

¹³C NMRおよびESR法を用いた一次元ニッケル-パラジウム混合金属錯体 [Ni_{1-x}Pd_xBr(chxn)₂](NO₃)₂(0.00≤χ≤1.00)の金属原子価とスピン構造の研究

Metal Valence and Spin Structures in 1-D Ni-Pd Mixed-Metal Complexes,
[Ni_{1-x}Pd_xBr(chxn)₂](NO₃)₂(0.00≤χ≤1.00), Studied by ¹³C NMR and ESR Measurements

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Abstract

¹³C solid-state NMR and ESR spectra were observed in [Ni_{1-x}Pd_xBr(chxn)₂](NO₃)₂ (0.00 ≤ χ ≤ 1.00; chxn: 1*R*, 2*R*-diamonocyclohexane), where the antiferromagnetically coupled paramagnetic-Br-Ni³⁺-Br-Ni³⁺-Br-chains are formed at χ=0.00, while the mixed-valence-Br-Pd²⁺-Br-Pd⁴⁺-Br-state is formed at χ=1.00. The ¹³C NMR signals at C_α coordinating to Ni atoms in mixed-metal complexes afforded the marked decrease of intensity with increasing χ from 0.00. This result seems to be attributed to the effect of the strong spin fluctuation on paramagnetic Ni³⁺ sites, and was supported by ESR spectrum measurement.

1. Introduction

Halogen-bridged one-dimensional (1-D) complexes, expressed as X-M-X-M-X-(M: Ni, Pd, Pt; X: Cl, Br, I), have been very interested because they show interesting physical properties, such as solitons,^{1,2} polarons,¹ large third-order nonlinear optical susceptibilities³ and spin-Peierls transition.⁴ Among these complexes, [MBr(chxn)₂]₂(chxn: 1*R*, 2*R*-diamonocyclohexane) have been reported to form a mixed-valence diamagnetic structure of -Br-Pd²⁺-Br-Pd⁴⁺-Br- for M=Pd,⁵ whereas an averaged paramagnetic structure of -Br-Ni³⁺-Br-Ni³⁺-Br- for M=Ni,⁶ and the novel Ni-Pd mixed-metal complexes, [Ni_{1-x}Pd_xBr(chxn)₂]₂(0.00 ≤ χ ≤ 1.00), were recently prepared⁷ by applying the electrochemical oxidation technique.⁷ The valence structures of these complexes have been intensively studied by various measurements⁷⁻⁹ as competition between an averaged valence structure-Br-Ni³⁺-Br-Ni³⁺-Br-and a mixed-valence structure-Br-Pd²⁺-Br-Pd⁴⁺-Br-. We previously reported the ¹³C NMR spectra⁸ and ¹H T₁ results⁸ in [Ni_{1-x}Pd_xBr(chxn)₂]₂, where the formation of paramagnetic Pd³⁺ sites and the Ni-spin fluctuation owing to the strong magnetic coupling with Pd³⁺ sites formed both sides of Ni³⁺ were observed at χ ≤ 0.93.⁸

In the present study, we performed ¹³C

NMR and ESR spectra measurements in [Ni_{1-x}Pd_xBr(chxn)₂](NO₃)₂ to investigate the effect of counteranion through the hydrogen-bond network.

2. Experimental

A series of crystals of Ni-Pd mixed-metal nitrate compounds, [Ni_{1-x}Pd_xBr(chxn)₂](NO₃)₂ (0.00 ≤ χ ≤ 1.00), were obtained by the electrochemical oxidation⁷ of methanol solutions of [Ni(chxn)₂]₂Br₂ and [Pd(chxn)₂]₂Br₂ with various mixing ratios at room temperature with a dc current of 20 μA. As an electrolyte, ammonium nitrate¹⁰ was used. Mixing ratios of Pd to Ni in crystals were determined by a Shimadzu AA-6200 atomic absorption spectrometer.

To identify the obtained crystals, the powder X-ray diffraction and IR spectra were measured using a Phillips X'pert PW3050/00 diffractometer and a Jasco FT-IR 6100 spectrometer, respectively. A Bruker MSL-300 spectrometer was used for the measurement of ¹³C CP-MAS NMR spectra at a Larmor frequency of 75.468 MHz and with a sample spinning rate of ca. 4 kHz at room temperature. TMS and solid adamantane were used as external standards of chemical shift. The ESR spectra were obtained with an X-band JEOL-FE1XG spectrometer on powder samples under a modulation field of 10 G with a frequency of 100

kHz at room temperature.

3. Results and discussion

The observed ^{13}C NMR spectra in the mixed-metal complexes, $[\text{Ni}_{1-x}\text{Pd}_x\text{Br}(\text{chxn})_2](\text{NO}_3)_2$ ($0.00 \leq x \leq 1.00$), are shown in Figure 1.

