^{13}C Solid NMR, ESR and IR Studies on -M(II)-X-Pt(IV)-X- Type Complexes, [M(*en*)$_2$][PtX$_2$(*en*)$_2$](NO$_3$)$_4$ (M: Pd, Pt; X: Cl, Br)

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Abstract

IR and ^{13}C NMR measurements in hetero-metal complexes, [Pd(*en*)$_2$][PtX$_2$(*en*)$_2$](NO$_3$)$_4$ (X: Cl, Br) afforded two kinds of signals assignable to Pd and Pt moieties, indicating the formation of the Pd(II)-X- Pt(IV)-X- type chain structure. Weak ESR signal observed in [Pt(*en*)$_2$][PtCl$_2$(*en*)$_2$](NO$_3$)$_4$ suggested the formation of only small amounts of spin soliton.

1. Introduction

More than 150 halogen-bridged one-dimensional (1-D) mixed-valence complexes formulated as [M(AA)$_2$][MX$_2$(AA)$_2$]Y$_4$ (M: Pt, Pd, Ni, Cu; X: Cl, Br, I; AA: ethylendiamine (*en*), 1*R*, 2*R*-cyclohexanediamine (*chxn*), *etc.*; Y$^-$: X$^-$, ClO$_4^-$, BF$_4^-$, *etc.*) have so far been synthesized[1-3]. ESR[4,5] and NMR studies[5] of [M(*en*)$_2$]-[MX$_2$(*en*)$_2$](ClO$_4$)$_4$ in solid state have shown the presence of paramagnetic M(III) sites with temperature independent concentrations (10^{-4}- 10^{-5} [4, 5] in molar ratio to the M(II) and M(IV) sites). Observed M(III) sites expressed as -M(II)-X-M(IV)-X-M(III)-M(II)- X-M(IV)- X- were shown to form spin solitons[4-6].

Recently, we prepared[7] a nitrate complex, [Pt(*en*)$_2$][PtCl$_2$(*en*)$_2$](NO$_3$)$_4$, and discussed[7] the comparison of peak frequency for overtone in Pt-Cl stretch vibration between that excited by an Ar$^+$ and that by a near infrared lasers from observed Raman spectra[7] in a temperature range of 10- 300 K and reported[7] that the decrease of the overtone peak frequency of near infrared excitation were larger than that of visible excitation. In the present studies, we undertake to synthesize mixed metal complexes [M(*en*)$_2$][PtX$_2$(*en*)$_2$](NO$_3$)$_4$ (M: Pd, Pt; X: Cl, Br), and study their structure and the formation of spin-solitons by measuring the IR, ^{13}C NMR and ESR spectra.

2. Experimental

[M(*en*)$_2$][PtX$_2$(*en*)$_2$](NO$_3$)$_4$ (M: Pt, Pd; X: Cl, Br)[8] were prepared by dissolving equimolar amounts of [M(*en*)$_2$]X$_2$ [9, 10] and [PtX$_2$(*en*)$_2$]X$_2$ [1] in an aqueous solution of NH$_4$NO$_3$. Obtained crystals were recrystallized from an aqueous solution. IR absorption measurement was carried out with a Nicolet Nexus 670 FTIR spectrometer. A Bruker MSL-300 spectrometer was used for the measurement of ^{13}C CP/ MAS NMR spectra at a Larmor frequency of 75.47 MHz and a sample spinning rate of 4- 5 kHz at room temperature. TMS and solid adamantane were used as external standards of chemical shift. ESR spectra were observed with a Bruker EMX-T spectrometer.

3. Results and Discussion

IR spectra observed in [M(*en*)$_2$][PtX$_2$(*en*)$_2$](NO$_3$)$_4$, [M(*en*)$_2$][PtX$_2$(*en*)$_2$](ClO$_4$)$_4$ are shown in Figure 1.

