

Selected Paper

Metal Valence Structures and Magnetic Interactions in Halogen-Bridged 1-D Ni–Pd Mixed-Metal Complexes Studied by ^{13}C and ^{1}H Solid State NMR

Noriyoshi Kimura,* Aki Josako, Masataka Kano,[1] Kenji Kisoda,[2] Toshio Manabe,[3] Masahiro Yamashita,[3] and Ryuichi Ikeda[1]

Department of Chemistry, Faculty of Education, Wakayama University, Wakayama 640-8510

[1]Department of Chemistry, University of Tsukuba, Tsukuba 305-8571

[2]Department of Physics, Faculty of Education, Wakayama University, Wakayama 640-8510

[3]Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397

Received April 2, 2004; E-mail: nkimura@center.wakayama-u.ac.jp

^{13}C NMR spectra at room temperature and the temperature dependences of ^{1}H T_1 in the solid state were measured in $[Ni_{1-x}Pd_xX(chxn)_2]X_2$ (*X*: Cl, Br; chxn: 1*R*,2*R*-cyclohexanediamine; $0.0 \leq x \leq 1.0$), where antiferromagnetically coupled paramagnetic –X–Ni^{3+}–X–Ni^{3+}–X– chains were formed at $x = 0.00$, while the mixed-valence –X–Pd^{2+}–X–Pd^{4+}–X– state was made at $x = 1.00$. ^{13}C signals at α-carbons in chxn coordinating to Pd atoms showed a doublet assignable to Pd^{2+} and Pd^{4+} in $x = 1.00$, while, with a slight decrease of x from 1.00, a clear broadening and a shift to low-field of signals, indicating conversion into the averaged Pd^{3+} state, were observed. This can be explained by the fluctuation of the Pd valency caused by neighboring paramagnetic Ni^{3+} sites introduced in small amounts in the 1-D chain. The x dependences of the chemical shifts of β- and γ-carbons are also attributable to the effect from a partial mixing of the paramagnetic Pd^{3+} sites. The values of ^{1}H T_1 and its temperature dependence observed in the ranges of 100–300 K and $x \leq 0.13$ for $[Ni_{1-x}Pd_xBr(chxn)_2]Br_2$ could be explained by a model of strong exchange interactions between Ni^{3+} and Pd^{3+} as well as Ni^{3+} sites. Gradual changes in the T_1 value and slope with increasing x from 0.00 to 0.93 are attributable to the variation of the exchange interaction value, which depends upon the number of Ni–Ni pairs.

Halogen-bridged quasi-one-dimensional (1-D) complexes[1–3] consisting of alternate arrangements of metals (M) (M: Cu, Ni, Pd, Pt) and halogens (X) (X: Cl, Br, I), expressed as –X–M–X–M–X–, have been of interest because of their almost isolated 1-D structure in which various metal valencies, such as M^{2+}, M^{3+}, and M^{4+}, can be formed. Among those, $[MX(chxn)_2]X_2$ (chxn: 1*R*,2*R*-cyclohexanediamine, $C_6H_{10}(NH_2)_2$; X: Cl, Br) have been reported to form a mixed-valence diamagnetic structure of –X–M^{2+}–X–M^{4+}–X– for M = Pd,[1] whereas they have shown an averaged paramagnetic structure of –X–M^{3+}–X–M^{3+}–X– for M = Ni.[2]

Recently, crystals of Ni–Pd mixed-metal complexes, $[Ni_{1-x}Pd_xX(chxn)_2]X_2$ ($0.0 \leq x \leq 1.0$),[4,5] consisting of homogeneously mixed crystalline lattices of the two kinds of metal complexes with the isomorphous structure (*I*222) were prepared by applying the electrochemical oxidation technique.[4,5] Concerning these series of complexes, the x dependence of the ESR spectra[6] was measured, and a continuous change of the spectrum-width with x was obtained. A remarkable result was that the evaluated spin susceptibility[6] showed no linear relation with x, but was almost constant up to $x \approx 0.6$ with increasing x. This suggests that the majority of diamagnetic Pd^{2+} and Pd^{4+} metal sites behave like paramagnetic Pd^{3+} at concentrations lower than $x = 0.6$. A change in the Pd valence was also observed in the IR spectra[4,5] of the N–H stretching bands in both the Pd^{2+} and Pd^{4+} units, which showed a gradual shift to that in the Ni^{3+} unit.

