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High-Resolution Solid-State NMR Studies of Natural Abundant ^{15}N Observed in Halogen-Bridged One-Dimensional Complexes, $[NiX(chxn)_2]X_2$ and $[Pd(chxn)_2][PdX_2(chxn)_2]Y_4$ (chxn = (1*R*,2*R*)-Diaminocyclohexane; Y = X (Halogen), NO_3, and ClO_4)

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We performed solid-state NMR measurements of ^{15}N nuclei with a low natural abundance in chxn ligands in halogen-bridged Pd and Ni complexes with a one-dimensional (1-D) structure. Spectra obtained for ^{15}N bonded to Pd^{2+}, Pd^{4+}, and Ni^{3+} were clearly separated from each other, and it was shown that information on electronic and magnetic structures of 1-D chains was obtained more sensitively than from ^{13}C NMR data. A characteristic new result is a marked broadening of the signal from nitrogen bonded to the Pd^{4+} in $[Pd(chxn)_2][PdBr_2(chxn)_2]Br_4$, which is expected to be closely connected with polarons formed on 1-D chains.

Valence structures and electron spin dynamics in halogen-bridged metal complexes have effectively been studied by applying magnetic resonance techniques, i.e., ESR,[1] NMR,[2–4] and NQR[5] using electron and nuclear spins as sensitive probes for the detection of subtle changes of valence electrons and spin magnetism.

As for solid-state NMR studies so far reported, ^1H NMR relaxation measurements have revealed dynamic properties of spin solitons and polarons diffusing along 1-D chains in $[Pd^{II}(chxn)_2][Pd^{IV}Br_2(chxn)_2]Br_4$ (chxn = (1*R*,2*R*)-diaminocyclohexane),[3,4,6] and also the fluctuation of magnetic structure in $[Ni^{III}X(chxn)_2]X_2$ (X = Cl and Br) with strong 1-D antiferromagnetic interactions.[4,7]

On the other hand, the ^{13}C high-resolution NMR spectrum measurement of ligands bonded to metals has provided information of subtle differences in the metal valence structure in various halogen-bridged Pt, Pd, and Ni complexes by observing the ^{13}C chemical-shift in ligands: en, chxn, etc.[2,4] From observed ^{13}C shift values, for example, the spin structure of 1-D chains in Ni–Pd mixed metal complexes, $[Ni_{1-x}Pd_xX(chxn)_2]X_2$ ($0.0 \leq x \leq 1.0$; X = Cl and Br) could be estimated.[8] However, since carbon atoms in the chxn ligand have no direct bonds to metal atoms, ^{13}C data cannot necessarily afford enough information for subtle changes of valence structures on metal atoms occurring in 1-D chains. In fact, although the above Ni–Pd mixed metal complexes gave ^{13}C spectra for α-carbons (carbon next to nitrogen) in chxn ligands bonded to Ni and Pd atoms with different chemical shift values,[8] resolution is not sufficient and spectra overlap. Accordingly, limited discussion on the metal valence structure could not be avoided.

Undoubtedly, the spectrum observation for ^{15}N atoms ($I = 1/2$) directly bonded to metals can afford more reliable information of the metals. However, observation in natural abundance has been difficult work because of the low natural abundance (0.37%) and a small magnetic moment, both being ca. 1/3 of those of ^{13}C. The enrichment of this isotope in the chxn ligand containing two optically active carbon atoms is a costly and time consuming experiment. So far, no ^{15}N NMR studies of chxn ligands in halogen-bridged complexes containing both enriched and natural abundant ^{15}N have been reported. Only ^{15}N measurements for halogen-bridged metal complexes in the natural abundance concentration have been reported for 1,2-diaminoethane (en) complexes by Clark et al.[9,10]

In the present study, we intended to measure natural abundant ^{15}N NMR spectra of the chxn ligand in halogen-bridged complexes in solid state to determine whether the ^{15}N NMR technique is applicable to halogen-bridged complexes, and also if its measurement is useful for obtaining accurate information of the valence structure of metals in these metal complexes.

