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Magnetic Properties of Some Triangular Trinuclear Complexes of $[\mathrm{Ru_2M}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-O})(\mathrm{py})_3]^{n+}$ with a Diamagnetic Ion M

Hanako Kobayashi,* Norikiyo Uryû,† Iwao Mogi,†† Ryo Miyamoto,†††
Yasunori Ohba,†††† Masamoto Iwaizumi,†††† Yoichi Sasaki,‡ Akihiro Ohto,‡‡ and
Tasuku Ito‡‡

Department of Physics, Toin University of Yokohama, Yokohama 225
†Faculty of Engineering, Nagasaki University, Nagasaki 852
††Institute of Materials Research, Tohoku University, Sendai 980-77
†††Faculty of Science, Hirosaki University, Hirosaki 039
††††Institute of Chemical Reaction Science, Tohoku University, Sendai 980-77
‡Faculty of Science, Hokkaido University, Sapporo 060
‡‡Faculty of Science, Tohoku University, Sendai 980-77

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The magnetic susceptibilities and the electron paramagnetic resonances (EPRs) of four complexes: $[\mathrm{Ru_2M}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-O})(\mathrm{py})_3]^{n+}$ (M=Zn(II), Mg(II), and Ru(II): $n=0$; and Rh(III): $n=1$) salts were observed. These are magnetic dimers of Ru(III). The results were analysed under the assumptions that the strong antiferromagnetic superexchange interaction (J_3) is working through μ_3-O bridge and that the antiferromagnetic superexchange interaction (J_1) through $\mu\text{-}(\mathrm{CH_3COO})_2\text{–M(dia)–}(\mathrm{CH_3COO})_2$ is very weak compared to those of double μ-acetato bridges (J_2's) and of the μ_3-O bridge between Ru(III) ions considering the Goodenough–Kanamori rule. The fitting assuming a probability for each path showed the antiferromagnetic interactions through μ_3-O were much stronger than that of the symmetric trimer M=Ru(III). J_1/k's were −1.4—−6.5 K (J_1; −97—−450 m^{-1}), J_2/k's were −40—−110 K (J_2; −2780—−7640 m^{-1}), and J_3/k's were −500—−900 K (J_3; −34700—−62500 m^{-1}). Samples of M=Rh(III) and Ru(II) seem to show weak ferromagnetism.