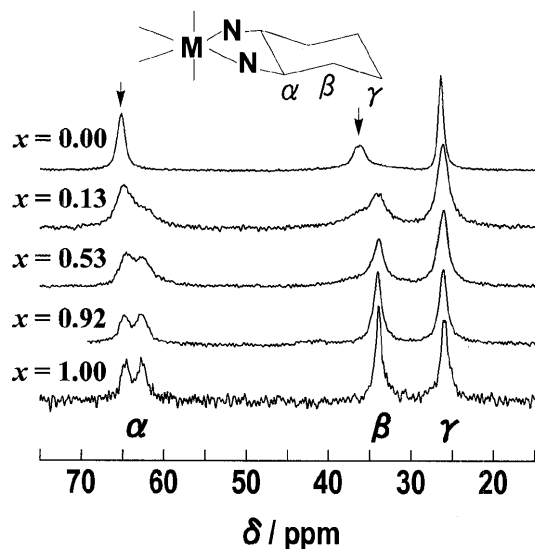


Fig. 1 ^{13}C CP-MAS NMR spectra observed in Ni-Pd mixed-metal complexes, $[\text{Ni}_{1-x}\text{Pd}_x\text{Br}(\text{chxn})_2](\text{NO}_3)_2$ ($0.0 \leq x \leq 1.0$). α , β and γ denote the carbon position in a cyclohexane ring. The arrows show the carbon signals of 65.3 and 36.4 ppm for Ni chelate rings.

In $x = 1.00$, an observed doublet line was attributed to α -carbons in Pd^{2+} and Pd^{4+} moieties,¹¹ while, in $x = 0.00$, a single C_α line showed the formation of an averaged paramagnetic Ni^{3+} site.¹¹ We also simulated the observed C_α signals in $[\text{Ni}_{1-x}\text{Pd}_x\text{Br}(\text{chxn})_2](\text{NO}_3)_2$ by assuming the Gaussian-type line-shape in the mixed-metal range into two components corresponding to Ni and Pd sites, and showed the results of decomposition in Figure 2.

With increasing x from 0.00, C_α and C_β signals of 65.3 and 36.4 ppm, respectively, in Ni chelate rings afforded the marked decrease of intensity, and, in $x = 0.53$, the corresponding Ni site peaks showed only the slight signals of Ni C_α and C_β with a ratio of *ca.* 10 %. The Ni signals at $x > 0.53$ were unable to be observed by the marked broadening. This behavior seems to be attributed to the strong spin fluctuation on Ni^{3+} sites. The powder ESR spectra of $[\text{NiBr}(\text{chxn})_2](\text{NO}_3)_2$, $[\text{NiBr}(\text{chxn})_2]\text{Br}_2$ and $[\text{Ni}_{1-x}\text{Pd}_x\text{Br}(\text{chxn})_2](\text{NO}_3)_2$ at room temperature are shown in Figure 3.

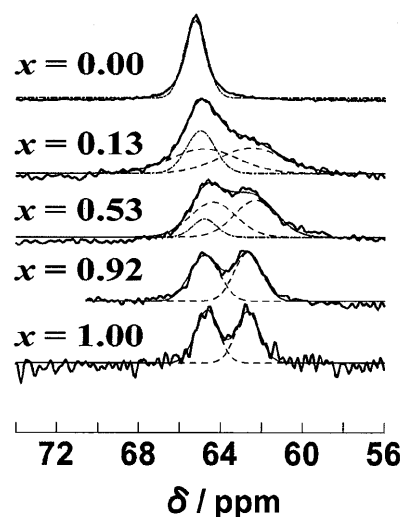


Fig. 2 The α -carbon signals decomposed into two components corresponding to Ni and Pd sites in $[\text{Ni}_{1-x}\text{Pd}_x\text{Br}(\text{chxn})_2](\text{NO}_3)_2$.