Experimental

$[NiX(chxn)_2]X_2$[11] and $[Pd(chxn)_2][PdX_2(chxn)_2]Y_4$ (Y = X, NO_3, and ClO_4)[12] were synthesized according to methods reported in the literature.[11,12] Crystals obtained were identified by taking X-ray powder patterns, which were explained well by the reported lattice parameters.[11,12]

^{15}N CP-MAS NMR spectra were recorded at room temperature with fine crystals containing natural abundant ^{15}N using a JEOL ECA-500 spectrometers by applying cross polarization (CP), proton decoupling and magic-angle spinning (MAS). The proton decoupling was performed with a contact time of 2 ms. Sample spinning rates of 3–5 kHz were employed for samples in a holder of 4 mm in diameter with an inner volume of ca. 50 µL. Spectra were obtained by signal averaging of 2000–30000 acquisitions corresponding to 4 to 60 h depending on relaxation times (T_1). ^{15}N shift values were determined with external glycine ($\delta(^{15}NH_2) = -347.6$ from $CH_3{}^{15}NO_2$).

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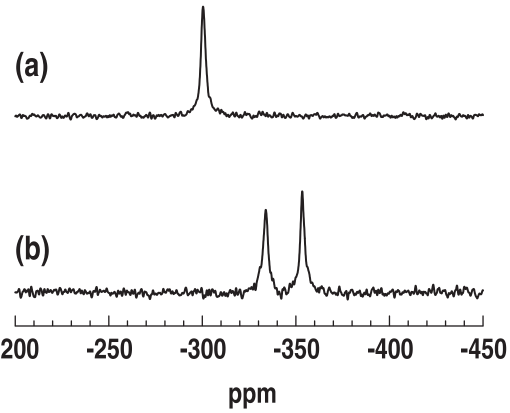

Figure 1. ^{15}N CP-MAS NMR spectra observed at room temperature in (a) [NiCl(chxn)$_2$]Cl$_2$ and (b) [Pd(chxn)$_2$][PdCl$_2$(chxn)$_2$]Cl$_4$.

^{13}C CP-MAS NMR measurements were performed with a Bruker MSL-300 spectrometer at room temperature.

UV–visible–near IR spectra were recorded on a Jasco V-570 spectrometer. ESR spectra were obtained with Bruker EMX-T and Jeol JES-FE1XG spectrometers on powder samples (ca. 0.1 g) under a modulation field of 10 G with a frequency of 100 kHz at room temperature.

Results and Discussion

As examples of present measurements of natural abundant ^{15}N nuclei in solid metal complexes, spectra observed in [NiCl(chxn)$_2$]Cl$_2$ and [Pd(chxn)$_2$][PdCl$_2$(chxn)$_2$]Cl$_4$ are shown in Figures 1a and 1b, respectively. The former was obtained after accumulation of 3000 acquisitions for 4 h, while the latter was with 2300 acquisitions for 16 h because of the long T_1. Both gave us sufficient S/N ratios for analyzing the spectra. These results support our contention that ^{15}N NMR measurement in solid samples with natural-abundance concentration can easily provide useful data for the electronic and magnetic structures in metal complexes containing metal–nitrogen bonds.

The spectrum of the Ni complex exhibited a single resonance line at -300.3 ppm supporting the averaged spin structure of –Cl–Ni^{3+}–Cl–Ni^{3+}–Cl– in good agreement with the reported ^{13}C NMR data.[2] On the other hand, a doublet clearly separated by 19.7 ppm observed in the ^{15}N spectrum for [Pd(chxn)$_2$][PdCl$_2$(chxn)$_2$]Cl$_4$ was attributed to nitrogen atoms in Pd^{2+} and Pd^{4+} moieties in the Pd complex. This resolution was not complete in the ^{13}C spectra at the α-position in a cyclohexane ring in the ligand.[8]

^{15}N NMR spectra of [Pd(chxn)$_2$][PdBr$_2$(chxn)$_2$]Y$_4$ (Y = Br, NO$_3$, and ClO$_4$) are shown in Figure 2. Each ^{15}N resonance line in the complexes is split into a doublet consisting of a sharp and a broad line. These splittings are expected to be explicable by considering that two kinds of nitrogen atoms coordinated to the Pd^{2+} and Pd^{4+} atoms are placed in slightly different electronic environments, as given above.

In ^{13}C NMR spectra of [Pd(chxn)$_2$][PdBr$_2$(chxn)$_2$]Y$_4$ (Y = Br, NO$_3$, and ClO$_4$) shown in Figure 3, the obtained splitting widths at α-carbons for Y = NO$_3$ and ClO$_4$ were estimated to be ca. 2 and 3 ppm, respectively, in the present study, but we could not resolve the α-carbon signals in [Pd(chxn)$_2$][PdBr$_2$(chxn)$_2$]Br$_4$[8] because the ^{13}C signals for Pd^{2+} and Pd^{4+} sites were broadened and overlapped with each other. These results mean that the chemical shift measurement of the ^{15}N NMR probe is more sensitive than that of the ^{13}C NMR for distinguishing Pd^{2+} from Pd^{4+} and to determine the metal valence state in the chain.