We measured the ^{13}C spectra and the ^{1}H NMR relaxation of $[Ni_{1-x}Pd_xX(chxn)_2]X_2$, and the preliminary result was reported,[7] where the presence of Pd^{3+} sites at $x \leq 0.7$ and a strongly coupled antiferromagnetic 1-D structure at $x \leq 0.13$ were shown. In the present study, we performed ^{13}C NMR spectrum and ^{1}H NMR relaxation measurements over the whole range of $0.0 \leq x \leq 1.0$ in more detail, and analyzed the obtained NMR data to determine the local spin structure in the 1-D chain.

Experimental

A series of crystals of Ni–Pd mixed-metal complexes, $[Ni_{1-x}Pd_xX(chxn)_2]X_2$ (X: Cl, Br; $0.0 \leq x \leq 1.0$), were obtained by the electrochemical oxidation[4,5] of methanol solutions of $[Ni(chxn)_2]X_2$ and $[Pd(chxn)_2]X_2$ with various mixing ratios at 300–320 K with a dc current of 10–20 μA.[4,5] As electrolytes, tetramethylammonium chloride[5] and tetra-*n*-butylammonium bromide[4] were used. The mixing ratios of Pd to Ni in crystals were determined by ICP emission spectrometry.

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 Nicolet NEXUS 670 FT-IR spectrometer, respectively. A Bruker MSL-300 spectrometer was used for measuring the ^{13}C 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

Published on the web October 9, 2004; DOI 10.1246/bcsj.77.1815

standards of the chemical shift. The ^{1}H NMR spin–lattice relaxation time (T_1) was measured at 54.3 MHz by the inversion recovery method in the range of 100–300 K using a home-made spectrometer.[8]

Results and Discussion

The x dependences of the observed ^{13}C CP/MAS NMR spectra at room temperature for $[Ni_{1-x}Pd_xCl(chxn)_2]Cl_2$ and $[Ni_{1-x}Pd_xBr(chxn)_2]Br_2$ are shown in Figs. 1 and 2, respectively. In both systems, three kinds of carbon sites (α, β, and γ) in a chxn ligand were observed as separated peaks. At $x = 1.00$, a doublet line observed for the α-carbon (C_α) was attributed to carbons in Pd^{2+} and Pd^{4+} moieties,[9] while, in $x = 0.00$, a single α line showed the formation of an averaged paramagnetic Ni^{3+} site.[9] We decomposed C_α signals in $[Ni_{1-x}Pd_xX(chxn)_2]X_2$ by assuming a Gaussian-type lineshape in the mixed-metal range into two components corresponding to the Ni and Pd sites; the results of the decomposition are shown in Fig. 3. Two decomposed peaks observed at low and high fields were assigned to C_α in the $Ni(chxn)_2$ and $Pd(chxn)_2$ moieties, respectively, by comparing chemical-shift values of the C_α signals in $x = 0.00$ with that in 1.00. The x dependences of the chemical shift and the line-width of α-carbons in both moieties are shown in Fig. 4. With increasing x from 0.00, C_α signals in Ni chelate rings, whose intensity gradually decreased almost proportionally to the Ni concentration, gave nearly the same values of the shift and a line-width up to ca. $x = 0.8$. This result implies that Ni atoms are always in the trivalent state, even in a short –Ni–X–Ni–X– chain separated by neighboring Pd sites.

