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

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Version of record first published: 24 Sep 2006.

To cite this article: R. Ikeda , A. Ghosh , L. S. Prabhumirashi , D. Nakamura & M. Yamashita (1992): Spin Dynamics in 1-D Mixed Valence Complex $[Pt(En)_2][PtCl_2(en)2](C1O_4)_4$ Studied by Proton Magnetic Resonance, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 216:1, 181-187

To link to this article: http://dx.doi.org/10.1080/10587259208028770

Mol. Cryst. Liq. Cryst. 1992, Vol. 216, pp. 181–187
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Printed in the United States of America

SPIN DYNAMICS IN 1-D MIXED VALENCE COMPLEX $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ STUDIED BY PROTON MAGNETIC RESONANCE

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Abstract ^1H NMR spin-lattice relaxation time T_1 of the above complex in the solid state was measured from 100 K to room temperature. The presence of paramagnetic Pt^{III} sites trapped in the 1-D chains was observed at low temperatures. T_1 was shortened upon heating, and the observed T_1 data were well explained by the model that the trapped unpaired electrons are thermally excited and diffuse along the chain. The observed spin motion is attributable to the neutral soliton by referring to the data of ESR and the electrical conductivity.

INTRODUCTION

The halogen-bridged $-M^{II}-X-M^{IV}-X-$ type mixed valence complexes have been intensively studied as the 1-D charge-density-wave systems with Peierls distortion[1,2]. By noting to the two-fold degeneracy of this chain structure, the formation of the domain wall, for example, $-M^{IV}XM^{II}XM^{IV}XM^{IV}XM^{II}XM^{IV}-$ or $-M^{IV}XM^{II}XM^{IV}XM^{III}-XM^{II}XM^{IV}-$, has been theoretically derived in a similar manner to the soliton revealed in *trans*-polyacetylene[3, 4]. The recent ESR study on single crystals of $[Pt(en)_2][PtX_2(en)_2](ClO_4)_4$ (X: Cl, Br, I; en: ethylenediamine) has shown the presence of the paramagnetic Pt^{III} sites whose concentration(*ca.* 10^{20} mol^{-1}) is temperature independent[5, 6].

It is noted that the ESR linewidth is gradually reduced with increasing temperature suggesting the motional narrowing. These ESR results are consistent with the idea of the domain-wall soliton including the paramagnetic Pt^{III} site. In the present study, we investigate the dynamic behaviour of the electron spins in 1-D chains by measuring the ^1H NMR spin-lattice relaxation time.

EXPERIMENTAL

$[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ crystals synthesized according to the reported method[7] were recrystallized from water. Columnar crystals of 2-5 mm long were collected(*ca.* 1 g) and used for the NMR measurement. A pulsed NMR spectrometer constructed in IMS[8] was used to determine ^1H spin-lattice relaxation time(T_1) by employing the inversion recovery method. Differential scanning calorimetry (DSC) was carried out using a Du Pont 9900 thermal analyzer in IMS.

RESULTS AND DISCUSSION

The DSC measurement revealed a phase transition at 293 ± 1 K with a transition enthalpy of 12 kJ mol^{-1}. The ^1H NMR T_1 measurement at a Larmor frequency of 60 MHz carried out below the phase transition temperature(T_{tr}) showed marked nonexponential behaviour of the ^1H magnetization recovery. An example of the observed data is shown in Figure 1. This curve can be divided roughly into two T_1

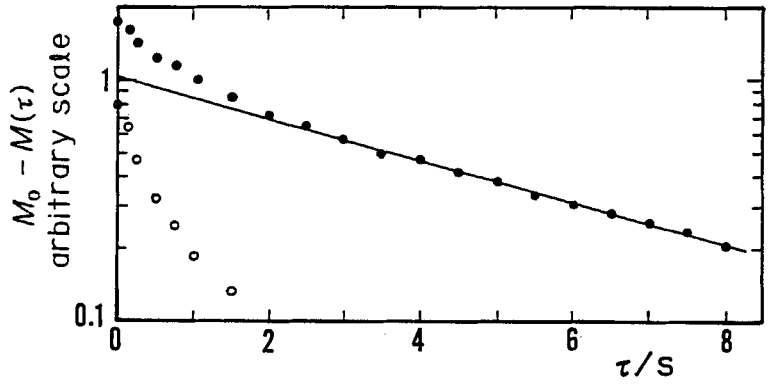

FIGURE 1. Recovery of ^1H magnetization, $[M(\tau) - M_0]$(●) observed at 227 K(60 MHz). The slope of solid line affords the long T_1(4.85 s). Magnetization of the short T_1 component(○) is given by the difference between the observed magnetization and the solid line.

