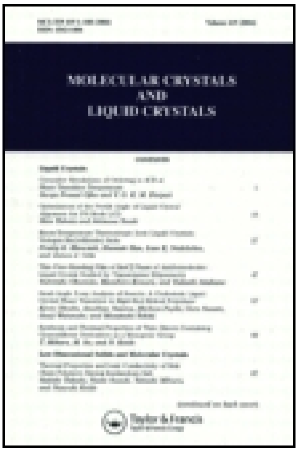

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Crystal Structure of a Molecular Building Block with π-π Intermolecular Interaction

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Mononuclear iron(II) compound [Fe(4tpt)$_2$(NCS)$_2$(MeOH)$_2$]·MeOH (**1**) (4tpt = 2,4,6-tri(4-pyridyl)-1,3,5-triazine) was synthesized and characterized by X-ray single crystal diffraction, Mössbauer spectra, magnetic susceptibilities, electronic spectra and IR spectra. The crystal structure of **1** was determined. Crystal data for **1**: $C_{42}H_{40}O_4N_{14}S_2Fe_1$, space groupe *P-1*, Z=2, a=7.091(1), b=10.630(2), c=28.251(7) Å, α=89.77(1)°, β=90.072(9)°, γ=84.45(1)°, V=2119.5(7)Å3, $R1$=0.069. The compound **1** has two 4tpt ligands, and forms π-π stacking between the 4tpt ligands in the neighboring complexes along the b axis. The assembly of the constituent complexes forms 1-D zigzag chains because of the strong π-π stacking between the neighboring complexes. Two methanol molecules are contained in the space between the 1-D zigzag chains.

Keywords iron(II) compound; π-π stacking; 1-D chain

INTRODUCTION

Self-assembly has been recognized as a most efficient process that organizes individual molecular components into highly ordered supramolecular species[1]. The designed construction of supramolecules from molecular building blocks is noted as one of most challenging issues facing synthetic chemistry today. During the past few years, many one-, two- and three-dimensional coordination polymers have been generated from transition metal templates with rigid and flexible pyridyl containing bidentate or multidentate organic spacers[2]. In addition, self-assembly of molecules driven by coordination to transition metal ions has become an important tool to explore the cooperative nature of the spin-crossover phenomenon[3]. Particularly, the ligands of the polypyridine type have been proved to be particularly suitable for metallosupramolecular chemistry as well as for the field of the spin-crossover phenomenon. Real et al reported that the iron(II) compound with four pyridine derivatives and two NCS- counter anions $[Fe(tvp)_2(NCS)_2]\cdot CH_3OH$[4], where tvp is 1,2-di-(4-pyridyl)-ethylene, forms two-dimensional networks organized in parallel stacks of sheets made up of edge-shared Fe_4 rhombuses. The fully interlocked networks are catenane supramolecular systems, and the compound exhibit spin-crossover behavior. Supramolecular systems have attracted the attention of many research groups because of their photochemical and magnetic properties that can result from the interaction among their subunits. However, the number of polymeric spin-crossover compounds reported up to now is still small[4-10]. Here we reported the self-assembly of 2,4,6-tri(4-pyridyl)-1,3,5-triazine (4tpt), rigid trifunctional spacer ligand, and iron(II) ions. The resulting assembly of formula $[Fe(4tpt)_2(NCS)_2(MeOH)_2]\cdot MeOH$ (**1**) is the mononuclear iron(II) compound formed 1-D zigzag chain by very strong π-π intermolecular interaction, and is in the high-spin state.

EXPERIMENTAL SECTION

Preparation of the Compound 1

The 4tpt ligand was prepared as described previously[11]. The compound **1** was prepared by the addition of $Fe(NCS)_2$ to 4tpt ligand in $CHCl_3$/MeOH at room temperature. The single crystals suitable for X-ray diffraction were yielded by slow diffusion for one week. The crystals were effloresced because of removing of MeOH solvent molecules in air.

Mössbauer Spectroscopy

The Mössbauer spectra (isomershift vs metal iron at room temperature) were measured using a Wissel MVT-1000 Mössbauer spectrometer with a ^{57}Co/Rh source in the transmission mode. All isomer shifts are given relative to α-Fe at room temperature. The measurements at low temperature were performed with a closed-cycle helium refrigerator cryostat (Iwatani Co., Ltd.).

Crystallographic Study

X-ray crystallographic data at 90 K ($C_{42}H_{40}O_2N_7S_1Fe_1$): *F.W.* = 924.84, violet platelet (0.3*0.1*0.05), triclinic, space group *P-1*, a = 7.091(1), b = 10.630(2), c = 28.251(7) Å, α= 89.77(1), β= 90.072(9), γ= 84.45(1)°, V = 2119.5(7) Å^3, Z = 2, D_{calcd}=1.449 gcm^{-3}. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-K_α radiation. The data were collected at 90 K to a maximum 2θ value of 55.0°. For **2**, among the 10751 reflections, 6079 were unique (R_{int}=0.066) and 2550 with $I>3\sigma(I)$ were used to solve the structure with SIR92. Final R values gave $R1$=0.059 for $I>3\sigma(I)$, R=0.094 and R_w=0.136 for all data; linear absorption coefficient $\mu(MoK_\alpha)$ = 18.35 cm^{-1}. The non-hydrogen atoms were refined anisotoropically. Hydrogen atoms were included but not refined.