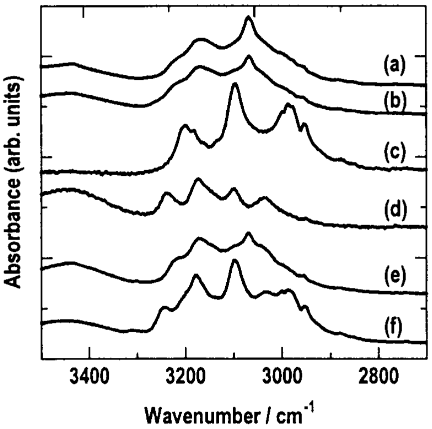

Figure 1. IR absorption spectra observed at room temperature in $[M(en)_2][PtCl_2(en)_2](NO_3)_4$ (M: Pt; X: Cl (**a**), M: Pt; X: Br (**b**), M: Pd; X: Cl (**c**), M: Pd; X: Br (**d**)), $[M(en)_2][PtCl_2(en)_2](ClO_4)_4$ (M: Pt (**e**), M: Pd (**f**)).

The peaks around 3100 cm^{-1} were assigned to the C-H stretching mode of ethylenediamine by referring the reported shift values in Raman spectra observed in $[M(en)_2][PtCl_2(en)_2](ClO_4)_4$[11]. It was also reported that C-H stretching mode was split into two groups because of two kinds of ethylenediamine molecules coordinated to M(II) and Pt(IV). In the present IR spectra, the shape of signals in nitrate-salts are similar to those in perchlorate given above, and this fact proves that both homo- and hetero-complexes in nitrate-salts are consistent with the expectation of the formation of M(II) and Pt(IV) moieties. The more peaks for hetero-complexes than that for homo- can be attributable to larger difference for frequencies of C-H stretching modes between $[Pd(en)_2]$ and $[PtX_2(en)_2]$ moieties than that between $[Pt(en)_2]$ and $[PtX_2(en)_2]$ moieties.

^{13}C NMR spectra observed in $[M(en)_2][PtX_2(en)_2](NO_3)_4$ at room temperature are shown in Figure 2.

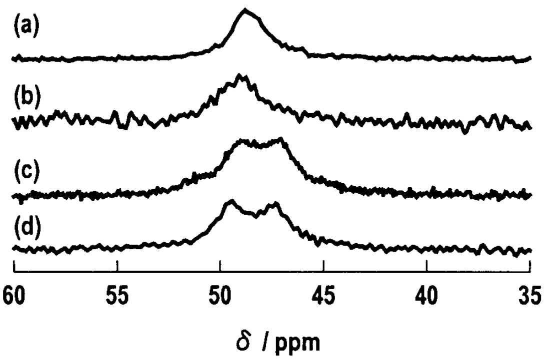

Figure 2. ^{13}C CP/ MAS NMR spectra observed in $[M(en)_2][PtX_2(en)_2](NO_3)_4$ (M: Pt; X: Cl (a), M: Pt; X: Br (b), M: Pd; X: Cl (c), M: Pd; X: Br (d)).

Chemical-shift values are summarized in Table 1.

Table 1. ^{13}C chemical shifts of polymer and monomer complexes in solid and aqueous solution states.

Compound	δ / ppm (solid)	Compound	δ / ppm (solution)
$[Pt(en)_2][PtCl_2(en)_2](NO_3)_4$	48.5	$[Pt(en)_2]Cl_2$	49.49
$[Pt(en)_2][PtBr_2(en)_2](NO_3)_4$	49.0	$[PtCl_2(en)_2]Cl_2$	49.67
$[Pd(en)_2][PtCl_2(en)_2](NO_3)_4$	47.1, 48.9	$[Pd(en)_2]Cl_2$	48.43
$[Pd(en)_2][PtBr_2(en)_2](NO_3)_4$	47.4, 49.6		
$[Pd(en)_2][PdCl_2(en)_2](ClO_4)_4$	48.4, 51.2		

