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A ^{1}H NMR Study on the Electronic State of a Chloride-bridged Tetrakis(acetamidato)dirhodium Complex

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A temperature dependence of ^{1}H NMR spin-lattice relaxation time in a zig-zag chain of chloride-bridged tetrakis(acetamidato)dirhodium was measured. The observed ^{1}H relaxation was well explained by the fluctuation of the magnetic dipolar interaction between proton and paramagnetic electron spins, where each unpaired spin is coupled by the one-dimensional antiferromagnetic interaction above 35 K. The slight change of the electronic state in the Rh dimer was observed below 35 K.

Halide-bridged one-dimensional (1-D) chains of binuclear-metal complexes (MMX chains) composed of metal dimers such as Ni_2, Pd_2, Pt_2, show various kinds of electronic states. According to the ordering of charges and spins, four kinds of electronic states are proposed, e.g., the averaged-valence state, the charge-density-wave (CDW) state, the charge-polarization state, and the alternate charge-polarization state.[1]

Recently, 1-D chains of halide-bridged Rh_2 complexes $[Rh_2(acam)_4X]_n$ (Hacam = acetamide, X = Cl, Br, and I) have been synthesized.[2] Rh_2 units are connected by a halide ion and arranged to a zig-zag structure, as shown in Figure 1. The fact that a crystallographically unique Rh atom can be seen in the crystal structure at 193 K[2] suggests that $Rh_2{}^{5+}$ units are in an averaged-valence state at high temperatures, i.e., the unpaired spin is delocalized in a dimer, and each Rh seems to have the same charge of +2.5. Moreover, the unpaired spin is found to be in the $\delta^*{}_{RhRh}$ SOMO orbital in the Rh_2 complexes,[2,3] while the HOMO is the σ_{MM} orbital in other MMX chains of Ni_2, Pd_2, and Pt_2. Therefore, the 1-D electronic state of Rh_2 complexes is expected to show unique characteristics in the charge ordering and spin–spin interactions due to some differences of a symmetry of the SOMO orbital and the structure of the Rh_2 complex from those of other MMX complexes.

In the present study, we measured the ^{1}H NMR spin–lattice relaxation time to reveal the 1-D spin structure in the zig-zag chain of the chloride-bridged Rh_2 complex.

The 1-D chain of chloride-bridged tetrakis(acetamidato)dirhodium was prepared according to the literature.[2] The temperature dependence of ^{1}H NMR spin–lattice relaxation time (T_1) was measured with a homemade apparatus[4] using the π-τ-$\pi/2$ pulse sequence in the temperature region of 4–300 K. A Larmor frequency of 53.1 MHz was employed. The sample temperature was controlled by a Chino SU10-2121LNN temperature controller and measured with a chromel-constantan thermocouple within ±1 K.

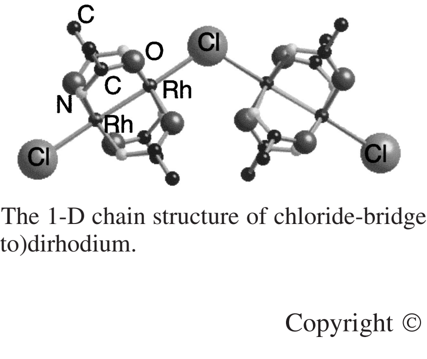

Figure 1. The 1-D chain structure of chloride-bridged tetrakis-(acetamidato)dirhodium.

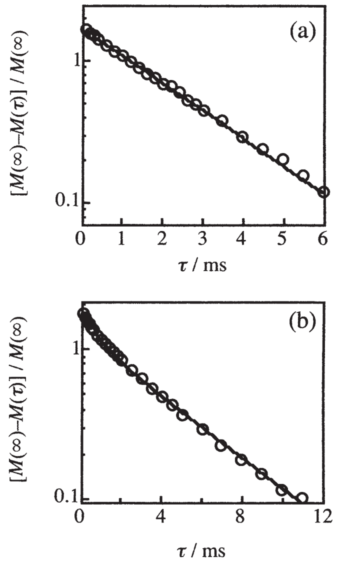

Figure 2. The ^{1}H NMR magnetization recoveries at a delay time τ after $\pi/2$ pulse at 200 K (a) and 30 K (b). Fitted curves are shown by solid lines.

^{1}H magnetization recoveries after a $\pi/2$ pulse are shown in Figure 2. The recovery above 35 K could be fitted with a single exponential curve as shown in Figure 2a, indicating that all protons are relaxed through a single process. On the other hand, a rapidly relaxing portion became distinguishable below 35 K, and the recovery curve was reproduced with a superposition of two kinds of single exponential curves as shown in Figure 2b. The existence of two T_1 components suggests two kinds of protons under different circumstance. Below 12 K, the recovery could not be fitted with a double-exponential curve.

