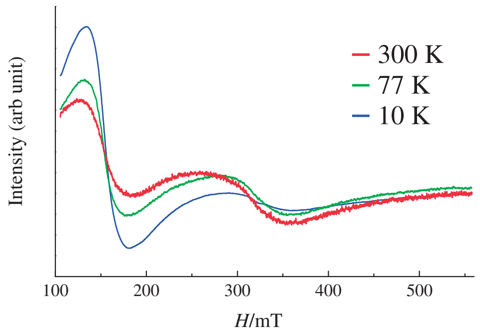


Figure 2. Temperature dependence of ESR spectra for **1**.

10 K due to a weak antiferromagnetic interaction ($\theta = -0.66(4)$ K).

The temperature dependence of ESR spectra for **1** is shown in Figure 2. The ESR signals corresponding to the HS state and the LS state of Fe^{III} site are observed at about 300 mT ($g \approx 2.05$) and at about 150 mT ($g \approx 4.25$), respectively, in the temperature range between 10 and 300 K. The ESR signal ratio of the LS state to the HS state increases with decreasing temperature, which is consistent with the temperature dependence of $\chi_M T$. Therefore, these results indicate that the spin state of $Fe^{III}O_3S_3$ is the spin equilibrium of the HS and LS states, where the HS and LS states are clearly distinguishable in the time scale (10^{-10} s) of ESR spectroscopy.

Figure 3 shows the ^{57}Fe Mössbauer spectra of **1** at 300, 77, and 10 K.[10] The single quadrupole doublet of Fe^{III} was observed despite of the coexistence of the HS and LS states in the ESR measurement between 10 and 300 K. The ^{57}Fe Mössbauer spectra of HS and LS states should be distinguishable, if the time scale of spin equilibrium is slower than that of the ^{57}Fe Mössbauer spectroscopy ($\tau = 10^{-7}$ s).[6] On the other hand, the averaged spectra of HS and LS states are observed, if the time scale of spin equilibrium is faster than that of the ^{57}Fe Mössbauer spectroscopy.[7] Therefore, the ^{57}Fe Mössbauer spectra of **1** shown in Figure 3 indicates that the rapid spin equilibrium in which the HS and LS state exchange in the time scale faster than that of ^{57}Fe Mössbauer spectroscopy occurs at the $Fe^{III}O_3S_3$ site. The relaxation process between HS and LS states at the $Fe^{III}O_3S_3$ site is considered to be a tunneling process.[12]

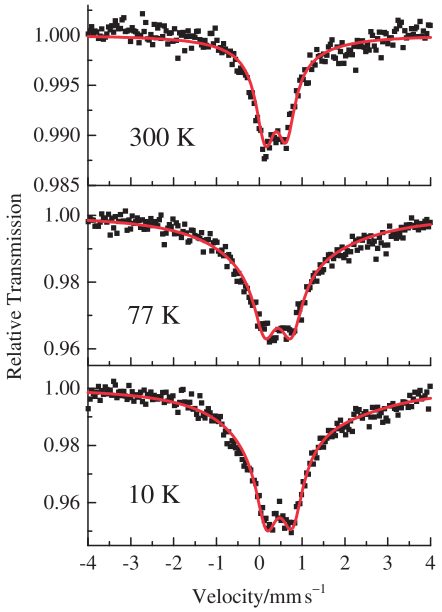


Figure 3. Temperature dependence of ^{57}Fe Mössbauer spectra for **1**. Solid line represents the least-squares fitting curve.

In summary, we found the rapid spin-equilibrium phenomenon between the HS and LS states at the $Fe^{III}O_3S_3$ site in **1**, which is the first report for an assembled metal complex system. The time scale of spin equilibrium was estimated at $10^{-10} < \tau < 10^{-7}$ s from the analysis of ESR and ^{57}Fe Mössbauer spectroscopy.

References and Notes

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1. N. Tajima, J. Fujisawa, N. Naka, T. Ishihara, R. Kato, Y. Nishio, K. Kajita, *J. Phys. Soc. Jpn.* **2005**, *74*, 511.
2. S. Uji, H. Shinagawa, T. Terashima, T. Yakabe, Y. Terai, M. Tokumoto, A. Kobayashi, H. Tanaka, H. Kobayashi, *Nature* **2001**, *410*, 908.
3. O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, *Science* **1996**, *272*, 704.
4. N. Kojima, W. Aoki, M. Itoi, Y. Ono, M. Seto, Y. Kobayashi, Y. Maeda, *Solid State Commun.* **2001**, *120*, 165.
5. M. Itoi, A. Taira, M. Enomoto, N. Matsushita, N. Kojima, Y. Kobayashi, K. Asai, K. Koyama, T. Nakano, Y. Uwatoko, J. Yamaura, *Solid State Commun.* **2004**, *130*, 415.
6. M. Cox, J. Darken, B. W. Fitzsimmons, A. W. Smith, L. F. Larkworthy, K. A. Rogers, *J. Chem. Soc., Dalton Trans.* **1972**, 1192.
7. K. R. Kunze, D. L. Perry, L. J. Wilson, *Inorg. Chem.* **1977**, *16*, 594.
8. M. Leitheiser, D. Coucouvanis, *J. Inorg. Nucl. Chem.* **1977**, *39*, 811.
9. MossWinn 3.0 Dr. Zoltan Klencsar, http://www.mosswinn.com/english/index.html.
10. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
11. H. Ōkawa, N. Matsumoto, H. Tamaki, M. Ohba, *Mol. Cryst. Liq. Cryst.* **1993**, *233*, 257.
12. P. Gütlich, H. A. Goodwin, *Topics Current Chemistry: Spin Crossover in Transition Metal Compounds*, Springer, **2004**, Vol. 233–235.