^{13}C NMR signals of $[Pt(en)_2][PtX_2(en)_2](NO_3)_4$ (X: Cl, Br) exhibited a single resonance line, 48.5 and 49.0 ppm, respectively. These values indicate that local electronic distributions around CH_2 carbon in Pt(II) and Pt(IV) units in the chain were quite analogous. In fact, $\delta = 49.49$ ppm in monomer complexes $[Pt(en)_2]^{2+}$ and 49.67 ppm in $[PtCl_2(en)_2]^{2+}$ were obtained in aqueous solutions. In $[Pd(en)_2][PdCl_2(en)_2](ClO_4)_4$, it is expected that two peaks appeared at 48.4 and 51.2 ppm are assignable to CH_2 carbons in Pd(II) and Pd(IV) sites, respectively, by comparing chemical shift of $[Pd(en)_2]Cl_2$ in solution. On the other hand, ^{13}C NMR signals in hetero-metal complexes, $[Pd(en)_2][PtX_2(en)_2](NO_3)_4$ (X: Cl, Br) exhibited two lines, 47.1 and 48.9 ppm for chloro- and 47.4 and 49.6 ppm for bromo-complexes. Observed two peaks of equal intensity at up- and down-fields were assignable to carbons in Pd(II) and Pt(IV) units, respectively. This is because ^{13}C chemical shifts observed in these complexes are close to values in Pd(II) and Pt(IV). These results clearly indicate that the present polymer complexes have a -Pd(II)-X-Pt(IV)-X- chain structure formed by the two kinds of metals with the same concentration.

Powder ESR spectra observed in $[Pt(en)_2][PtCl_2(en)_2](NO_3)_4$ and $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ are shown in Figure 3.

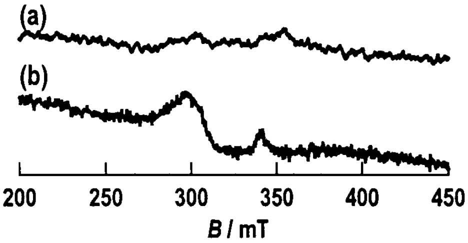

Figure 3. Powder ESR spectra observed at room temperature in $[Pt(en)_2][PtCl_2(en)_2](NO_3)_4$ (**a**) and $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ (**b**). Samples of *ca.* 0.1 g were used in both measurements.

From observed line-shape and width in nitrates, we estimated spin concentrations to be *ca.* 10^{-6} in molar ratio. This spin concentration is roughly two orders of magnitude smaller than in perchlorate as shown in Fig. 3 (**b**). The low concentration of paramagnetic sites observed in nitrate implied that the formation of the spin soliton in nitrate seem to be more difficult than those in perchlorate, probably because it is expected that the strength of hydrogen bonds between amines and counter anions (NO_3^- and ClO_4^-) is different·

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References and Notes

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[8] Elemental analysis: Calculated for $[Pt(en)_2][PtCl_2(en)_2](NO_3)_4$: C, 10.1; H, 3.40; N, 17.7; Cl, 7.47 %. Found: C, 9.94; H, 3.52; N, 17.8; Cl, 8.18 %. Calculated for $[Pt(en)_2][PtBr_2(en)_2](NO_3)_4$: C, 9.25; H, 3.11; N, 16.2; Br, 15.3 %. Found: C, 8.99; H, 3.29; N, 15.7; Br, 16.3 %. Calculated for $[Pd(en)_2][PtCl_2(en)_2](NO_3)_4$: C, 11.2; H, 3.75; N, 19.5 %. Found: C, 10.9; H, 3.95; N, 19.3 %. Calculated for $[Pd(en)_2][PtBr_2(en)_2](NO_3)_4$: C, 10.1; H, 3.40; N, 17.7 %. Found: C, 9.81; H, 3.33; N, 16.9 %.

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