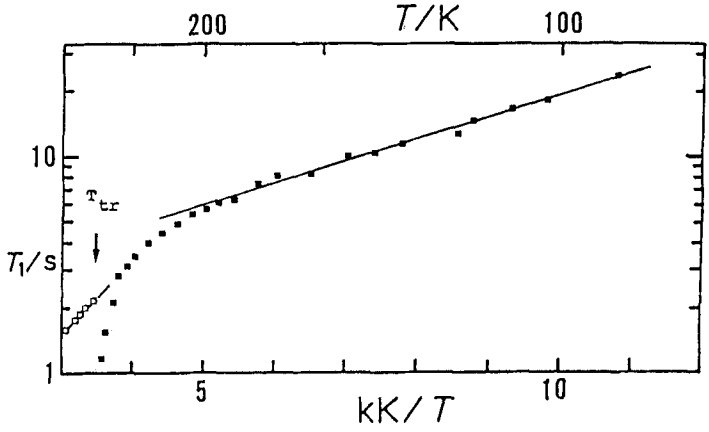

FIGURE 2. The temperature dependence of long T_1 observed at 60 MHz. Slopes of the solid lines give activation energies of 10.8 and 60 meV below and above the phase transition temperature, T_{tr}, respectively.

components: The long T_1 which is always the major component could be uniquely determined, while the short or minor component gave no single T_1 value, but distributed T_1 values as shown in Figure 1. The temperature dependence of the long T_1 was shown in Figure 2. Upon heating, T_1 decreased gradually up to *ca.* 250 K, then sharply to T_{tr}. After a sudden increase at T_{tr}, T_1 again showed a slow decrease with a further heating to 320 K.

The ^1H magnetization ratio of the short to long T_1 component was also temperature dependent as shown in Figure 3. The magnetization ratio of *ca.* 0.5 at 170 K decreased gradually on heating, and became almost zero at T_{tr}, and only the long component was observed around T_{tr}. Above T_{tr}, a single T_1 could be obtained.

These relaxation data can be explained as follows: The presence of temperature-independent paramagnetic Pt^{III} sites with a concentration of *ca.* 10^{20} mol^{-1} revealed by the ESR study[6] implies that the fluctuation of magnetic field made by the unpaired electron is strong enough to be detected by the ^1H relaxation measurement. At sufficient low temperatures, we can expect that these paramagnetic sites are trapped at impurity or defect sites in the chains and/or the chain ends near the grain boundaries in crystals[6]. In this state, protons located near a Pt^{III} site feel a strong magnetic field due to the electron, and its magnitude depends upon the distance(R) to the electron. T_1 is proportional to R^{-6} in the neighbourhood of the electron where the spin-diffusion among protons is ignorable[9,10].

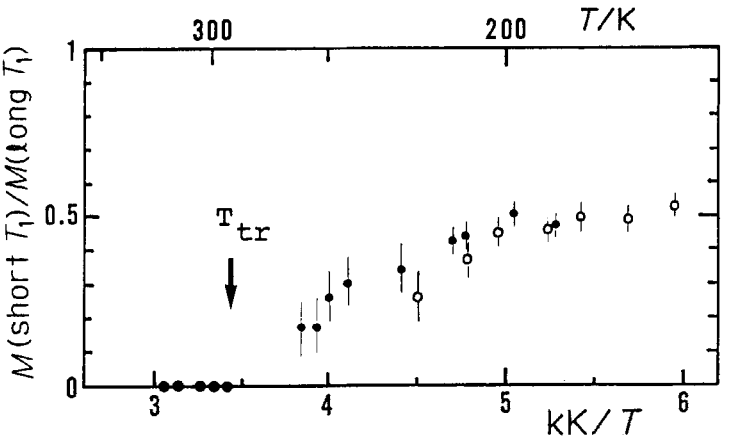

FIGURE 3. Temperature dependence of the magnetization ratio of the short to long T_1 component observed at 60(●) and 30 MHz(○).

For these protons, there should be a distribution of T_1 which agrees well with the nonexponential behaviour observed for the short T_1 component. This explanation can be supported by the fact that the magnetization of the short T_1 component roughly showed an exponential change when plotted it against the square root of time[9].

For the protons far from the unpaired electrons, the paramagnetic field is so weakened that the spin-diffusion mechanism among protons becomes the main origin of the relaxation[9,10]. Since the exponential T_1 behaviour is expected for these protons, the observed long T_1 component is attributable to these protons remote from the paramagnetic electrons.