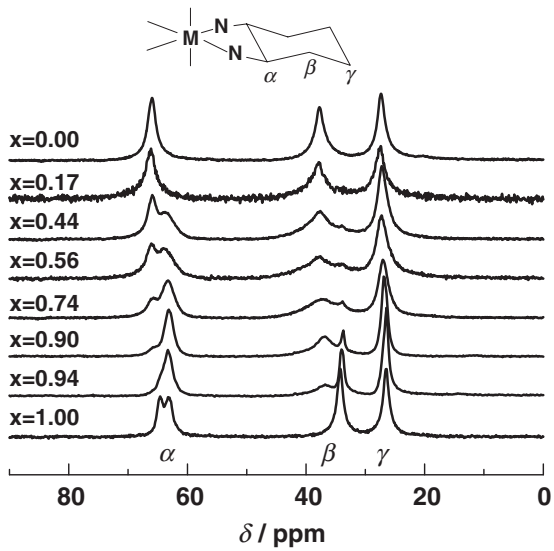

Fig. 1. ^{13}C CP/MAS NMR spectra observed at room temperature in $[Ni_{1-x}Pd_xCl(chxn)_2]Cl_2$ and carbon positions in a cyclohexanediamine ligand in a M(chxn) chelate ring.

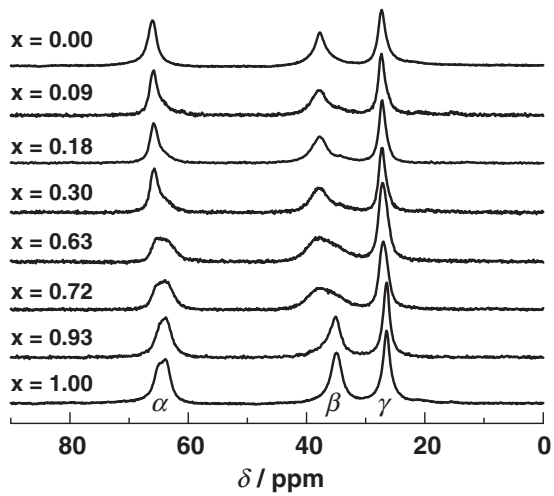

Fig. 2. ^{13}C CP/MAS NMR spectra observed at room temperature in $[Ni_{1-x}Pd_xBr(chxn)_2]Br_2$.

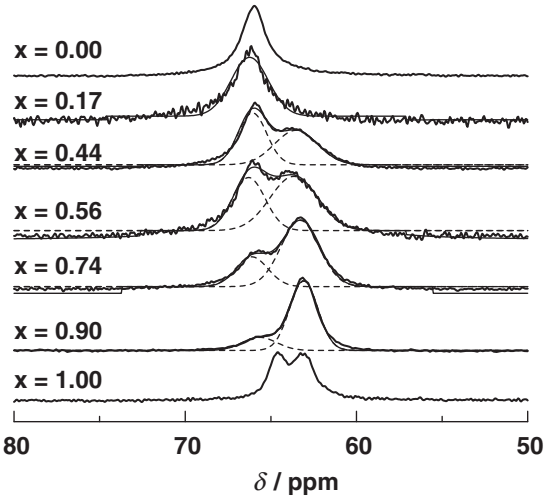

Fig. 3. α-Carbon signals decomposed into two components corresponding to Ni and Pd sites in $[Ni_{1-x}Pd_xCl(chxn)_2]Cl_2$.

On the other hand, corresponding signals in Pd rings afforded a marked broadening and a continuous shift to the low field with decreasing x from 1.00, as shown in Fig. 4. It is noted that an inclusion of 6–7% Ni gave a single C_α line in Pd chelate rings. This implies that the magnetic circumstances at C_α in all Pd chelate rings are almost the same even in the presence of Ni^{3+} with a ratio of 1:15. The observed Pd C_α shift value around $x = 0.9$ seems not to be explained by the rapid exchange between the Pd^{2+} and Pd^{4+} sites, because the observed value is different from the split two shifts observed at $x = 1.00$ and also their averaged value. Since the low-field shift with increasing a Ni concentration observed at Pd C_α is mainly explainable by a paramagnetic shift,[10,11] the above results together with the signal broadening in the Pd C_α lines with mixing Ni are attributable to a gradual conversion into paramagnetic Pd^{3+} sites in the chain and the chain ends. The Pd^{3+} sites seem to be formed by the strong magnetic interaction with neighboring Ni^{3+} from Pd^{2+} and Pd^{4+} sites. If the Pd^{3+} sites move rapidly along the chain by forming neutral-solitons or polarons, Pd takes an electronic and magnetic structure averaged by those in Pd^{2+}, Pd^{4+}, and a small amount of Pd^{3+}. This model can explain the observed single line of Pd C_α and also the continuous low-field shift with the increase of Ni, which should favor the creation of more Pd^{3+} sites.