The temperature dependence of ^{1}H NMR T_1 was plotted in Figure 3. The constant T_1 value of 3 ± 1 ms was obtained in the temperature region of 35–300 K. From the previous report,[2] the temperature dependence of the magnetic susceptibility for this complex could be expressed by the antiferromagnetic 1-D Heisenberg model with $J = -4.3$ K ($\mathcal{H} = -2J\Sigma S_i S_{i+1}$). According to this spin structure, we assume that the ^{1}H relaxation in this temperature range is caused by a fluctuation of the magnetic dipolar interaction between proton and paramagnetic electron spins. If conditions of $\omega_I\tau_c \ll 1$ and $\omega_S\tau_c \ll 1$ are fulfilled where ω_I and ω_S are nuclear and electronic angular Larmor fre-

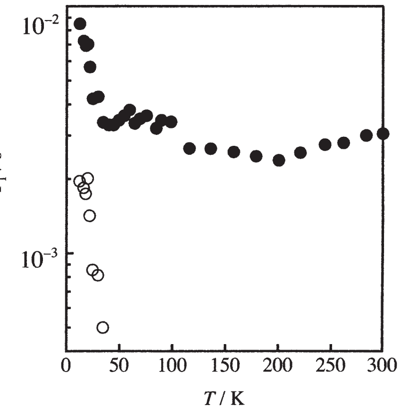

Figure 3. The temperature dependence of ^{1}H spin–lattice relaxation time (T_1) measured at 53.1 MHz. Long and short T_1 components are shown as ● and ○, respectively.

quencies, respectively, and τ_c is the electron spin correlation time, T_1 can be expressed as[5]

$$T_1^{-1} \approx \sum_i \frac{20}{15} \frac{\gamma_I^2 g^2 \mu_B^2 S(S+1)}{r_i^6} \tau_c \tag{1}$$

where γ_I, g, μ_B, S, and r_i are the gyromagnetic ratio of a proton, the g factor, the Bohr magneton, the effective electron spin and the distance from a paramagnetic electron to a proton, respectively. τ_c is given by

$$\tau_c^{-1} = T_{1e}^{-1} + \tau_f^{-1} \tag{2}$$

where T_{1e} and τ_f denote the electron spin–lattice relaxation time and the correlation time for electron spin flips, respectively. Since T_{1e} is generally temperature dependent, while τ_f is independent, we can approximately write $\tau_c = \tau_f$ above 35 K, because almost temperature independent T_1 values were obtained in this range. According to Moriya,[6] the electron spin exchange frequency ω_{ex} is expressed as

$$\omega_{ex}^2 = \frac{2}{3} \frac{J^2}{\hbar^2} zS(S+1) \tag{3}$$

and

$$\omega_{ex}^2 = \frac{\pi}{2\tau_f^2} \tag{4}$$

where z is the number of the nearest neighbors of a paramagnetic spin; in this 1-D system, $z = 2$. Since the right-hand side except τ_c in Eq 1 can be calculated by using crystal data,[2] we can get a relation between ^{1}H T_1 and J values. We assume that the spin density is a half on each Rh, and two protonic sites at NH and CH_3 groups in ligands afford the same averaged T_1 value because almost a single T_1 was determined above ca. 35 K. By using $J = -4.3$ K estimated for this complex, T_1 value was calculated to be 4 ms in good agreement with observed T_1 above 35 K. This result indicates that the antiferromagnetic 1-D spin structure in this complex mainly governs the ^{1}H relaxation.

Below 35 K, both long and short T_1 values increased upon cooling. The T_1 increases suggest that the exchange interaction becomes comparable to the thermal energy in this temperature range and the short-range ordering of antiferromagnetically coupled spins takes place.

The presence of two T_1 components and the short T_1 value less than ca. 4 ms, however, cannot be explained by the magnetic dipolar interaction in the averaged-valence state of the Rh dimer. In ESR measurement, we recently observed unusual change in the spectral line-width below ca. 50 K. The ESR spectrum at room temperature showed a broad single-line with a peak-to-peak line-width of 122 ± 2 mT. With reducing temperature, the line-width was decreased, and a spectral structure with an anisotropic g factor was observed below ca. 120 K.[2] On the other hand, the spectrum was broadened, and its structure was disappeared below 50 K. At 28 ± 1 K, the single-line with the peak-to-peak width of 50 ± 2 mT was obtained. Below 28 K, the spectra became to be sharpened again. The line broadening observed below 50 K is probably attributed to rapid electronic relaxation due to spin fluctuation for some reconstruction of electronic state in the zig-zag chain, which was also observed by ^{1}H NMR. The detailed analysis of ESR spectra is currently under way.

Since no marked change in the magnetic susceptibility was reported below 50 K,[2] the antiferromagnetic 1-D spin structure itself seems to be maintained, it can be said that local electronic state in the Rh dimer was slightly changed in this temperature range. Detailed studies on the 1-D electronic structure below 50 K are in progress.

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