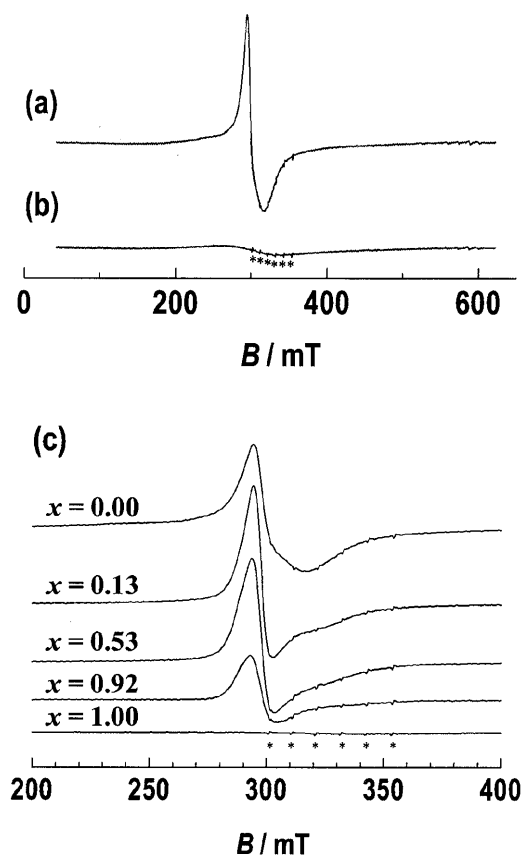


Fig. 3 ESR spectra for a powder samples of $[\text{NiBr}(\text{chxn})_2](\text{NO}_3)_2$ (a), $[\text{NiBr}(\text{chxn})_2]\text{Br}_2$ (b) and $[\text{Ni}_{1-x}\text{Pd}_x\text{Br}(\text{chxn})_2](\text{NO}_3)_2$ (c). The lines with asterisks are the marker signals from doped Mn^{2+} in MgO .

The intensity and linewidth of ESR spectrum observed in $[\text{NiBr}(\text{chxn})_2](\text{NO}_3)_2$ are larger and sharper than those of $[\text{NiBr}(\text{chxn})_2]\text{Br}_2$, and these differences are explained by considering the strong fluctuation of electron spins on the Ni^{3+} sites in $[\text{NiBr}(\text{chxn})_2](\text{NO}_3)_2$. This expla-

nation is consistent with the magnitudes of J values estimated from susceptibility measurements.¹⁰

The ESR spectra of the mixed-metal complexes, [Ni_{1-x}Pd_xBr(chxn)₂](NO₃)₂, are more sharper than that of pure Ni complex, [NiBr(chxn)₂](NO₃)₂, and this behavior seems that the exchange interaction between Ni³⁺ spins in [Ni_{1-x}Pd_xBr(chxn)₂](NO₃)₂ should be weaker than that in [NiBr(chxn)₂](NO₃)₂. This result agrees with the reported ESR⁷ and ¹H NMR T_1 analyses⁸ in [Ni_{1-x}Pd_xBr(chxn)₂]Br₂. Since an isolated Ni³⁺ site is magnetically coupled with nearest-neighbor Ni³⁺ through diamagnetic Pd²⁺ or Pd⁴⁺ sites, a remarkable broadening of Ni site at $x \geq 0.53$ shown in Fig. 1 seem to be afforded by the strong spin fluctuation.

On the other hand, the corresponding signals to Pd rings in [Ni_{1-x}Pd_xBr(chxn)₂](NO₃)₂ afforded a gradual broadening with decreasing x from 1.00 as shown in Fig. 1. In $x = 1.00$, a doublet line observed for C_α is attributed to carbons in Pd²⁺ and Pd⁴⁺ moieties¹¹, and most of Pd atoms are expected to take the valencies of diamagnetic Pd²⁺ and Pd⁴⁺ even in the presence of Ni³⁺ for $x \leq 0.53$. The x dependency of chemical shift of C_β could be also explained by the valencies of both Pd²⁺ and Pd⁴⁺ for $x \leq 0.53$. It has been reported that the Pd C_α signals of ¹³C NMR spectra in [Ni_{1-x}Pd_xBr(chxn)₂]Br₂⁸ show the formation of paramagnetic Pd³⁺ sites from analyses of line-width and shift of signals. This difference of Pd valences between nitrate and bromide could be explained by the differences of d_{z²} orbital energy levels between Pd²⁺ and Pd⁴⁺ sites, which were estimated by the CT excitation energies as shown in reference.¹² This remarkable result depends on the distances^{5,12} between Pd²⁺ and Pd⁴⁺ sites, and these distances seem to be attributed to the strength of hydrogen bond through counteranion in the interchain. We also tried to measure the IR spectra corresponding to N-H stretching bands in the whole range of 0.00 ≤ x ≤ 1.00 for both nitrate and bromide, and the stronger hydrogen bond was measured for bromide.

4. Summary

We measured ¹³C CP-MAS NMR and ESR

spectra of 1-D mixed-metal complex, [Ni_{1-x}Pd_xBr(chxn)₂](NO₃)₂. By the simulation of C_α NMR lines in the mixed-metal range into two components corresponding to Ni and Pd sites, the single and doublet lines for Ni and Pd, respectively, were obtained. With increasing x from 0.00, Ni C_α and C_β signals afforded the marked decrease of intensity, and, in $x = 0.53$, the corresponding C_α and C_β showed only the slight signals with a ratio of ca. 10%. This behavior seems to be attributed to the effect of the strong spin fluctuation on Ni³⁺ sites, and was also supported by ESR spectra data in the present study.

On the other hand, the behavior of Pd valency is different from that of bromide, which showed a single line for Pd site, and this difference could be explained by the differences of d_{z²} orbital energy levels between Pd²⁺ and Pd⁴⁺ sites from CT excitation energy measurements.

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