Molecular Motions in Halogen-Bridged One-Dimensional Pt Complexes, $[Pt^{II}(en)_2][Pt^{IV}X_2(en)_2](ClO_4)_4$ (X = Cl, Br) Studied by ^{2}H and ^{1}H NMR

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^{2}H and ^{1}H NMR measurements were performed on crystalline $[Pt(en)_2][PtX_2(en)_2](ClO_4)_4$ (X = Cl, Br), where the protonated and partially deuterated ethylenediamines (en's), $NH_2(CH_2)_2NH_2$, $NH_2(CD_2)_2NH_2$ and $ND_2(CH_2)_2ND_2$ were used as ligands. Measurements of ^{2}H and ^{1}H NMR spin-lattice relaxation times showed the presence of motions of en chelate rings at the temperatures near the phase transitions, whereas broad ^{2}H NMR spectra and the reported X-ray diffraction data showed no marked motions. These results were consistently explained by introducing the en puckering motion between highly asymmetric potential wells with an energy difference of 10 - 13 kJ mol^{-1}. This difference was shown to be much larger than 2 - 5 kJ mol^{-1}, reported for the iodo-complex, $[Pt(en)_2][PtI_2(en)_2](ClO_4)_4$.

Key words: Phase Transition; NMR; Spin-lattice Relaxation; Molecular Motion.

1. Introduction

Halogen-bridged mixed-valence complexes $[Pt(en)_2][PtX_2(en)_2](ClO_4)_4$ (en = ethylenediamine; X = Cl, Br, I) with a one-dimensional -X-Pt^{II}-X-Pt^{IV}-X- structure have been intensively studied because of optical [1], magnetic [2] and structural interests [3]. Characteristic electronic excitations in mixed valence states [4], and charge and spin migrations along the one-dimensional chains have been revealed. $[Pt(en)_2][PtI_2(en)_2](ClO_4)_4$ was shown to have a structural phase transition with an order-disorder type as for the conformation of "en" chelate rings at 150 - 160 K [5]. We showed from studies of ^{1}H and ^{2}H NMR spectra and spin-lattice relaxation times T_1 that the disorder of the en conformation in the high-temperature phase is not static but dynamic, where the puckering motion of Pt(en) chelate rings between δ and λ conformations was well explained by the model of two-site jumps between two asymmetric potential wells with an energy difference of 2 - 5 kJ mol^{-1} [6]. On the other hand, the above complexes with X = Cl or Br were shown to have structural phase transitions at 293.2 [7] and 297.8 K [7] for Cl and Br, respectively, where the conformations of en-chelate rings having two possible conformations δ and λ in the $Pt(en)_2$ moieties are changed from $\delta\lambda$ or $\lambda\delta$ in the low-temperature monoclinic phase ($P2_1/m$) [7] to $\lambda\lambda$ or $\delta\delta$ in the high-temperature orthorhombic phase (Ibam) [7]. This structural change, resulting in no disordered structure for the conformation of en chelate rings in the high-temperature phase, is different from that in the iodo-complex. We reported [8] ^{1}H NMR T_1 results in the present chloro- and bromo-complexes, and an observed T_1 decrease upon heating from *ca.* 200 K to phase transition temperatures was attributed to thermal motions. In the present study, we performed ^{2}H and ^{1}H NMR measurements on these complexes and we discuss the dynamics of the chelate rings in the neighborhood of the phase transitions in order to reveal the mechanism of the phase transition by comparing the new results with those obtained for the previous iodo-complex.

