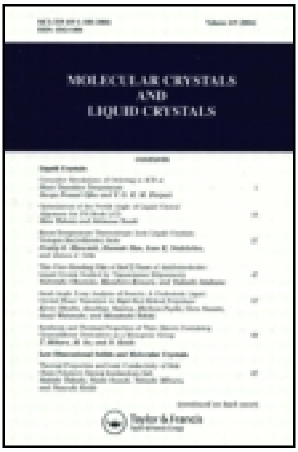

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Spin Polarization in Infinite Zigzag Chains of $[Rh_2(HNCOCH_3)_4Cl]_n$

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A temperature dependence of ^{13}C CPMAS NMR was measured for revealing the local electron spin structure in $[Rh_2(acam)_4Cl]_n$ (Hacam=acetamide). Observed two sharp peaks were assigned to carbons of crystallographycally nonequivalent CH_3 groups and a broad one to C in the C=O group. A large high-field shift of -125 ppm was observed in C (C=O), indicating a negative spin polarization on this carbon. From the temperature dependence of Fermi contact shifts, the hyperfine coupling constant of each carbon was determined. By considering hyperfine coupling constants, it is found that a marked amount of electron spins are distributed on C (C=O) with the negative polarization, and a small positive spin exists even on the terminal carbons in methyl groups. ^1H MAS NMR spectra can be explained by the superposition of different shift lines, implying that spin polarization is also generated on hydrogen atoms.

Keywords: Rhodium complex; Acetamidato complex; Dinuclear complex; Electron spin polarization; ^{13}C CPMAS NMR; Hyperfine coupling constant

INTRODUCTION

Halide bridged tetrakis(acetamidato)dirhodium cation radicals

$[Rh_2(HNCOCH_3)_4X]_n$ (X=Cl, Br, I) have a 1D zigzag chain structure supported by hydrogen bonds between ligands in neighboring dimers as illustrated in Figure 1[1]. These complexes have unique features: (1)an odd spin exists on a Rh_2^{5+} unit dimer, and SOMO (singly occupied molecular orbital) is supposed to be the $d_{\delta*}$ molecular orbital in a metal dimer[1], (2) the zigzag alignment of dimers gives rise to an overlap between SOMO's[2], (3) the $d_{\delta*}$ SOMO is symmetry-allowed to delocalize onto the π system of the bridging ligand[2]. By comparison with 1D metal complexes with local d_σ HOMO, it can be presumed that interdimer magnetic interaction is small, in other words, variable by a slight change of their chain structures. It is also likely that the distribution of electron spin on the ligands is relatively large. From these reasons, their magnetic property is expected to be sensitively changed with temperature, and governed not only by the metal-metal interactions but also by the interaction through ligands.

In this study, to understand the structure of electronic spin in these rhodium complexes in detail, the distribution of electron spin on the ligand were investigated by the measurements of temperature dependence of ^{13}C CPMAS NMR and ^{1}H MAS NMR spectra in $[Rh_2(HNCOCH_3)_4Cl]_n$.

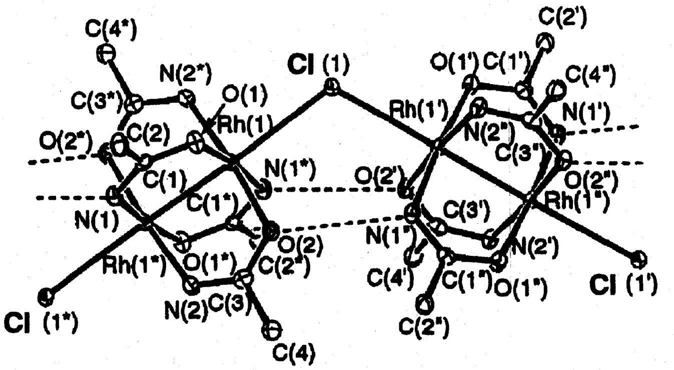

FIGURE 1 Zigzag chain structure in $[Rh_2(HNCOCH_3)_4Cl]_n$[1].

EXPERIMENTAL

$[Rh_2(HNCOCH_3)_4Cl]_n$ was obtained by the method previously reported[1]. The ^{13}C CPMAS NMR spectra were measured at 75.6 MHz with a BRUKER MSL 300 NMR spectrometer with a $\pi/2$ pulse of 5 μs long and a contact time of 1 ms. The magic angle spinning rate was set between 5 and 7 kHz in a temperature range 175-330 K. ^1H NMR spectrum was measured in the same NMR system as mentioned above at a frequency of 300.13 MHz with a spinning rate of 6 kHz at 300 K.

