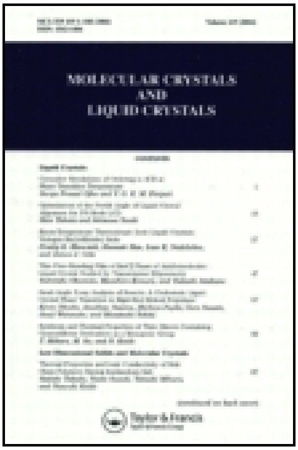

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Moussbauer Spectroscopic Study of the Reentrant Phase Transitions in TBA[Fe(tdas)$_2$]

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MÖSSBAUER SPECTROSCOPIC STUDY OF THE REENTRANT PHASE TRANSITIONS IN TBA[Fe(tdas)$_2$]

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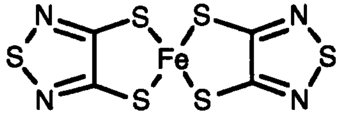
Abstract Temperature dependence of ^{57}Fe Mössbauer spectra for TBA[Fe(tdas)$_2$] is measured to obtain the information on the spin state and the phase transitions. The large quadrupole splitting due to the S = 3/2 spin state increases reenteringly in the intermediate temperature region (190 – 230 K on cooling and 200 – 240 K on heating). The small increase in the quadrupole splitting and the continuous decrease in the isomer shift suggests the 3/2 spin state does not change, supporting the interpretation of the magnetic susceptibility.

INTRODUCTION

Recently the metal complexes of π-electron rich multi-sulfur ligand have been investigated widely because of their attractive solid state characteristics such as electrical, optical and magnetic properties.[1] In the previous paper we have reported on the iron(III) complex of 1,2,5-thiadiazole-3,4-dithiolate (H$_2$tdas), TBA[Fe(tdas)$_2$] (TBA = tetrabutylammonium).[2] The X-ray structure determination have shown the [Fe(tdas)$_2$]$^-$ anion has a dimeric structure in which the iron(III) atom adopts a square pyramidal coordination. The dimerization occurs through the formation of intermolecular Fe – S bond of 2.501 Å. According to this dimeric structure, magnetic susceptibility of TBA[Fe(tdas)$_2$] have been interpreted by an antiferromagnetically coupled S = 3/2 dimer model having a coupling constant J / k_B of 118 K. Interestingly the complex shows a reentrant magnetic phase transitions having a hysteresis as shown in Fig. 1. A sudden increase and recovery of the paramagnetic susceptibility (χ_p) are observed in the intermediate temperature region. During this phase transition the value of J / k_B decreases by about 10 %.

There have been some ambiguity in the spin states of the $[Fe(tdas)_2]^-$ anion. The temperature dependence of χ_p can be interpreted in terms of either S =3/2 or S = 5/2 spin state. The abruptly increased χ_p values in the intermediate temperature region are also explained not only by the decrease in coupling constant but also by a change in spin state to S = 5/2 or 1/2. Thus we have carried out a ^{57}Fe Mössbauer spectroscopic study on TBA$[Fe(tdas)_2]$ to obtain the information on spin state and reentrant behavior.



$[Fe(tdas)_2]^-$

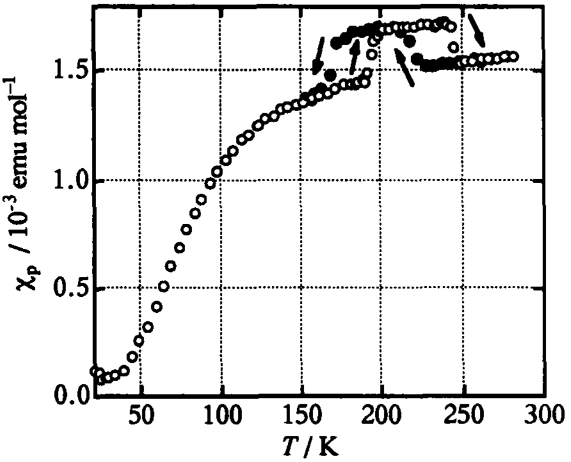


Fig. 1 Temperature dependence of paramagnetic susceptibility for TBA$[Fe(tdas)_2]$.