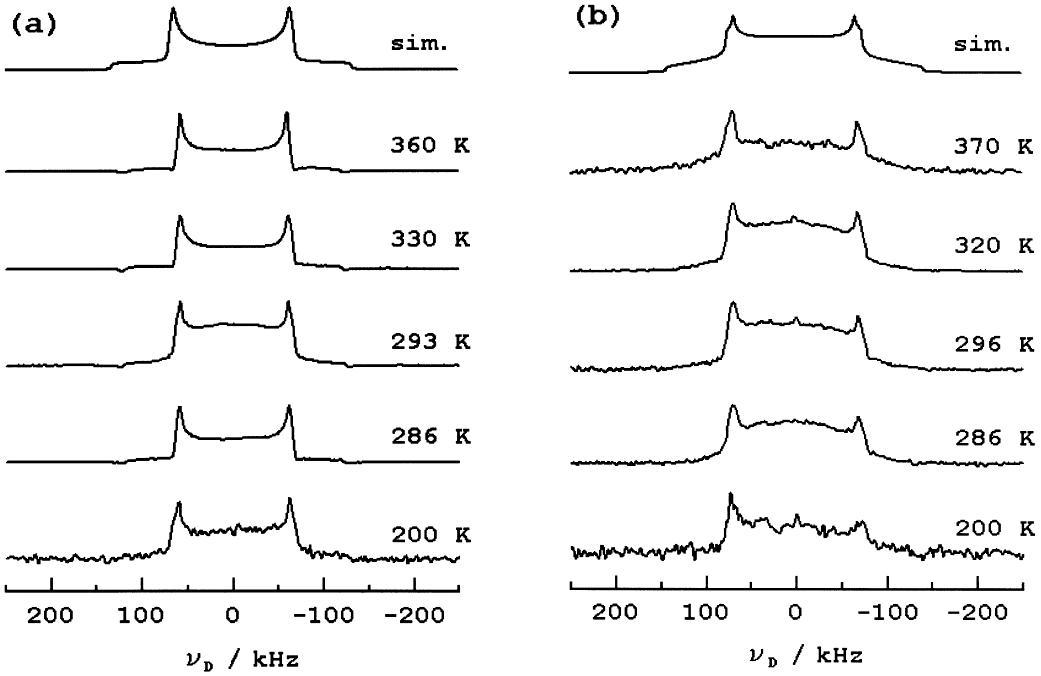

Fig. 1. Temperature dependences of ^{2}H NMR spectra observed in (a) $[Pt(NH_2(CD_2)_2NH_2)_2][PtCl_2(NH_2(CD_2)_2NH_2)_2](ClO_4)_4$ (**PtCl-CD**) and (b) $[Pt(ND_2(CH_2)_2ND_2)_2][PtCl_2(ND_2(CH_2)_2ND_2)_2](ClO_4)_4$ (**PtCl-ND**). The top spectra shown in (a) and (b) are simulated for the highest temperature spectra observed.

2. Experimental

$[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ (abbreviated to **PtCl**) was prepared according to [9] and recrystallized from water at room temperature. The partially deuterated analogs, $[Pt(NH_2(CD_2)_2NH_2)_2][PtCl_2(NH_2(CD_2)_2NH_2)_2](ClO_4)_4$ (**PtCl-CD**) and $[Pt(ND_2(CH_2)_2ND_2)_2][PtCl_2(ND_2(CH_2)_2ND_2)_2](ClO_4)_4$ (**PtCl-ND**) were obtained by using ethylenediamines, $NH_2(CD_2)_2NH_2$ and $NH_2(CH_2)_2NH_2$, respectively, as the starting materials, and **PtCl-ND** repeated crystallizations from D_2O. $[Pt(en)_2][PtBr_2(en)_2](ClO_4)_4$ (**PtBr**) synthesized [9] analogously to **PtCl** was recrystallized from water.

The phase transition temperatures (T_{tr}) were determined with a Seiko Instrument DSC 120 calorimeter using sealed aluminum vessels.

The ^{2}H NMR spectra and spin-lattice relaxation times (T_{1D}) were observed with a Bruker MSL-300 spectrometer at a Larmor frequency of 46.051 MHz at 200 - 370 K using a VT-1000 temperature controller. The quadrupole pulse sequence [10] with a $\pi/2$ pulse width of 3.5 - 5.0 μs was employed for the spectrum measurement, and the inversion recovery method was used for the T_{1D} determination.

The ^{1}H NMR T_{1H} was determined with a home-made pulsed spectrometer [11] at 54.3 and 21.3 MHz, using the inversion recovery method.