These explanations agree well with the reported analysis of the N–H stretching band in the IR spectra,[4,5] indicating a con-

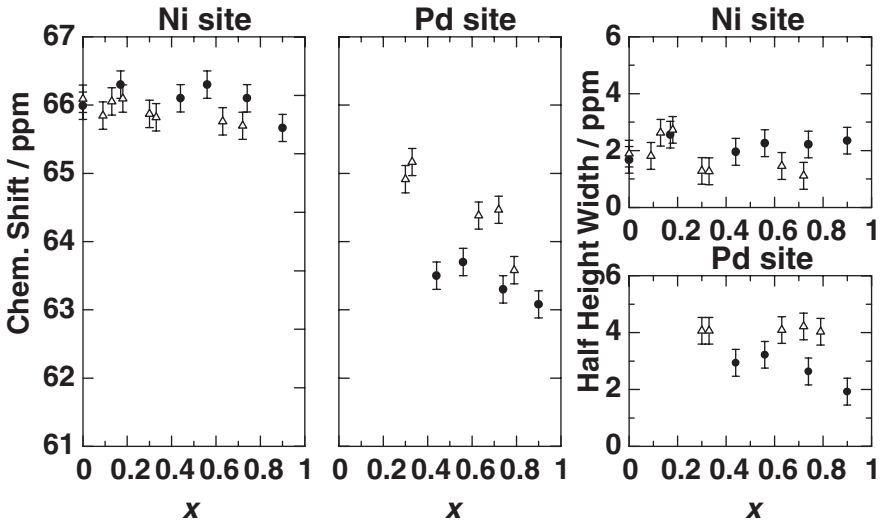

Fig. 4. Concentration (x) dependences of the chemical shift (left) and the half-height width (right) corresponding to Ni and Pd C_α signals observed in $[Ni_{1-x}Pd_xCl(chxn)_2]Cl_2$ (●) and Ni and Pd C_α signals observed in $[Ni_{1-x}Pd_xBr(chxn)_2]Br_2$ (△).

version into Pd^{3+} sites in the presence of Ni^{3+} in $x \leq 0.96$.[4,5] It has been reported from the XP spectra study[4] that the oxidation states of the Pd^{2+} and Pd^{4+} gradually approach the Pd^{3+} state with decreasing x from 1.00. This suggests that the formation of Pd^{3+} becomes easy with the x decrease. In the present study, the split of two peaks from the Pd^{2+} and Pd^{4+} sites observed at $x = 1.00$ became a broad single line with decreasing x, consistent with the XPS result. It is noted that a marked x dependence of ^{13}C chemical shifts values could be explained by the paramagnetic shift,[10,11] because the observed shift values of C_α were different from the averaged value of the split of the two shifts observed at $x = 1.00$. The extent of the observed shifts is very close to the spin-susceptibility data obtained by an ESR measurement.[6] This result is also consistent with the above expectation from the XPS study.[4]

The x dependences of the chemical shifts observed for C_β and C_γ are shown in Fig. 5. Opposite directions of shift were

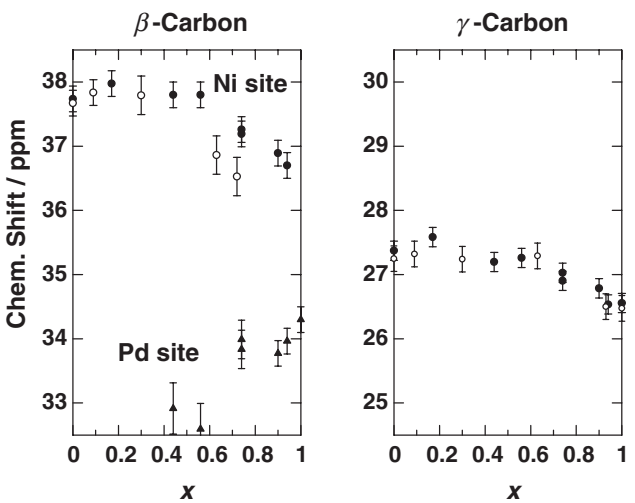

Fig. 5. Concentration (x) dependences of the chemical shift corresponding to Ni (●) and Pd (▲) C_β and C_γ signals (●) observed in $[Ni_{1-x}Pd_xCl(chxn)_2]Cl_2$ and Ni C_β (○) and C_γ signals (○) observed in $[Ni_{1-x}Pd_xBr(chxn)_2]Br_2$.