The decrease of the short T_1 magnetization observed with increasing temperature implies the decrease in the number of protons placed in the strong magnetic field due to the fixed paramagnetic spins. Since the paramagnetic Pt^{III} density is constant, this result suggests that the fixed paramagnetic sites decrease in number, that is, some of the fixed electron spins can move along the chain apart from the trapped sites by obtaining thermal excitation energies, and the number of moving electrons increases with temperature.

In case the electron spins can diffuse rapidly enough, the protons in the chain feel the averaged magnetic field. This reduces the proton T_1 which was controlled by the spin diffusion at low temperatures. The T_1 decrease observed upon heating can be explained by this mechanism. At the same time, the decrease of trapped electrons with

increasing temperature reduces the short T_1 magnetization in conformity with the data shown in Figure 3. The presence of only single T_1 values observed above T_{tr} indicates that the paramagnetic electrons can move along the chains covering almost the whole crystals.

The present model of the electron-spin migration can be supported by the temperature-dependence study of the ESR linewidth[6] which showed a gradual narrowing upon heating attributable to some motional effect. The activation energies for this motion evaluated from the temperature gradient of the ESR linewidth were reported to be 12 and 55 meV below and above T_{tr}, respectively[6]. On the other hand, the activation energies derived from the ^1H T_1 data shown in Figure 2 are 10.8 and 60 meV in the same order in good agreement with the ESR results. This indicates that the ESR narrowing and the NMR T_1 decrease arise from the same origin of the electron-spin diffusion.

One-dimensionality of the electron-spin motion was investigated by measuring the Larmor-frequency dependence of ^1H T_1. It has been shown that T_1 is proportional to the square root of the frequency when the electron diffusion is one-dimensional[11,12]. The frequency dependence of the long T_1 observed at 200, 250 and 300 K are shown in Figure 4. We can see that this relationship is well satis-

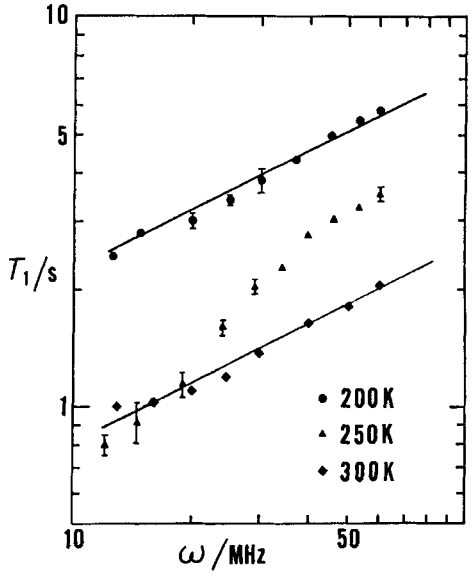

Figure 4. Frequency(ω) dependences of the long T_1 observed at 200, 250 and 300 K. Solid lines are proportional to ω.

fied with the data at 200 and 300 K supporting the present interpretation of T_1. On the other hand, the data at 250 K deviated appreciably from this law. This is explainable by the effect of molecular motions arising from the phase transition because it was found that the conformation change of en ligands take place at the phase transition[13]. Since the rapid T_1 decrease associated with the phase transition already started from *ca.* 200 K as shown in Figure 2, the contribution from slow lattice motions to the relaxation can be expected even at 250 K.

We can assume from the above discussion that the paramagnetic Pt^{III} sites were formed as impurities in the stage of crystallization rather than made by thermal excitation of the d_z electrons in Pt^{II} atoms which was reported to be required a much higher energy of *ca.* 1.5 eV[14].

The Pt^{III} sites introduced in $-Pt^{II}-X-Pt^{IV}-X-$ chains can be presumed to form the domain wall between the doubly-degenerate ground state of the distorted 1-D system which has been theoretically treated analogously to the soliton in polyacetylene[3,4]. In the present compound, it has been reported that the electrical conductivity along the chain is quite small(*ca.* 10^{-15} Scm^{-1} at room temperature) and has a high activation energy(1.4 eV)[15] implying that the diffusion of the electronic charges is ignorable. Since the present NMR relaxation is controlled by diffusing electron spins, the model of neutral soliton seems to be acceptable.

The most part of the present experiments was performed in IMS, Okazaki, Japan. The authors express their thanks to IMS Instrument Center for using the NMR and DSC apparatus. The authors are also grateful to Professors T. Mitani and K. Nasu, and Drs. H. Okamoto and K. Toriumi in IMS for their helpful discussion.

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