3. Results and Discussion

Differential Scanning Calorimetry (DSC)

The DSC measurements revealed phase transitions at (295 ± 4), (293 ± 5) and (298 ± 3) K with transition enthalpies ΔH_{tr} of (8.8 ± 1.0), (11 ± 1.0) and (9.0 ± 1.0) kJ mol^{-1} in **PtCl**, **PtCl-CD** and **PtCl-ND**, respectively. The phase transition temperature (T_{tr}) of **PtBr** was observed at (303 ± 4) K with a ΔH_{tr} of 12 kJ mol^{-1}. The T_{tr}'s of **PtCl** and **PtBr** agree well with 293.2 [7] and 297.8 K [7], respectively, determined by measurements of the temperature dependence of lattice parameters [7].

^{2}H NMR in $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$

The temperature dependences of the ^{2}H NMR spectra of **PtCl-CD** and **PtCl-ND** are shown in Figs. 1(a)

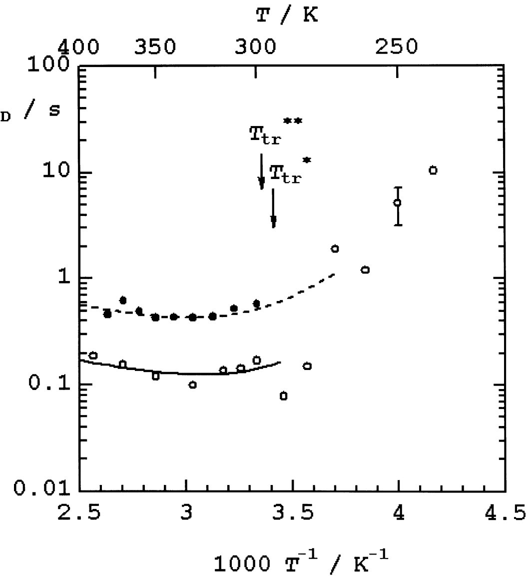

Fig. 2. ^{2}H NMR spin-lattice relaxation times (T_{1D}) in $[Pt(NH_2CD_2)_2NH_2)_2][PtCl_2(NH_2(CD_2)_2NH_2)_2](ClO_4)_4$ (**PtCl-CD**) (○) and $[Pt(ND_2(CH_2)_2ND_2)_2][PtCl_2(ND_2(CH_2)_2ND_2)_2](ClO_4)_4$ (**PtCl-ND**) (●). Broken and solid lines are the best-fitted theoretical values. T_{tr}^{*} and T_{tr}^{**} are phase transition temperatures for **PtCl-CD** and **PtCl-ND**, respectively, determined by DSC.

and (b), respectively. At 200 - 370 K both complexes yielded spectra with a small η (< 0.05) and e^2Qqh^{-1} values of (180 ± 5) and (190 ± 10) kHz for **PtCl-CD** and **PtCl-ND**, respectively. The reported data [12, 13] imply that the CD_2 and ND_2 groups are almost rigid.

The temperature dependences of ^{2}H T_{1D} in **PtCl-CD** and **PtCl-ND** are shown in Figure 2. Upon heating from *ca.* 200 K to T_{tr}, T_{1D} in **PtCl-CD** decreased. After a sudden increase at T_{tr}, T_{1D} in both **PtCl-CD** and **PtCl-ND** showed a minimum at *ca.* 320 K. This T_{1D}-minimum is expected to be connected with motions of Pt-en chelate rings, as observed in $[Pt(en)_2][PtI_2(en)_2](ClO_4)_4$ [6]. Since X-ray diffraction [7] of **PtCl** showed a change in the ethylenediamine conformations in the $Pt(en)_2$ moieties from the δ-λ or λ-δ form in the low-temperature phase to λ-λ or δ-δ in the high-temperature phase, one can assume that the δ and λ conformations have different energies. If the energy difference is much larger than the thermal energy, the above T_{1D} data are consistent with the results of ^{2}H NMR spectra with e^2Qqh^{-1} of the almost rigid CD_2 and ND_2 groups. Here, it is expected that T_{1D} is dominated by the fluctuation of the EFG caused by the puckering motion in the asymmetric double minimum potential shown in Figure 3. Using the rigid quadrupole interaction parameters of $e^2Qq_{\text{rigid}}h^{-1}$ and η_{rigid}, T_{1D} is written by assuming $\eta_{\text{rigid}} = 0$ as [14]

