NMR study on Ru-based quantum spin systems of [Ru(acac)₃] and [{Ru(acac)₂}₂(μ-OEt)₂]

S. Nakajima, M. Masuko, A. Oosawa, T. Goto, T. Hashimoto, A. Endo, and T. Hayashita

Faculty of Science and Technology, Sophia University
7-1 Kioicho Chiyodaku Tokyo 102-8554 Japan

E-mail: gotoo-t@sophia.ac.jp

Abstract. Tris(β-diketonato)ruthenium(III) complexes of mononuclear [Ru(acac)₃] and binuclear [{Ru(acac)₂}₂(μ-OEt)₂] are spin-1/2 quantum spin magnets. In both systems, Ru and surrounding O₆ atoms consist of octahedral geometry, and in the binuclear complex, two (acetylacetonato) ruthenium complexes are bridged by two oxygen atoms of ethoxyl groups, making up a dimer with Ru-Ru bond. The electronic state of ruthenium is easily controlled by changing the methyl groups on the acetylacetonate to the different substituents such as electronegative trifluoromethyl group. We expect to introduce a new degree of freedom, a charge fluctuation into the dimer spin system. In this study, we investigate the spin state of monomer and dimer quantum spin systems by means of ¹³C,¹⁹F,¹⁰¹Ru-NMR at low temperatures. In the former [Ru(acac)₃], we observed Curie-like temperature dependence in the Knight shift down to 1.5 K, indicating that the system was simply in the paramagnetic state. The dimer system [{Ru(acac)₂}₂(μ-OEt)₂] on the other hand showed the NMR signal with very long T₁ at zero shift position at low temperatures, indicating that the system was the spin singlet state. In order to investigate the effect of substitution, we also report on results of mer-[Ru(ehfa)₃] and [Ru(fhea)₃], for which methyl groups are substituted by trifluoromethyl groups.

1. Introduction
In the studies of quantum spin dimer systems reported so far, most interest is concentrated on destroying the singlet ground state by applying an external magnetic field[1], a high pressure[2-3], or substituting non-magnetic impurity[4-7]. These perturbations, by inducing triplet sites or creating unpaired spins, lead the system to the magnetic state, which undergoes a phase transition at low temperatures with an assist of inter-dimer interactions. In particular, a field-induced long range magnetic order is known as the magnon Bose-Einstein condensation (BEC) [8].

We introduce into the dimer system a new degree of freedom, a valence fluctuation. By tuning valence of each atom to be fractional value, we expect the wave function of the dimer to be a superposition of the two states in which an extra electron is located at an either atom, and to bear a possibility of an exotic ground state. As a candidate of valence fluctuating dimer, we have chosen as a kernel atom Ru, which is stable in various valence state 2, 3 and 4. In order to realize a valence fluctuating dimer compound in the solid state form which is stable in atmosphere of air, we have adopted a method developed by one of our the present authors A. E.[9] to substitute methyl groups on the acetylacetone with more electronegative one such as trifluoromethyl group. This method allows one to adjust the potential surrounding Ru ions by changing the number of substituent group in six...
methyl groups in a dimer so as to obtain a fractional valence state without making a solid solution between hetero-valent ions.

In this preliminary report we demonstrate by NMR technique the variation of magnetism in synthesized five compounds of tris(β-diketonato)ruthenium(III) complexes of monomer systems [Ru(acac)₃] and those with different number of CF₃ substituted, and a dimer system [{Ru(acac)₂(μ-OEt)}₂].

2. Experimental

The list of samples investigated is shown in Table 1 and their molecular structure in Fig. 1, where (a) and (b) are those of a monomer and a dimer without CF₃ substitution respectively, (c), the partially-substituted, (d), the fully-substituted and (e), the fully-substituted and with the counter cation of potassium. The nominal valence of Ru is expected to be +3 except for the last one which has +2. The details of the sample synthesis is shown in ref. 10. As for [{Ru(acac)₂(μ-OEt)}₂], there are the two enantiomers with and without a mirror symmetry. We have investigated both types of this sample, meso and racemi.