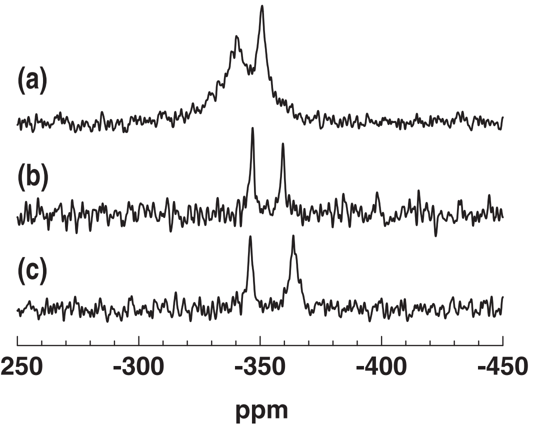

Figure 2. ^{15}N CP-MAS NMR spectra observed in [Pd(chxn)$_2$][PdBr$_2$(chxn)$_2$]Y$_4$ (Y = (a) Br, (b) NO$_3$, and (c) ClO$_4$).

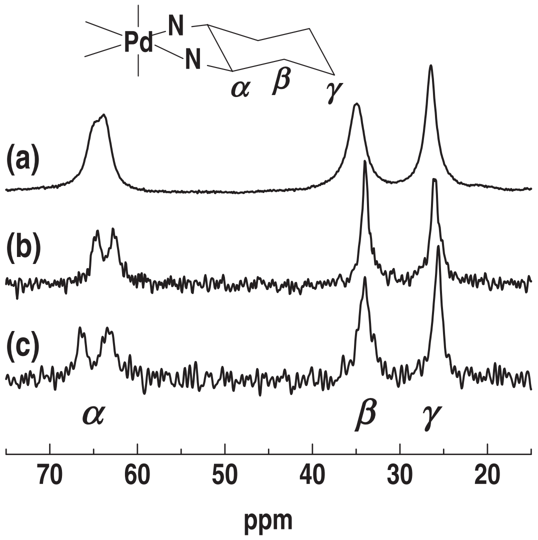

Figure 3. ^{13}C CP-MAS NMR spectra observed in [Pd(chxn)$_2$][PdBr$_2$(chxn)$_2$]Y$_4$ (Y = (a) Br, (b) NO$_3$, and (c) ClO$_4$). α, β, and γ denote carbon positions in a cyclohexane ring.

Powder ESR spectra observed at room temperature in [NiBr(chxn)$_2$]Br$_2$ and [Pd(chxn)$_2$][PdBr$_2$(chxn)$_2$]Y$_4$ (Y = Br and NO$_3$) are shown in Figure 4. The strong and broad signal observed in [NiBr(chxn)$_2$]Br$_2$ is attributable to unpaired electron spins in Ni^{3+} with a strong antiferromagnetic interaction between neighboring sites in 1-D chins.[13] On the other hand, the spectrum for the Pd complex with Y = Br showed a weak but sharp signal. This signal can be ascribed to the thermally activated paramagnetic Pd^{3+} sites on the chain by referring to the reported data.[12,13] These paramagnetic spins with a concentration of ca. 10^{-3} per Pd site have been shown to

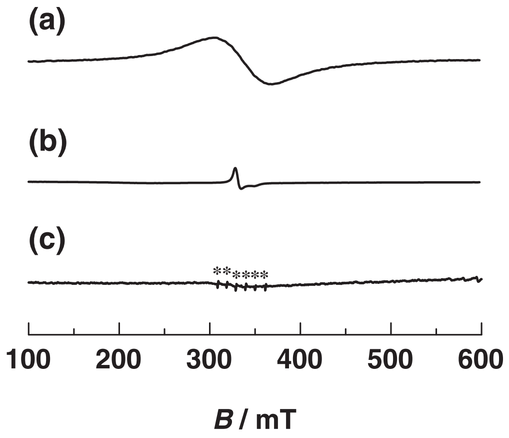

Figure 4. Powder ESR spectra observed at room temperature in (a) $[NiBr(chxn)_2]Br_2$, (b) $[Pd(chxn)_2][PdBr_2(chxn)_2]Br_4$, and (c) $[Pd(chxn)_2][PdBr_2(chxn)_2](NO_3)_4$. Lines with asterisks are marker signals from doped Mn^{2+} in MgO.