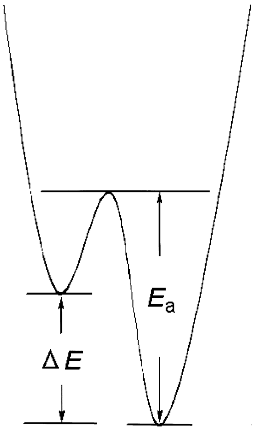

Fig. 3. The model of asymmetric potential wells used for the two-site jumps of C-D and N-D bonds.

$$\frac{1}{T_{1D}} = C_D \frac{4a}{(1+a)^2}\left[\frac{\tau_D}{1+\omega_D^2\tau_D^2} + \frac{4\tau_D}{1+4\omega_D^2\tau_D^2}\right], \quad (1)$$

$$C_D = \frac{1}{10}\left(\frac{3e^2Qq_{\text{rigid}}}{4\hbar}\right)^2 \sin^2 2\theta, \quad (2)$$

where ω_D and τ_D are the angular NMR frequency of ^{2}H and the correlation time, respectively. θ is the angle between the C-D or N-D bond and the flipping axis. The population parameter a is defined for the unequal-two-well potential in Fig. 3 as

$$a = \exp\left(\frac{\Delta E}{RT}\right). \quad (3)$$

Here ΔE is the difference between the deep and the shallow well. τ_D is written as

$$\tau_D = \frac{1}{1+a}\tau_0 \exp\left(\frac{E_a}{RT}\right), \quad (4)$$

where E_a and τ_0 are the activation energy for jumps from the deep to the shallow minimum and the correlation time at infinite temperature. The best fitted broken and solid lines in Fig. 2 were obtained using (1), (3) and (4) with C_D, ΔE, τ_0 and E_a as parameters. The determined parameters are shown in Table 1 for **PtCl-CD** and **PtCl-ND**. The 2θ values were estimated

Table 1. Motional constants (C), reductions of ^{1}H NMR second moments (ΔM_2), potential energy differences (ΔE), correlation times at the infinite temperature (τ_0) and activation energies (E_a) of the puckering motion of Pt(en) chelate rings in asymmetric potential wells in $[Pt(en)_2][PtX_2(en)_2](ClO_4)_4$ determined for ^{2}H and ^{1}H NMR relaxation times obtained in the high-temperature phase.

Compound	$C/10^9\,s^{-2}$	$\Delta M_2/mT^2$	ΔE/kJ mol^{-1}	$\tau_0/10^{-13}$ s	E_a/kJ mol^{-1}
$[Pt(NH_2(CD_2)_2NH_2)_2][PtCl_2(NH_2(CD_2)_2NH_2)_2](ClO_4)_4$	62.0 ± 5	—	12.8 ± 0.5	6.6 ± 2.0	32.4 ± 1.0
$[Pt(ND_2(CH_2)_2ND_2)_2][PtCl_2(ND_2(CH_2)_2ND_2)_2](ClO_4)_4$	18.3 ± 5	—	13.0 ± 0.5	7.0 ± 1.0	32.7 ± 0.5
$[Pt(NH_2(CH_2)_2NH_2)_2][PtCl_2(NH_2(CH_2)_2NH_2)_2](ClO_4)_4$	6.1 ± 0.5	0.13 ± 0.04	13.0 ± 1.0	6.6 ± 1.0	31.7 ± 1.0
$[Pt(NH_2(CH_2)_2NH_2)_2][PtBr_2(NH_2(CH_2)_2NH_2)_2](ClO_4)_4$	6.1 ± 0.5	0.13 ± 0.04	13.0 ± 1.0	6.6 ± 1.0	31.0 ± 1.0
$[Pt(NH_2(CH_2)_2NH_2)_2][PtCl_2(NH_2(CH_2)_2NH_2)_2](ClO_4)_4$*	5.6 ± 0.5	0.12 ± 0.04	10.2 ± 1.0	1.4 ± 4.0	34.1 ± 1.0