RESULT AND DISCUSSION

Mössbauer Spectroscopy

The variable temperature Mössbauer spectra of the compound **1** are shown in Figure 1. Before efflorescence for **1**, the wide doublet with *Q.S.* (quadrupole splitting) = 2.43 mms^{-1} and *I.S.* (isomer shift) = 1.21 mms^{-1} was observed at 80 K, which corresponded to the high-spin state of iron(II) compounds. The crystals were effloresced because of removing of MeOH solvent molecules at room temperature. After removing of MeOH molecules at 293 K for **1**, the wide doublet with *Q.S.* = 2.14 mms^{-1} and *I.S.* = 1.09 mms^{-1} was also observed at 293 K, showing that the iron(II) takes the high-spin state. After efflorescence at 293 K for **1**, two wide doublet with *Q.S.* = 2.47 and 3.44 mms^{-1} and *I.S.* = 1.22 and 1.19 mms^{-1} was observed at 80 K, showing that there are two high-spin iron(II) sites in the compound **1**. Mössbauer spectrum after removing of MeOH molecules at 80 K for **1** were different from that before removing of the solvent, it is suggested that the structure after removing of MeOH molecules is different from that before removing of MeOH molecules.

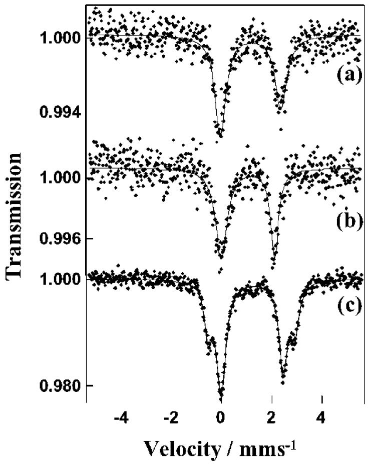

FIGURE 1 Mössbauer spectra for the compound 1. (a) at 80 K, (b) at 293 K and (c) at 80 K after efflorescence at 293 K.

Structure of the Compound

The compound **1** was in the high-spin state, when it is synthesized in MeOH solution. The X-ray analysis was successfully carried out for compound **1** at 90 K. Figure 2 shows that the compound **1** with high-spin state crystallize in the triclinic *P-1* space group. The single crystal X-ray analysis for **1** revealed that each iron(II) atoms are octahedrally coordinated by four nitrogen atoms in two 4tpt ligands and in two NCS$^-$ counter anions, and two oxygen atoms in two MeOH molecules, i.e. a N_4O_2 donor set. The values of the bond lengths are consistent with those for typical high-spin iron(II) compounds. The Fe-O distances are shorter than the Fe-N distances, which induce a pronounced distortion of the FeN_4O_2 octahedron. The 4tpt ligands form slightly distorted planes. The dihedral angles between triazine and pyridine rings for **1** are equal to 5.877°, 1.328° and 8.122°, respectively. The two 4tpt ligands in the compounds are found to be nearly coplanar to one another. The least-square plane of a slightly distorted 4tpt ligand makes an angle of 1.056° with the one of another 4tpt ligand for **1**. The counter anion NCSe$^-$ and solvent molecules are coordinated by *trans* position to each other.

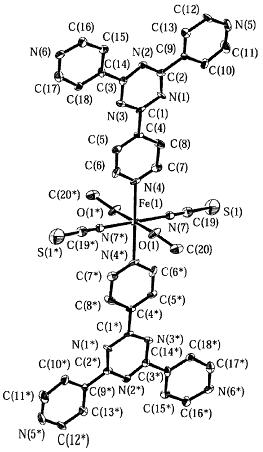

FIGURE 2 ORTEP view of 1. All hydrogen atoms are omitted for clarity.

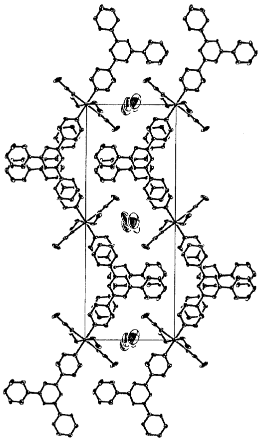

FIGURE 3 Structure of the π-π stacking between compounds. All hydrogen atoms are omitted for clarity.

The compound **1** forms π-π stacking in the 4tpt ligands between the compounds along the *b* axis (Figure 3). In order to the strong π-π stacking between the constituent complexes, these complexes form 1-D zigzag chains. Two methanol molecules are contained in the space between the 1-D zigzag chains. The crystal structures removing of MeOH molecules for **1** could not be determined, because removing of MeOH molecules induces cracks in the crystal, which makes the X-ray single crystal analysis impossible.

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