RESULTS AND DISCUSSION

^{13}C CPMAS NMR Spectrum

A temperature dependence of ^{13}C CPMAS NMR spectra is shown in Figure 2. In the spectrum at 300 K, two relatively sharp and a broad peaks were observed. Two sharp peaks observed at 91 and 46 ppm are attributed to two crystallographically nonequivalent methyl groups in the ligand, but one-to-one correspondence between them cannot be determined at present stage. The broad peak of -125 ppm can be attributed to the carbon in C=O group, which is located close to Rh. The broad width comes from the effect of much fast paramagnetic relaxation of an electron spin on the Rh dimer. The most remarkable result is that a quite large high-field shift of -125 ppm was observed in the C=O carbon. This value differs by several hundred ppm from the common shift of +200 ppm in diamagnetic compounds. From the comparison of electronic structures with various dirhodium complexes,

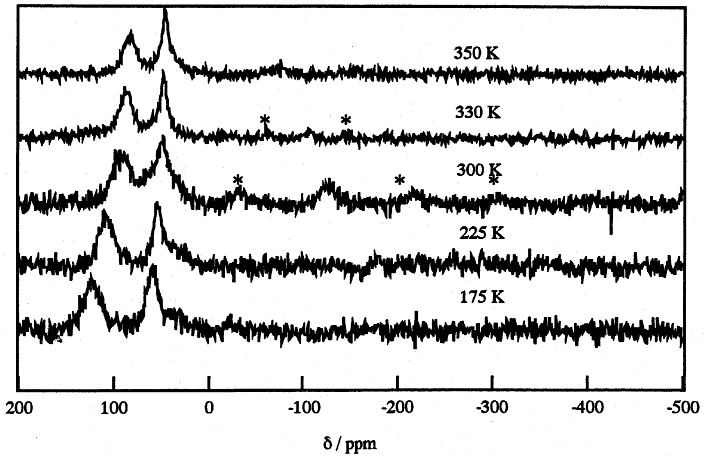

FIGURE 2 Temperature dependence of ^{13}C CPMAS NMR spectrum. The peaks marked with * are spinning side bands.

it was proposed that the matal-ligand bond contains π overlap between the Rh d_{δ^*} and the ligand p_π orbitals[1]. Taking into consideration of these facts mentioned above, it is likely that a considerable amount of electron spins is distributed on the C (C=O), and its spin is negatively polarized.

The observed shifts δ is descried by a sum of the temperature-dependent Fermi contact δ_{Fermi}[3] and pseudo contact δ_{pseudo} shift[4], and temperature independent diamagnetic shift δ_{dia} ;

$$\delta = \delta_{\mathrm{Fermi}} + \delta_{\mathrm{pseudo}} + \delta_{\mathrm{dia}} ,$$

$$\delta_{\mathrm{Fermi}} = \frac{g_{\mathrm{iso}}\mu_{\mathrm{B}}}{\gamma/2\pi} \cdot \frac{A}{3k_{\mathrm{B}}T},$$

$$\delta_{\mathrm{pseudo}} = (g_{\mathrm{para}}^2 - g_{\mathrm{perp}}^2)\frac{\mu_{\mathrm{B}}^2}{12kT} \cdot (3\cos^2\theta - 1)/r^3,$$

where A and γ are the hyperfine coupling constant and the gyromagnetic ratio of ^{13}C, g_{para}, g_{perp}, and g_{iso} are parallel, perpendicular, and isotropic value of g-tensor. The magnitude of A is directly related to the spin polarization. At first, δ_{pseudo} shifts of respective ^{13}C were determined by the method reported in [3]. In this estimation, experimentally determined g_{para} and g_{perp} in the frozen solution of $[\mathrm{Rh_2(acam)_4Cl_2}]^{-\cdot}$ were used[1]. Then, $\delta_{\mathrm{Fermi}} + \delta_{\mathrm{dia}}$ values were obtained by subtracting δ_{pseudo} from δ, and $\delta_{\mathrm{Fermi}} + \delta_{\mathrm{dia}}$ values were plotted versus reciprocal temperature in Figure 3. Here, one peak of methyl carbon with a higher shift than the other was related to the carbon with larger

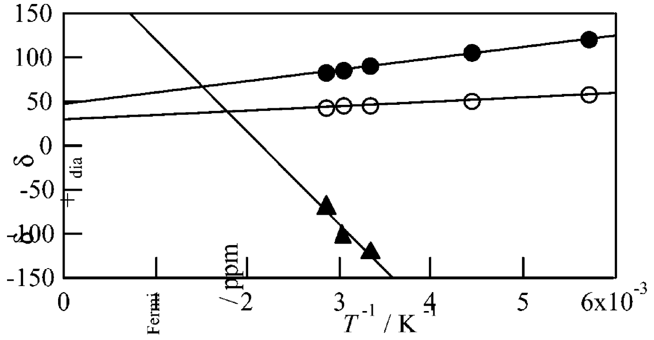

FIGURE 3 Temperature dependencies of Fermi contact shifts of the peaks assigned to carbons in CH$_3$ (● ,○) and C=O (▲). The solid lines are fitted by $\delta_{\mathrm{Fermi}} \propto T^{1}$.