* Low-temperature phase

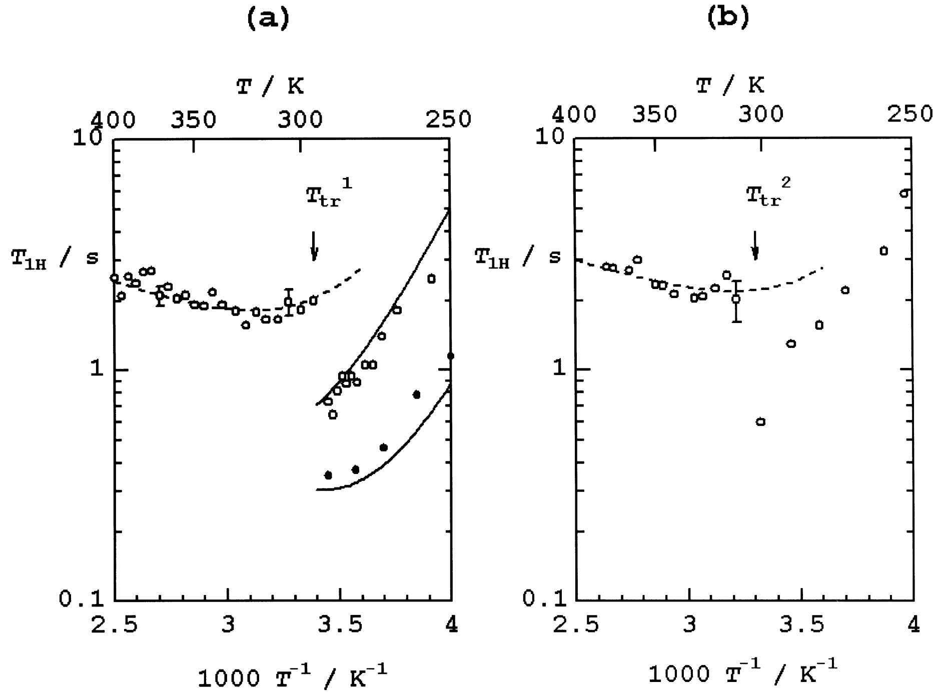

Fig. 4. ^{1}H NMR spin-lattice relaxation times (T_{1H}) observed in (a) $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ (**PtCl**) at Larmor frequencies of 54.3 (○) and 21.3 (●) MHz and (b) $[Pt(en)_2][PtBr_2(en)_2](ClO_4)_4$ (**PtBr**) at 54.3 MHz. Broken and solid lines are the best-fitted theoretical values. T_{tr}^1 and T_{tr}^2 are phase transition temperatures in **PtCl** and **PtBr**, respectively, determined by DSC.

to be 68 and 28.5° for **PtCl-CD** and **PtCl-ND**, respectively, from (2), using $e^2Qq_{\text{rigid}}h^{-1}$ of (180 ± 10) and (190 ± 10) kHz for **PtCl-CD** and **PtCl-ND**, respectively, given in [12] and [13]. These angles can be explained by the onset of the conformational change of en-chelate rings, because the jump angles by the conformational change between λ and δ were estimated to be *ca.* 60 and 30° for the C-D and N-D bond directions, respectively, by use of the structural data [7]. The ΔE values obtained for chloro-complexes in the present study are larger than 2 - 5 kJ mol^{-1}, determined for the iodo-complex [6]. This difference can be explained by the loose crystal packing of the iodo-complex [5, 15], which is favorable for the puckering motion. In fact, it is concluded from X-ray and neutron diffraction measurements [5, 7, 15] that the steric hindrance for the motion around en-ligands in intrachain for iodo-complex [5, 15] is smaller than that for the chloro-complex [7]. From these reports and the present studies of ^{2}H NMR spectra and T_{1D} measurements, most of the en-ligands in the chloro-complex have stable δ-λ or λ-δ and δ-δ or λ-λ conformations in the low and high-temperature phases, respectively, and the puckering motion of the en-skeleton takes place in the large asymmetric double minimum potential, but the lifetime, *i.e.*, the population of the excited state is quite low because of the high ΔE value. This asymmetric motional model is supported by the results of the ^{2}H NMR simulation spectra in **PtCl-CD** and **PtCl-ND** shown in Figure 1. We simulated the spectra in **PtCl-CD** and **PtCl-ND** for two-site jumping C-D and N-D bonds, respectively, taking place between two directions with angles of 68 and 28.5° in the same order, and between two potential wells with an energy differences of ΔE = 12.8 and 13.0 kJ mol^{-1} by applying the $e^2Qq_{\text{rigid}}h^{-1}$ = 180 and 190 kHz and the η_{rigid} = 0.05 values given above. Here, we assumed that the jumping rate at 350 K is rapid enough compared with the observed linewidth. We see that the spectra observed above room temperature are mostly reproduced by the simulation.