EXPERIMENTAL

TBA$[Fe(tdas)_2]$ was prepared in a general method described previously.[1]

^{57}Fe Mössbauer spectra were obtained using a Mössbauer driving system from Wissenschaftliche Electronik GmbH, consisting of an MDU-1200 driving unit, a DFG-1200 digital function generator and an MTV-1000 velocity transducer, incorporating with a Model 5500 multichannel analyzer from EG&G ORTEC. The temperature dependence of the Mössbauer spectra in the range 80 – 295 K were measured by keeping the sample (10 mgFe cm^{-2}) in a cryostat. A 1.5 GBq ^{57}Co(Rh) Mössbauer source from Amersham International plc. was kept at room temperature. The temperature of the sample was controlled by a DTC2 digital temperature controller from Oxford Instruments. A platinum resistor was used to measure the temperature. The spectra were computer fitted to Lorentzian lines on a personal computer and the values of isomer shift are given relative to α-iron foil at room temperature.

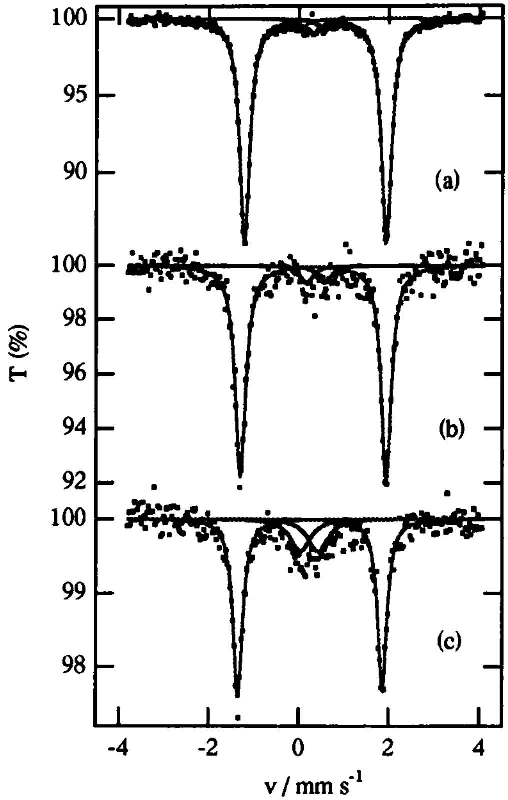
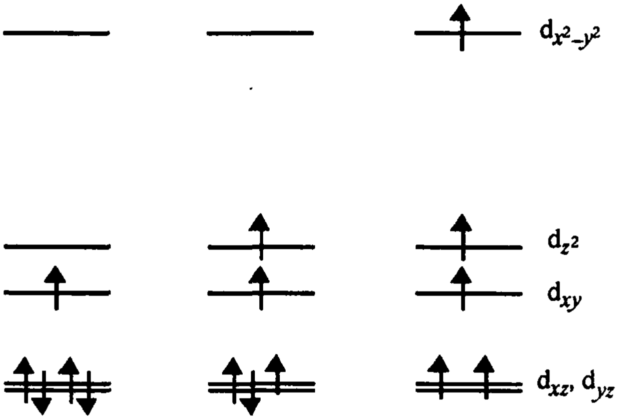


Fig. 2 ^{57}Fe Mössbauer spectra for TBA[Fe(tdas)$_2$]. (a) at 80 K, (b) at 200 K on cooling, (c) 295 K.

RESULTS AND DISCUSSION

A doublet due to the large quadrupole splitting was observed at each temperature as shown in Fig. 2. An additional weak absorption having a much smaller quadrupole splitting was also observed. Since the relative intensity of the minor peaks are decreased monotonically on cooling, this component does not associate with the phase transitions. Judging from the values of the isomer shift (δ) and the quadrupole splitting (Δ), the minor peaks are attributed to Fe(III) impurities having a S = 5/2 spin state. The amount of the impurities are estimated to be less than 6 % from the spectrum at 80 K.