obtained for C_α and C_β coordinating to Pd, whereas the x dependence of C_γ showed the same tendency as that of C_α. These characteristic features of the chemical shifts are explicable by the signs of the electron-spin densities on the carbon atoms in the presence of a contact interaction through the bidentate σ-bond system, as reported in Ref. 10, 11. The small shift from 0.00 to 1.00 of C_γ is explainable by a cancellation of the sign of the electron-spin densities through the bidentate σ-bond system.

We performed measurements of the ^1H NMR spin–lattice relaxation time (T_1) in a temperature range of 100–300 K for $[Ni_{1-x}Pd_xBr(chxn)_2]Br_2$ ($0.0 \leq x \leq 1.0$). The T_1 measurement is a sensitive probe to obtain information concerning magnetic interactions along the chain from a dynamical point of view compared with the spectrum measurement. The ^1H magnetization recovery curves observed after the inversion-recovery pulse-sequence showed a non-exponential behavior over the whole range of x, including at $x = 0.00$ and 1.00. We could roughly divide the decay curves into two T_1 components, observed at all temperatures investigated, where the short T_1 component was always major, being 60–80% of the total observed magnetization. The ratio of the fast-relaxation magnetization gradually decreased with an increase of x from 0.00. The decrease in the observed fast component is attributable to the increase in the number of protons in Pd chelate rings remote from Ni sites. The temperature dependences of T_1 shown in Fig. 6 were derived from the fast component.

At $x \leq 0.13$, T_1 and its temperature dependence observed above ca. 100 K afforded no appreciated changes from those in the complex of $x = 0.00$. The T_1 temperature dependence in the pure Ni complex ($x = 0.00$) could be explained by the model of the strong exchange interaction in an $S = 1/2$ 1-D Heisenberg antiferromagnet,[12] and is expressed by the theoretical treatments[13] as

$$T_1^{-1} \propto \ln^{1/2}(2J/T) \quad (1)$$

in the range of $T/J < 0.5$, where the exchange interaction is given by

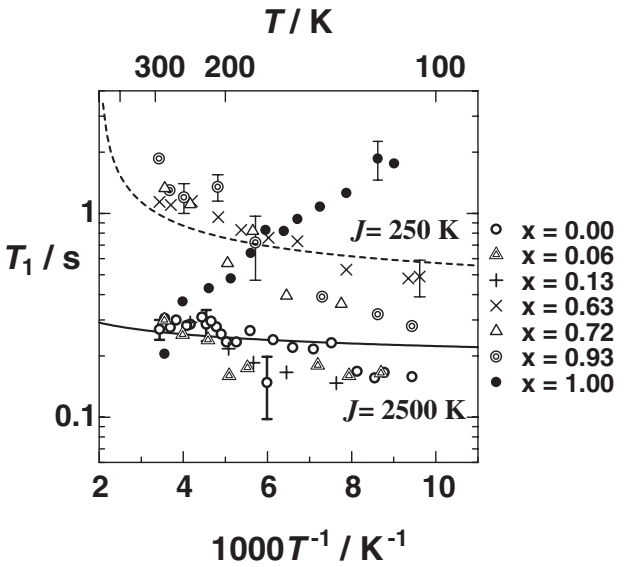

Fig. 6. Temperature dependences of ^{1}H T_1 observed at 54.3 MHz in $[Ni_{1-x}Pd_xBr(chxn)_2]Br_2$. Solid and broken lines indicate the fitted theoretical values of $x = 0.00$ and 0.63, respectively.