^{1}H NMR in [Pt(en)$_2$][PtX$_2$(en)$_2$](ClO$_4$)$_4$ (X = Cl, Br)

The temperature dependences of ^{1}H $T_{1\text{H}}$ in **PtCl** and **PtBr** are shown in Figs. 4(a) and (b), respectively. Upon heating, $T_{1\text{H}}$ decreased to T_{tr}, and $T_{1\text{H}}$ showed a minimum at *ca.* 320 K in both complexes. Using the asymmetric potential model, the relaxations in the high-temperature phase can be expressed by [16]

$$\frac{1}{T_{1\text{H}}} = C_{\text{H}}\frac{4a}{(1+a)^2}\left[\frac{\tau_{\text{H}}}{1+\omega_{\text{H}}^2\tau_{\text{H}}^2} + \frac{4\tau_{\text{H}}}{1+4\omega_{\text{H}}^2\tau_{\text{H}}^2}\right], \quad (5)$$

$$C_{\text{H}} = \frac{2}{3}\gamma_{\text{H}}^2\Delta M_2, \quad (6)$$

where γ_{H} and ΔM_2 denote the protonic gyromagnetic ratio and the reduction of M_2 by the onset of the motion in question, respectively.

The fitting calculation was performed above T_{tr}, using (3 - 6) with ΔE, τ_0, E_{a} and ΔM_2 as parameters. The best fitted T_1 curves are shown in Fig. 4, and the determined parameters for **PtCl** and **PtBr** are listed in Table 1.

The theoretical ^{1}H NMR M_2 values before and after the onset of ethylenediamine puckering motions were, respectively, estimated with the Van Vleck equation [17] for the rigid ethylenediamine molecules, and the following equation for the M_2(mot.) for the two-site jumps of the proton-proton vector directions [18]:

$$M_2(\text{mot.})_{ij} = \frac{9}{40}\gamma_{\text{H}}^2\hbar^2\left[\frac{1}{r_{jkA}^6}+\frac{1}{r_{jkB}^6}+\frac{3\cos^2\alpha-1}{r_{jkA}^3r_{jkB}^3}\right]. \quad (7)$$

$M_2(\text{mot.})_{jk}$, r_{jkA}, r_{jkB} and α are the motional M_2 contributed from the dipolar interaction between j-th and k-th protons, the inter-proton distance in the A and B conformations and the two-site jump angle of the vector between the j-th and k-th protons, respectively. Using the crystal structure data [7] and the standard values of bond angles and distances, we obtained M_2(rig.) = (0.228 ± 0.01) mT^2 and M_2(mot.) = (0.108 ± 0.005) mT^2. The difference between these values ΔM_2 = 0.120 mT^2 agrees well with ΔM_2 = (0.13 ± 0.04) mT^2 shown in Table 1.

Temperature dependences of ^{1}H $T_{1\text{H}}$ of **PtCl** observed below T_{tr} are shown in Figure 4(a). We should note that the frequency dependence of $T_{1\text{H}}$ in the low-temperature phase of **PtCl** is unexplainable by the BPP theory [19] requiring the ω^2 dependence for the low-temperature side of the minimum, but the observed $T_{1\text{H}}$ was roughly proportional to ω. This result can be explained by introducing a jumping model between asymmetric potential wells for the two conformations of the ethylenediamine molecules. We fitted (3 - 6) to the observed data. The best fitted T_1 curves and the determined values of parameters are shown in Fig. 4(a) and Table 1, respectively. These results imply that the decrease of $T_{1\text{H}}$ in the temperature range below T_{tr} can be attributed to the motion of the en-chelate ring.