form spin solitons and polarons as studied by the relaxation in ^{1}H NMR.[4,6] For $Y = NO_3$ however, ESR behavior was quite different from the Br salt and almost no signal was observed. This fact suggests that paramagnetic Pd^{3+} sites in Y = Br can be formed more easily than those in $Y = NO_3$. It is expected that the characteristic differences in these ESR spectra seem to relate with the broadened ^{15}N NMR spectrum and shift to low field in Y = Br compared with NO_3 as shown in Figure 2.

The ^{15}N spectrum of the monomer complex, $[Pd(chxn)_2]Br_2$, containing only Pd^{2+} atoms is shown in Figure 5a. The deconvoluted curves of ^{15}N and ^{13}C NMR spectra in $[Pd(chxn)_2][PdBr_2(chxn)_2]Br_4$ by assuming the presence of two components in both nuclei, and the Lorentzian-type line shape are shown in Figures 5b and 5c, respectively. This separation seems to be acceptable because the presence of a broad and a sharp peak is consistent for both nuclei. In this separation of ^{15}N spectra, one may expect a broad component in the noise level of the high field range. This might show a possibility for the presence of a quite broad component attributable to effects from low concentrations of paramagnetic spins forming solitons and polarons. Using results of this separation, we determined ^{15}N chemical-shift and peak-separation values as shown in Table 1. The absolute values of splitting widths of doublet lines were in the order of magnitude $Br < NO_3 < ClO_4$.

In Figure 5a, the doublet observed at −358.4 and −356.0 ppm with a splitting of 2.4 ppm in $[Pd(chxn)_2]Br_2$ is assignable to two kinds of N atoms placed in slightly different crystal fields by referring to previous ^{13}C NMR data.[2,4] Since the averaged shift value (−357.2 ppm) is close to the low value −350.5 ppm observed in the mixed-valence complex $[Pd(chxn)_2][PdBr_2(chxn)_2]Br_4$ shown in Figure 5b, the low and high shift lines at −340.5 and −350.5 ppm, respectively, can be assigned to ^{15}N coordinated to Pd^{4+} and Pd^{2+} sites, respectively.

Electronic spectra observed in $[Pd(chxn)_2][PdBr_2(chxn)_2]Y_4$ are shown in Figure 6. Strong bands observed around 1–2 eV are assignable to the charge transfer (CT) from Pd^{2+} to Pd^{4+}

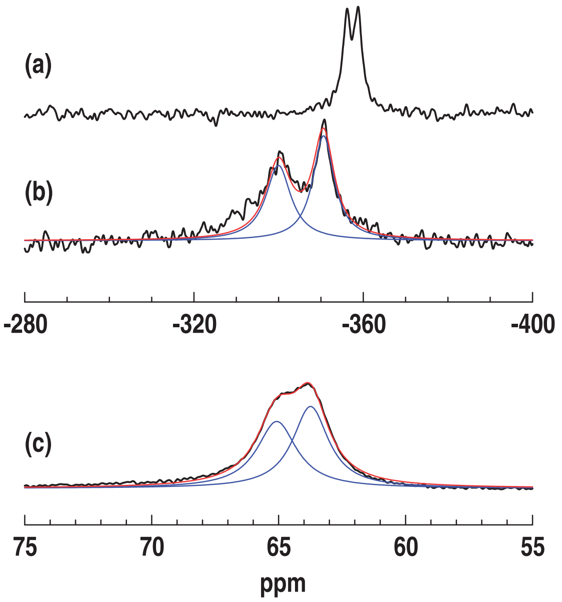

Figure 5. ^{15}N CP-MAS NMR spectra observed in (a) $[Pd(chxn)_2]Br_2$ and (b) $[Pd(chxn)_2][PdBr_2(chxn)_2]Br_4$, and ^{13}C NMR spectrum for α-carbon observed in (c) $[Pd(chxn)_2][PdBr_2(chxn)_2]Br_4$. The spectra of (b) and (c) reproduced from in Figures 2 and 3, respectively. Solid lines (red) indicate the best-fitted calculated values, and blue lines are two components corresponding to Pd^{2+} and Pd^{4+} sites.