$$H_{ex} = 2J \sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1}. \quad (2)$$

Since, according to Eq. 1, the absolute value and the temperature slope of T_1 depend on the exchange interaction (J), almost the same T_1 behavior below $x = 0.13$ implies that no change in the magnetic interactions in the strongly coupled antiferromagnetic 1-D structure takes place, although 10% of Ni is replaced by Pd. This seems to be unacceptable because the spin fluctuation at the end Ni^{3+} sites in the chain where the antiferromagnetic chain is intercepted by Pd should make a strong relaxation effect on protons. This disagreement is reasonably explained by considering the formation of Pd^{3+} in the Ni^{3+} chain, and a continuous 1-D coupling chain of paramagnetic M^{3+} sites is formed, although the coupling between Pd^{3+} and Ni^{3+} spins is smaller than that between the Ni^{3+} sites. This explanation is consistent with the reported ESR result.[4,6] By applying Eq. 1 to the temperature dependence of T_1 in $x = 0.00$, shown in Fig. 6, we roughly evaluated the J value to be ca. 2500 K, in agreement with the result given in Ref. 12. This value is comparable to 2700 ± 500 K estimated from the spin-susceptibility data.[6] For the sample of $x = 0.63$, we tried to estimate a rough value of J, which became ca. 250 K, as shown in Fig. 6. This value is quite small compared with that in $x = 0.00$, and seems to correspond to an effective interaction in a 1-D antiferromagnetic chain containing weak interactions in Ni–Pd and Pd–Pd pairs.

On the other hand, at $x = 1.00$, a gradual T_1 decrease observed upon heating from ca. 100 K was explained by the rapid diffusion of spin solitons formed by the impurity order of Pd^{3+}.[14] With a little reduction of x from 1.00, T_1 showed changes in its temperature dependency, giving a reversed temperature slope close to that in $x = 0.00$. However, the T_1 values themselves fall nearly in the same range of ca. 1 s in the presence of paramagnetic Ni^{3+}. This is quite unusual, because the relaxation generally becomes quite rapid when a small amount of paramagnetic species are introduced in diamagnetic systems. Since the formation of paramagnetic Ni^{3+} spins has been confirmed even at low concentrations by the ^{13}C NMR spectrum analysis given above, these almost isolated spins should make a strong ^{1}H NMR relaxation mechanism. The slow relaxation observed in a complex of $x = 0.93$, accordingly, implies that the spin fluctuation in Ni^{3+} is suppressed by some strong interactions. It is highly probable that an isolated Ni^{3+} site is magnetically coupled with nearest-neighboring paramagnetic Pd^{3+} sites formed from diamagnetic Pd^{2+} and Pd^{4+} sites. It is acceptable to propose a spin-structure model that a few Pd^{3+} sites are formed at both sides of the Ni^{3+}, and strong magnetic couplings between these M^{3+} sites hinder the rapid spin fluctuation. As described above in the discussion of chemical shifts, this model enables an easy diffusions of Pd^{3+} as neutral-solitons between two isolated Ni^{3+} sites. In fact, the long minor T_1 component observed as the other relaxation process gave ca. 2.0 s at 106 K at $x = 0.93$. This T_1 agrees well with that observed in the sample of $x = 1.00$. This T_1 can be attributed to ^{1}H in Pd^{2+} and Pd^{4+} chelate rings that receive averaged fluctuations made by rapidly diffusing neutral-solitons.

Another unusual relaxation behavior in ^{1}H T_1 in this mixed system is that the sign of the temperature slope of T_1 was reversed by introducing a small amount of Ni. It is noted, furthermore, that, with decreasing x, the slope became gentle and approached to that in $x = 0.00$. At the same time, T_1 decreased with decreasing x, and became close to those in $x = 0.00$. This behavior seems to be attributed to the magnitude of the magnetic coupling constant of J between paramagnetic spins. Since the couplings between Pd^{3+} spins and between Pd^{3+} and Ni^{3+} spins should be weaker than that between Ni^{3+} spins, the averaged J value seems to increase with decreasing x. This J variation seems to result in a decrease in T_1, and also its slope, with an x decrease, which can be derived from Eq. 1.