All the samples were powder with amount 0.2 g for NMR measurements; no enrich treatment was done for ¹³C-NMR. NMR spectra and longitudinal spin relaxation rate $T₁$ were measured at temperature region between 1.6-30 K and under magnetic fields around 1 T for ¹⁹F-NMR, 5 T for ¹³C-NMR and up to 12 T for $^{99/101}$Ru-NMR. NMR spectra have been obtained by plotting the spin-echo amplitude against the either external field or the resonance frequency. The temperature dependence of the resonance line-width and shift was determined from obtained spectra. $T₁^{-1}$ was determined by tracing the evolution of spin-echo amplitude with repetition rates $τ$ and fitting it with the function $1 - e^{-τ/T_1}$. These three quantities the resonance line shift, the line width and $T₁$ correspond to the uniform susceptibility, its distribution and fluctuation respectively, and allow one to investigate the Ru-4d spin state.

3. Results and Discussion

Figure 2 shows typical NMR spectra of the four monomer systems. First, we demonstrate by Ru-

![Figure 1. Schematic molecular structure of each sample: (a) [Ru(III)(acac)₃], (b) [{Ru(III)(acac)₂(μ-OEt)}₂], (c) mer-[Ru(III)(ehfa)₃], (d) [Ru(III)(fhfa)₃] and (e) K[Ru(III)(fhfa)₃].](image)
NMR the existence of the paramagnetism in the monomer sample [$\text{Ru}^{III}(\text{acac})_3$], where a spectrum with a huge width contributed both from the eqq-interaction and hyperfine field was observed. The center position of the spectrum was shifted from the zero shift position to lower side by approximately 2 T, indicating that $4d$ moments in trivalent Ru are paramagnetic and appreciably polarized in high field. This is consistent with the fact that $^{13}$C-NMR Knight shift exhibited the Curie-Weiss-like temperature dependence as shown in Fig. 3(a).

Next, we investigated the effect of trifluoromethyl group substitution. Figure 1(c)-(e) show the samples containing $\text{CF}_3$. The partially substituted system $\text{mer-}[\text{Ru}^{III}(\text{ehfa})_3]$ with the nominal Ru-valence of +3 shows a significant broadening and increase in the shift at low temperatures shown in Fig. 2(a) and (b) respectively, indicating that the spin state is nearly the same as in [$\text{Ru}^{III}(\text{acac})_3$]. Note here that the negative sign of the shift is a simple consequence of the negative hyperfine coupling between Ru-$4d$ spin and $^{13}$C/$^{19}$F-nuclei. The nuclear spin-lattice relaxation of these two was also very fast, that is, below 5 ms at 4 K. However, rigorously speaking, we cannot directly compare the resonance line shift in [$\text{Ru}^{III}(\text{acac})_3$] and $\text{mer-}[\text{Ru}^{III}(\text{ehfa})_3]$, because of the difference in the hyperfine coupling constant of C and F sites. Therefore, we cannot deny the possibility that the slight change in the spin state between the two.

The compound of $\text{K}[\text{Ru}^{II}(\text{fhfa})_3]$ that has the nominal valence +2 shows a diamagnetic behavior as expected. Both the shift and the line width do not change with temperature; they stay constant at very small value down to 1.8 K. $T_1$ is very long and exceed 50 sec at 1.8 K, as shown in Fig. 3 (c) and (d). These results indicate that Ru in $\text{K}[\text{Ru}^{II}(\text{fhfa})_3]$ is divalent and with $S=0$ spin state.