4. Summary

From ^{2}H and ^{1}H NMR measurements, the puckering motion of Pt(en) chelate rings between the δ and λ conformations was detected in [Pt(en)$_2$][PtX$_2$(en)$_2$](ClO$_4$)$_4$ (X = Cl, Br) in the range of 250 - 400 K. The obtained temperature dependences of ^{2}H and ^{1}H NMR T_1 were explained by two-site jumps between two asymmetric potential wells with energy differences of 10 - 13 kJ mol^{-1}. These large energy differences are consistent with the observed ^{2}H spectra and the X-ray diffraction study [7] requiring ordered conformations of en-chelate rings.

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[1] D. S. Martin Jr., in: Extended Linear Chain Compounds, Vol. 1, ed. J. S. Miller, Plenum Press, New York 1982, p. 409.

[2] A. Kawamori, R. Aoki, and M. Yamashita, J. Phys. C, **18**, 5487 (1985).

[3] H. J. Keller, in: Extended Linear Chain Compounds, Vol. 1, ed. J. S. Miller, Plenum Press, New York 1982, p. 357.

[4] R. J. H. Clark, in: Infrared Spectroscopy, Vol. 11, eds. R. J. H. Clark and R. E. Hester, John Wiley, New York 1984, p. 95.

[5] J.-F. Bardeau, A. Bulou, W. T. Klooster, T. F. Koetzle, S. Johnson, B. Scott, B. I. Swanson, and J. Eckert, Acta Crystallogr. **B52**, 854 (1996).

[6] N. Kimura, T. Hachisuka, Y. Nakano, and R. Ikeda, Phys. Chem. Chem. Phys. **3**, 1778 (2001).

[7] K. Toriumi, M. Yamashita, S. Kurita, I. Murase, and T. Ito, Acta Crystallogr. **B49**, 497 (1993); S. C. Huckett, B. Scott, S. P. Love, R. J. Donohoe, C. J. Burns, E. Garcia, T. Frankcom, and B. I. Swanson, Inorg. Chem. **32**, 2137 (1993).

[8] R. Ikeda, A. Ghosh, L. S. Prabhumirashi, D. Nakamura, and M. Yamashita, Mol. Cryst. Liq. Cryst. **216**, 181 (1992); N. Kimura, S. Ishimaru, H. Okamoto, M. Yamashita, and R. Ikeda, Synth. Metals **86**, 2151 (1997); N. Kimura, S. Ishimaru, R. Ikeda, and M. Yamashita, J. Chem. Soc. Faraday Trans. **94**, 3659 (1998).

[9] N. Matsumoto, M. Yamashita, and S. Kida, Bull. Chem. Soc. Japan **51**, 2334 (1978).

[10] J. H. Davis, K. R. Jeffrey, M. Bloom, M. I. Valic, and T. P. Higgs, Chem. Phys. Lett. **42**, 390 (1976).

[11] T. Kobayashi, H. Ohki, and R. Ikeda, Mol. Cryst. Liq. Cryst. **257**, 279 (1994).

[12] J. Seelig, Quart. Rev. Biophys. **10**, 353 (1977).

[13] M. J. Hunt and A. L. MacKay, J. Mag. Reson. **15**, 402 (1974).

[14] M. Mizuno, Y. Hamada, T. Kitahara, and M. Suhara, J. Phys. Chem. **103**, 4981 (1999).

[15] N. Matsumoto, M. Yamashita, S. Kida, and I. Ueda, Acta Crystallogr. **B35**, 1458 (1979); H. Endres, H. J. Keller, R. Martin, H. N. Gung, and U. Traeger, Acta Crystallogr. **B35**, 1885 (1979).

[16] D. C. Look and I. J. Lowe, J. Chem. Phys. **44**, 3437 (1966).

[17] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[18] E. R. Andrew and L. Latanowicz, J. Mag. Reson. **68**, 232 (1986).

[19] A. Abragam, The Principle of Nuclear Magnetism, Oxford University Press, Oxford 1961, Chapt. VIII.