Summary

We measured the ^{13}C NMR spectra at room temperature and temperature dependences of ^{1}H NMR T_1 of mixed-metal halogen-bridged 1-D complexes, $[Ni_{1-x}Pd_xX(chxn)_2]X_2$ (X: Cl and Br). By the decomposition of α-carbon (C_α) signals observed in both chloro- and bromo-complexes in the mixed-metal range into two components corresponding to Ni and Pd sites, single lines for both Ni and Pd, and the low-field shift and broadening of Pd C_α were obtained with decreasing x from 1.00. This result is unexplainable by the rapid exchange between Pd^{2+} and Pd^{4+} sites, but is attributable to the increase of paramagnetic Pd^{3+} sites, even introducing a small amount of Ni. The x dependences of the chemical shifts of C_β and C_γ could also be explained by the effect from the partial mixing of paramagnetic sites.

That the ^{1}H T_1 temperature dependences observed at $x \leq 0.13$ in $[Ni_{1-x}Pd_xBr(chxn)_2]Br_2$ show no appreciated changes from those in $x = 0.00$ was explained by the creation of Pd^{3+} sites, which enables completion of the strongly coupled 1-D Heisenberg chain. On the other hand, the introduction of a small amount of Ni^{3+} in diamagnetic Pd chains of $x = 1.00$

had no effect on T_1 from paramagnetic spins. This unusual result is attributable to a suppression of the Ni-spin fluctuation owing to the strong magnetic couplings with Pd^{3+} sites formed on both sides of Ni^{3+}. Gradual changes of the T_1 slope and the T_1 value, itself, with increasing x are explainable by a decrease of the exchange interaction (J) because of a decrease in the number of Ni–Ni pairs.

References

1 A. Hazell, *Acta Crystallogr.*, **C47**, 962 (1991).

2 K. Toriumi, Y. Wada, T. Mitani, and S. Bandow, *J. Am. Chem. Soc.*, **111**, 2341 (1989).

3 T. Kawashima, K. Takai, H. Aso, T. Manabe, K. Takizawa, C. Kachi-Terajima, T. Ishii, H. Miyasaka, H. Matsuzaka, M. Yamashita, H. Okamoto, H. Kitagawa, M. Shiro, and K. Toriumi, *Inorg. Chem.*, **40**, 6651 (2001).

4 M. Yamashita, T. Ishii, H. Matsuzaka, T. Manabe, T. Kawashima, H. Okamoto, H. Kitagawa, T. Mitani, K. Marumoto, and S. Kuroda, *Inorg. Chem.*, **38**, 5124 (1999).

5 T. Manabe, T. Kawashima, T. Ishii, H. Matsuzaka, M. Yamashita, K. Marumoto, H. Tanaka, S. Kuroda, H. Kitagawa, T. Mitani, and H. Okamoto, *Synth. Met.*, **116**, 415 (2001).

6 K. Marumoto, H. Tanaka, S. Kuroda, T. Manabe, and M. Yamashita, *Phys. Rev.*, **B60**, 7699 (1999).

7 N. Kimura, M. Kano, T. Manabe, M. Yamashita, and R. Ikeda, *Synth. Met.*, **120**, 777 (2001).

8 T. Kobayashi, H. Ohki, and R. Ikeda, *Mol. Cryst. Liq. Cryst. Sci. Technol.*, **257**, 279 (1994).

9 R. Ikeda, T. Tamura, and M. Yamashita, *Chem. Phys. Lett.*, **173**, 466 (1990).

10 I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *J. Am. Chem. Soc.*, **93**, 3922 (1971).

11 I. Morishima, K. Okada, and T. Yonezawa, *Chem. Commun.*, **1970**, 1535.

12 S. Takaishi, M. Kano, H. Kitagawa, Y. Furukawa, K. Kumagai, and R. Ikeda, *Chem. Lett.*, **2002**, 856.

13 S. Sachdev, *Phys. Rev.*, **B50**, 13006 (1994).

14 A. Ozawa, N. Kimura, H. Kitagawa, and R. Ikeda, *Synth. Met.*, **135–136**, 419 (2003).