The Mössbauer parameters are shown in Table 1. The value of the quadrupole splitting is quite large for an iron(III) complex. This indicates a large electric field gradient (EFG, $V_{zz} = eq$) at the iron nucleus, due to the inequivalent population of the 3d electrons. Fig. 3 shows the possible electron configurations for the square pyramidal structure. In the figure the estimated valence electron contribution to EFG[3] is also shown. $\langle r^{-3}\rangle$ is the reciprocal cube of the expectation value for the radial distribution of the Fe 3d orbital.



spin state	S = 1/2	S = 3/2	S = 5/2
valence electron contribution to EFG	$-\frac{4}{7}\langle r^{-3}\rangle$	$-\frac{6}{7}\langle r^{-3}\rangle$	0

Fig. 3 Possible electron configurations for square pyramidal structure and EFG.

Although both the 3d electrons of the iron atom and the charges on the surrounding atoms contribute to EFG at the nucleus of iron atom, the former does much more. Thus the magnitude of the quadrupole splitting is closely related to the spin state. The possibility of S = 5/2 state is readily ruled out because a quite small value of the quadrupole splitting is expected for this electron configuration. Thus the large quadrupole splitting implies that the spin state is 1/2 (low spin) or 3/2 (intermediate spin), but we can not distinguish them from the Mössbauer spectra by a cursory glance. The temperature dependence of magnetic susceptibility for TBA[Fe(tdas)$_2$] cannot be interpreted based on S = 1/2 dimer model but on S = 3/2 and 5/2 dimer model. Thus the spin state is concluded to be 3/2. This conclusion is reasonable because the Mössbauer parameters of TBA[Fe(tdas)$_2$] are close to those of square pyramidal 1,2-dithiolene complexes with S = 3/2, $[\mathrm{FeX(S_2C_2R_2)_2}]$[4,5] (X = pyridine and related ligands) as shown in Table 1.

The Mössbauer parameters are also essentially the same as to those of dimeric 1,2-dithiolene complexes[4,5] such as $\mathrm{TEA[Fe\{(S_2C_2(CN)_2\}_2]}$ and $\mathrm{TEA[Fe\{(S_2C_2(CF_3)_2\}_2]}$ (TEA = tetraethylammonium) whose spin state have been reported to be 1/2. The reported magnetic moments for the dimeric 1,2-dithiolene complexes are close to that of TBA[Fe(tdas)$_2$]; For example the effective magnetic moments[6] for $\mathrm{TEA[Fe\{(S_2C_2(CN)_2\}_2]}$ are 0.48 μ_B at 84 K and 1.67 μ_B at 301 K and for $\mathrm{TEA[Fe\{(S_2C_2(CF_3)_2\}_2]}$ 0.31 μ_B at 87 K and 1.39 μ_B at 299 K while those of TBA[Fe(tdas)$_2$] are 0.69 μ_B at 78 K and 1.88 μ_B at 281 K. Interestingly, the same Mössbauer and magnetic susceptibility between the tdas ligand and the 1,2-dithiolene complexes may suggest the possible 3/2 spin state for the

Table 1 ^{57}Fe Mössbauer parameters for Fe(III) complexes of tdas (this work) and 1,2-dithiolenes (ref. 6).

complex	δ^* / mm s^{-1}	Δ / mm s^{-1}	T / K
TBA[Fe(tdas)$_2$]	0.27	3.20	295
	0.37	3.15	80
(Ph$_4$P)[Fe(py){S$_2$C$_2$(CN)$_2$}$_2$]	0.27	2.51	295
	0.33	2.41	77
TEA[Fe(py){S$_2$C$_2$(CF$_3$)$_2$}$_2$]	0.28	2.54	295
	0.33	2.61	77
TEA[Fe(py)(S$_2$C$_6$Cl$_4$)$_2$]	0.23	3.12	295
	0.33	3.02	77
TBA[Fe(γ-pic){S$_2$C$_2$(CN)$_2$}$_2$]	0.26	2.61	295
	0.36	2.59	77
TEA[Fe{S$_2$C$_2$(CF$_3$)$_2$}$_2$]	0.23	2.50	295
	0.33	2.50	77
TEA[Fe{S$_2$C$_2$(CN)$_2$}$_2$]	0.24	2.81	295
	0.33	2.76	77
TBA[Fe(S$_2$C$_6$Cl$_4$)$_2$]	0.23	3.03	295
	0.32	3.02	77

[*] The values of δ for 1,2-dithiolene complexes are converted to those relative to α-iron foil by subtraction of 0.26 mm s^{-1}.

bisdithiolene complexes.