Table 1. Solid-State ^{15}N Chemical Shifts (δ) in Bromo-Bridged 1-D Palladium Complexes, $[Pd(chxn)_2][PdBr_2(chxn)_2]Y_4$ ($Y = Br, NO_3$, and ClO_4)

Compound	$\delta(^{15}N)$ ($\Delta\delta^{a)}$)
$[Pd(chxn)_2][PdBr_2(chxn)_2]Br_4$	−350.5, −340.5 (10.0)
$[Pd(chxn)_2][PdBr_2(chxn)_2](NO_3)_4$	−359.4, −346.8 (12.6)
$[Pd(chxn)_2][PdBr_2(chxn)_2](ClO_4)_4$	−363.9, −346.0 (17.9)

a) Splitting widths of doublet lines.

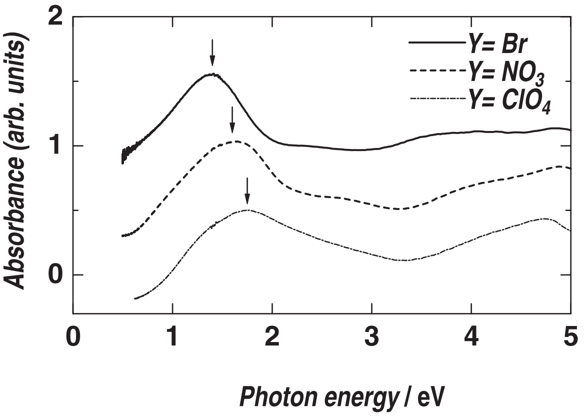

Figure 6. Electronic spectra of $[Pd(chxn)_2][PdBr_2(chxn)_2]Y_4$ observed in powder samples. Arrows show peak values of charge-transfer bands.

Table 2. M^{II}–X and M^{IV}–X (M = Pd and Pt; X = Cl and Br) Distances/pm in Halogen-Bridged 1-D Metal Complexes Determined by X-ray Diffraction

Compound	M^{II}–X	M^{IV}–X	Ref.
$[Pd(en)_2][PdCl_2(en)_2](ClO_4)_4$	303.3	232.4	15
$[Pd(en)_2][PdBr_2(en)_2](ClO_4)_4$	291.1	249.6	16
$[Pd(chxn)_2][PdBr_2(chxn)_2]Br_4$	278.2	252.1	17
$[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$	310.1	232.7	18
$[Pt(en)_2][PtBr_2(en)_2](ClO_4)_4$	300.1	248.4	18
$[Pt(chxn)_2][PtCl_2(chxn)_2]Cl_4$	283.4	232.4	19, 20
$[Pt(chxn)_2][PtCl_2(chxn)_2](ClO_4)_4$	339.6	231.5	20
$[Pt(chxn)_2][PtBr_2(chxn)_2]Br_4$	288.4	249.8	17

effected by the interaction between Pd^{2+} and Pd^{4+} through bridged halogen atoms;[13] the order of the band peak position is the same as the splitting widths given above. The observed CT excitation energies are believed to originate from the distortion of the bridging halogen atom from the midpoint between the neighboring two Pd atoms,[13] and this result is consistent with the single-crystal X-ray diffraction data.[14] The ^{15}N NMR result is also supported by consideration of differences in the electron overlap between the Pd^{2+} and Pd^{4+} $4d_{z^2}$ orbitals through the halogen p_z orbital.

In addition to the above assignment, we note X-ray studies[13,15–20] in which the M^{2+}–X distances are influenced by counter ions and ligands more markedly than the M^{4+}–X distances. In Table 2, M^{2+}–X and M^{4+}–X (M: Pd and Pt; X: Cl and Br) distances reported for 1D halogen-bridged metal complexes with en and chxn ligands are shown, where M^{2+}–X distances longer than those in M^{4+}–X imply that the M^{2+}–X bonds are more ionic, i.e., less covalent. These data clearly show that the M^{2+}–X distances are sensitive to ligands and counter ions much more than the M^{4+}–X distances.

These X-ray results[13,15–20] indicate that the electronic states in the M^{2+} sites are influenced by their circumstances much more than in M^{4+} sites because the M–X distances depend on the slight change of electronic states in the metal ions. The difference of these electronic states seems to be ascribed to the electron concentration on the metal ions, and the M^{2+} sites with more electrons can strongly couple with counter ions and ligands.