As for $[\text{Ru}^{III}(\text{fhfa})_3]$, which is in the intermediate state between the above two group shows a

**Figure 2.** Typical Ru- and F-NMR spectra for (a) [$\text{Ru}^{III}(\text{acac})_3$], (b) $\text{mer-}[\text{Ru}^{III}(\text{ehfa})_3]$, (c) $[\text{Ru}^{III}(\text{fhfa})_3]$ measured under constant field 0.693 T, and (d) $\text{K}[\text{Ru}^{II}(\text{fhfa})_3]$ under 0.695 T. The zero-shift position is shown by dashed arrows.

**Figure 3.** Temperature dependence of the resonance line shift (a) and the line width (b), where solid curve shows the Curie temperature dependence. Typical relaxation curves of the longitudinal spin relaxation (c) and the temperature dependence of $T_1^{-1}$ (d) in $\text{K}[\text{Ru}^{II}(\text{fhfa})_3]$. 
peculiar behavior. This compound is fully substituted by CF$_3$. However, Ru is oxidized by hydrogen peroxide, and expected to be in trivalent state with $S=1/2$. Actually, $T_1$ is very short below 10 ms, and the temperature dependence of the line width shows Curie-like behavior. However, the shift stays constant at low temperatures, and its magnitude is just identical to mer-K[Ru$^{III}$(fhfa)$_3$]. These results indicate that the valence state of Ru is effectively reduced to be III−Δ, and hence that the paramagnetism in this system is weakened. The result of these substitution effects is summarized in Table 2.

Finally, as for the dimer compound of [{Ru$^{III}$ (acac)$_2$}$_2$(μ-OEt)$_2$], $T_1$ is very long, irrespective of the sample is meso and raceme, that is, around 10 s at 4 K, and the resonance line is very sharp; the signal contains FID beat. These results indicate that the system is in non magnetic spinless state owing to the singlet coupling between the two spins in a dimer.

In summary, we have synthesized monomer and dimer compounds of Ru-complex, and investigated by NMR the substitution effect of trifluoromethyl group to find that the effective valence of Ru and hence its spin state is tunable by the substitution.

Acknowledgments
This research was supported by a Grant-in-Aid for Scientific Research on Innovative Areas “New Frontiers of Materials Science Opened by Molecular Degree of Freedom” (Grant No. 21110518) from the Ministry of Education, Science, Sports and Culture.

References
[1] Tanaka H, Oosawa A, Kato T, Uekusa H, Ohashi Y, Kakurai K and Hoser A, 2001 J. Phys. Soc. Jpn. 70 939
[2] Oosawa A, Fujisawa A, Osakabe T, Kakurai K and Tanaka H, 2003 J. Phys. Soc. Jpn. 72 1026
[3] Oosawa A, Kakurai K, Osakabe T, Nakamura M, Takeda M and Tanaka H, 2004 J. Phys. Soc. Jpn. 73 1446
[4] Oosawa A, Ono T, and Tanaka H, 2002 Phys. Rev. B 66, 020405(R)
[5] Suzuki T, Yamada F, Watanabe I, Matsuzaki T, Goto T, Oosawa A and Tanaka H, 2009 J. Phys. Soc. Jpn. 78 074705
[6] Goto T, Suzuki T, Kanada K, Saito T, Oosawa A, Watanabe I, and Manaka H, 2008 Phys. Rev. B 78 054422
[7] Saito T, Oosawa A, Goto T, Suzuki T, and Watanabe I, 2006 Phys. Rev. B74 134423
[8] Nikuni T, Oshikawa M, Oosawa A, and Tanaka H, 2000 Phys. Rev. Lett. 84 5868.
[9] Endo A, Hoshino Y, Hirakata K, Takeuchi Y, Shimizu K, Furushina Y, Ikekuchi H and Satō G.P. 1989 Bull. Chem. Soc. Jpn. 62 709
[10] Hashimoto T, Kawamoto Y, Ishtobi Y, Sasaki T, Fukuda Y, Yamagishi A, Sato H, Shimizu K, and Hayashita T, 2007 Chem. Lett. 36, 1174