δ_{pseudo} value, and the average δ_{pseudo} value for two kinds of C (C=O) was used as δ_{pseudo} for C (C=O). The δ_{Fermi} values of carbons (CH_3) increased linearly with T^{-1}, while that of C (C=O) decreased, implying that spin polarization on C (CH_3) is positive, on the other hand, that on C (C=O) is negative. The negative and rather small value of *A* of the C atom (C=O) is consistent with the model that the odd electron on d_{δ^*} is delocalized onto the HOMO of the acam ligand. Finally, *A* and δ_{dia} values were determined from the slopes and the *y* intercepts of δ_{fermi} variations, respectively. Obtained values are tabulated in Table 1. The presumed spin polarization on the ligands is given in Figure 4.

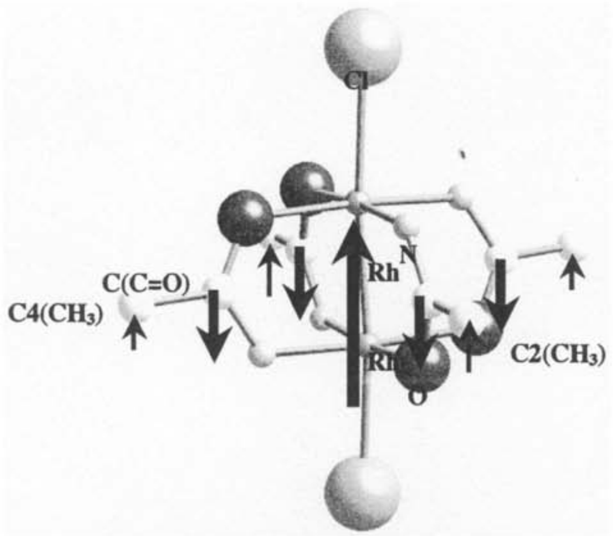

FIGURE 4 Spin polarization presumed from hyperfine coupling constants.

TABLE 1 Hyperfine coupling constants (*A*) , and diamagnetic shifts (δ_{dia}). C2 and C4 follow the notation in Figure 1.

	A / MHz	δ_{dia} / ppm
C2 (CH_3)	0.41	45
C4 (CH_3)	0.15	29
C (C=O)	-3.2	220

The estimated d_{dia} values are in the common range of values reported in diamagnetic compounds.

^{1}H MAS NMR Spectrum

A ^{1}H MAS NMR spectrum observed at 300 K is shown in Figure 5. The spectral shape is asymmetric and expanding to the high-field, indicating that there is several kinds of ^{1}H with different shift. This result implies the presence of spin polarization on hydrogen atoms.

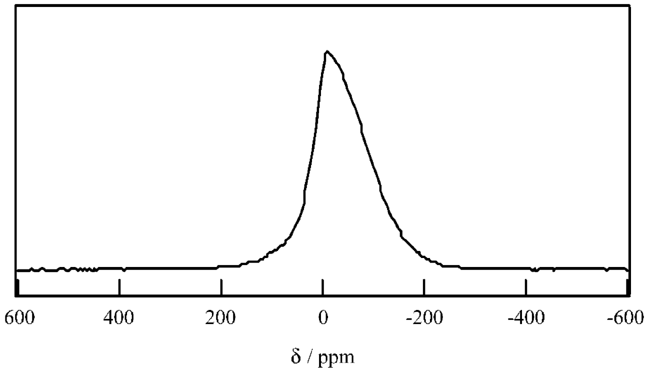

FIGURE 5 ^{1}H MAS NMR spectrum at 300 K.

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References

[1.] Z. Yang, M. Ebihara, T. Kawamura, T. Okubo, and T. Mitani, *Inorg. Chim. Acta*, **321**, 97(2001).

[2.] T. Kawamura, H. Katayama, N. Nishikawa, T. Yamabe, *J. Am. Chem. Soc.*, **111**, 8156(1989).

[3.] T. Kawamura, H. Kachi, H. Fujii, C. Kachi-terajima, Y. Kawamura, N. Kanematsu, N. Ebihara, K. Sugimoto, T. Kuroda-Sowa, and M. Munakata, *Bull. Chem. Soc. Jpn.*, **73**, 657(2000).

[4.] G. Maruta, S. Takeda, R. Imachi, T. Ishida, T. Nogami, and K. Yamaguchi, *J. Am. Chem. Soc.*, **121**, 424(1999).