Accordingly, we can expect by changing counter ions that the ^{15}N NMR lines for Pd^{2+} sites show the shift values spread more than that for Pd^{4+} sites. In fact, obvious differences were seen in the lower shift values observed in Y = Br, NO_3, and ClO_4, as shown in Table 1. This result also supports that the lower shift line at −350.5 ppm in Y = Br is assignable to the Pd^{2+} moiety.

The spectrum in Figure 5b shows two characteristic features compared with those in other mixed-valence Pd complexes, $[Pd(chxn)_2][PdBr_2(chxn)_2]Y_4$ (Y = ClO_4 and NO_3) given in Figure 2. One is that their averaged shift value in Y = Br is moved to lower field than in Y = ClO_4 and NO_3. The other is that the spectrum from ^{15}N coordinated to Pd^{4+} is much broader than that to Pd^{2+} as well as those in the other salts (Y = ClO_4 and NO_3) as shown in the results of the decomposition in Figure 5b.

As described above, since only the salt (Y = Br) among $[Pd(chxn)_2][PdBr_2(chxn)_2]Y_4$ (Y = Br, ClO_4, and NO_3) contains paramagnetic Pd^{3+} sites detectable by ESR, the observed characteristic spectra in Y = Br are expected to be related to effects from the paramagnetic spins.

It has been shown[6,13] that Pd^{3+} sites formed with a low concentration of 10^{-3} rapidly diffuse along the 1-D chains by forming neutral solitons and polarons. According to this model, all Pd ions in crystals feel an averaged magnetic field made by diffusing Pd^{3+} sites, and hence, this field can cause a low field shift of ^{15}N NMR lines.

The marked spectrum broadening at Pd^{4+} sites seems to be connected with the fluctuation of the unpaired electron spins on a small number of Pd^{3+} sites, but the reason why only one of two lines is remarkably influenced is not clearly understood at the present stage. One possible explanation is the effect from polarons formed along the –Pd^{2+}–Br–Pd^{4+}–Br– chain as schematically expressed as –Pd(2)–Pd(4)–Pd(3)–Pd(4)–Pd(2)– giving the chain a positive charge as well as a paramagnetic spin.[4] The formation of this quasi-particle was shown by the measurements of electronic spectra,[21] and ^{1}H NMR relaxation times.[4] The electrical conductivity[4,6] of this complex is much higher than those of other halogen-bridged chxn complexes[14] and also supports the occurrence of 1-D diffusion of polarons.[4,6] Although a polaron is expected to be delocalized over several metal sites,[4,6] applying the simple valence model given above, it can be shown that both sides of the paramagnetic Pd^{3+} are always Pd^{4+} sites even if the polaron diffuses along the chain. This model implies that Pd^{4+} sites receive effects from the paramagnetic spins more sensitively than Pd^{2+} sites, explainable by the broadened signal for ^{15}N bonded to Pd^{4+}. The ^{13}C NMR spectrum given in Figure 5c also shows that the low shift line is clearly broadened.

The above explanation which we showed only as a possible mechanism related to paramagnetic spins formed on the 1-D chain in $[Pd(chxn)_2][PdBr_2(chxn)_2]Br_4$, and contributions from other states containing paramagnetic spins cannot be ignored. More detailed discussion of this mechanism needs theoretical calculations on the electronic and magnetic structures of Pd^{3+} sites in the 1-D chain.

Summary

In the present study, it was shown that the natural abundant ^{15}N NMR measurement in solids can be performed without difficulties by applying conventional solid-state NMR techniques for halogen-bridged 1-D metal complexes with a low ^{15}N concentration in chxn ligands. The observed ^{15}N spectra provided more useful data for the electronic and magnetic structures in metal complexes than ^{13}C NMR spectra. Especially, the ^{15}N spectra for $[Pd(chxn)_2][PdBr_2(chxn)_2]Br_4$ clearly showed a doublet line assignable to Pd^{2+} and Pd^{4+}, while the ^{13}C signal could not be completely resolved. Moreover, the marked broadening of the Pd^{4+} signal observed in $[Pd(chxn)_2][PdBr_2(chxn)_2]Br_4$, which can be explained by the effect from paramagnetic spins such as in polarons, is the first report of the halogen-bridged mixed-valence system and is expected to give information on the behavior of paramagnetic spins formed along the 1D chain.

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