The isomer shift, a measure of the s electron density at the iron, is affected by the 3d electron density through a shielding effect. The value of isomer shift for TBA[Fe(tdas)$_2$] is practically the same as those of 1,2-dithiolene complexes. This implies that the expansion of the 3d electrons over the π-electron system of the ligand is the same though the tdas ligand has a larger π-electron system.

The temperature dependences of the isomer shift and quadrupole splitting are shown in Fig. 4. The open circles in Fig. 4 show the parameters measured with increasing temperature and closed circles with decreasing temperature. The values of isomer shift are increased continuously on cooling due to second-order Doppler shift. On the other hand, a reentrant behavior with a hysteresis is observed for quadrupole splitting; on decreasing the temperature the value of quadrupole splitting increased in the temperature region 190 – 230 K and on warming in 200 – 240 K. The value of the quadrupole splitting increases upto 3.25 mm s^{-1}. The amounts of change in the quadrupole splitting between the heating and cooling process are identical. The observed reentrant behavior is consistent with that observed in the magnetic susceptibility. Since no abrupt change in the isomer shift is observed in the temperature region in which the quadrupole splitting is discontinuous, the change in the electron distribution does not occur. The small but definite increase in the quadrupole splitting suggests no change in spin state; if the 3/2

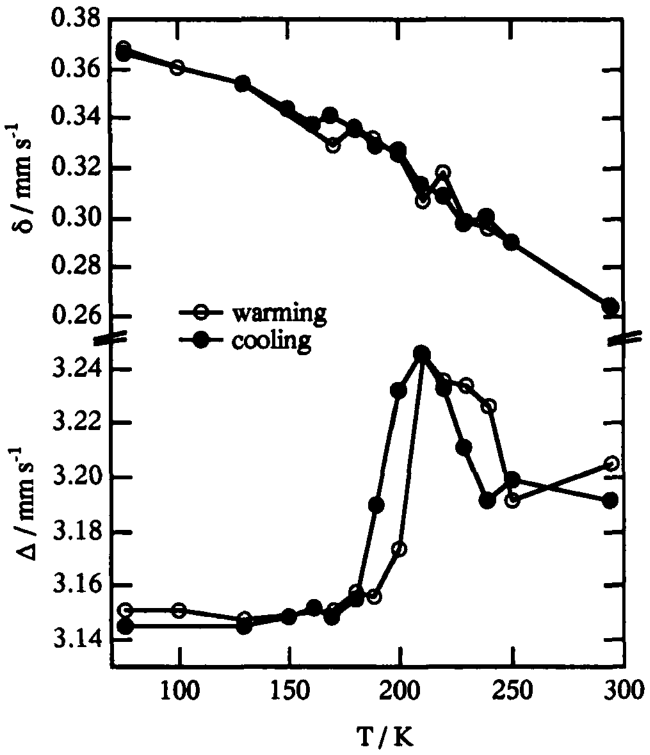


Fig. 4 Temperature dependence of isomer shift (top) and quadrupole splitting (bottom) for TBA[Fe(tdas)$_2$]

spin state changed to 1/2 or 5/2 the quadrupole splitting would be decreased more because the contribution of 3d electrons to EFG is smaller in S = 1/2 and 5/2 (Fig. 3). Thus the abrupt increase in the quadrupole splitting is associated with the change in intermolecular interactions. The intermolecular interactions concerning the Fe(III) atom is considered to be weakened during the phase transition since the coupling constant in the magnetic susceptibility decreased. The distortion of the molecular structure concurrently increases slightly since the quadrupole splitting increases during the transition.

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