Following the mixed Ruthenium–Rhodium trinuclear complex $[\mathrm{Ru_2Rh}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-O})(\mathrm{L})_3]^+$ (L=$\mathrm{H_2O}$ or pyridine) in Ref. 1, some triangular trinuclear complexes containing two paramagnetic Ru(III) ions and a diamagnetic ion were synthesized.[2] In the present paper we report magnetic properties of hexakis(μ-acetato-κO:$\kappa O'$)-μ_3-oxo-tris(pyridine)-*triangulo*-diruthenium(III)zinc(II)(*Ru–Ru*)(*2Ru–Zn*)- dichloromethane (1/1), $[\mathrm{Ru_2Zn}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-O})(\mathrm{py})_3]\cdot\mathrm{CH_2Cl_2}$, (**1**), hexakis($\mu$-acetato-$\kappa O$:$\kappa O'$)-$\mu_3$-oxo-tris(pyridine)-*triangulo*-magnesium(II)diruthenium(III)(*Ru–Ru*)(*2Ru–Mg*)-pyridine (1/1), $[\mathrm{Ru_2Mg}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-O})(\mathrm{py})_3]\cdot\mathrm{py}$, (**2**), hexakis($\mu$-acetato-$\kappa O$:$\kappa O'$)-$\mu_3$-oxo-tris(pyridine)-*triangulo*-rhodium(III)diruthenium(III)(*Ru–Ru*)(*2Ru–Rh*)perchlorate, $[\mathrm{Ru_2Rh}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-O})(\mathrm{py})_3]\mathrm{ClO_4}$, (**3**), and hexakis($\mu$-acetato-$\kappa O$:$\kappa O'$)-$\mu_3$-oxo-tris(pyridine)-*triangulo*-ruthenium(II)diruthenium(III)(Ru^{III}–Ru^{III})($2Ru^{\mathrm{III}}$–Ru^{II})-pyridine (1/1), $[\mathrm{Ru_2^{III}Ru^{II}}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-O})(\mathrm{py})_3]\cdot\mathrm{py}$, (**4**). In the following, these abbreviations are used: ($\mathrm{Ru_2ZnO}$) for **1**, ($\mathrm{Ru_2MgO}$) for **2**, ($\mathrm{Ru_2RhO}$) for **3**, and ($\mathrm{Ru_3^{III\ III\ II}O}$) for **4**. The Zn(II) ion in **1**, Mg(II) ion in **2**, Rh(III) ion in **3**, and Ru(II) ion in **4** are diamagnetic, that is, the structure of the complexes is a triangular trinuclear cluster, but they are dimers of Ru(III) ions from the viewpoint of magnetism. Figure 1 is a projection of the structure of the complex ion of $[\mathrm{Rh_3}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-O})(\mathrm{H_2O})_3]\mathrm{ClO_4}\cdot\mathrm{H_2O}$ quoted from Ref. 3. The central part of $[\mathrm{Ru_2^{III}Ru^{II}}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-O})(\mathrm{P(ph)_3})_3]$[4] analysed by X-rays shows a similar structure. The X-ray analysis results[3] in the former are: Rh(1)–Rh(2), 3.329×10^{-10} m; Rh(1)–Rh(3), 3.333×10^{-10} m; and Rh(2)–Rh(3), 3.325×10^{-10} m (monohydrate) and Rh(1)–Rh(2), 3.322×10^{-10} m; Rh(1)–Rh(3), 3.348×10^{-10} m; and Rh(2)–Rh(3), 3.325×10^{-10} m (dihydrate) respectively. In the latter, Ru(1)–Ru(2), 3.316×10^{-10} m; Ru(1)–Ru(3), 3.329×10^{-10} m; and Ru(2)–Ru(3), 3.342×10^{-10} m. Concerning these small differences of

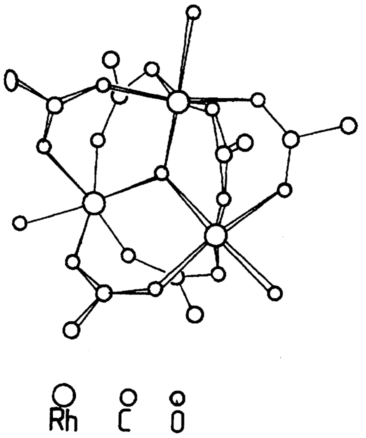

Fig. 1. A projection of the structure of the symmetric $[\mathrm{Rh_3}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-}\mathrm{O})(\mathrm{H_2O})_3]^+$ ion along the *a*-axis quoated from Ref. 3, p. 1737.

bond lengths between the homometallic complex ion and the mixed complex ion, magnetic properties will be calculated with the model of the structure shown in Fig. 1. Although these structure analyses show that the molecular orbital model analysis of magnetic properties would be suitable, in the present paper, the vector model[5] will be used as a first step. The structure of the triangular trinuclear cluster with two sites of magnetic ions has a possibility of showing the weak ferromagnetism[6] because it has the symmetry conditions to allow the antisymmetrical spin coupling in the cluster. As seen in Ref. 1, samples have been carefully prepared to prevent any contaminations by $(\mathrm{Ru_2MO})$ (abbreviated form) with M=Ru(III), namely a symmetric Ru(III) trimer, by $(\mathrm{RuM_2O})$, namely paramagnetic clusters containing a Ru(III) ion, or by $(\mathrm{Ru_2MO})$ with M=zero, that is dimers, especially dimers with very weak superexchange interactions between two Ru(III) ions. The results of the magnetic susceptibility measurements showed fairly different temperature dependences from those known in the triangular trinuclear clusters which consist of paramagnetic 3d ions and another ion.

Experimental

Materials. Preparations of $[\mathrm{Ru_2Zn}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-}\mathrm{O})(\mathrm{py})_3]\cdot\mathrm{CH_2Cl_2}$ (**1**) and $[\mathrm{Ru_2Mg}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-}\mathrm{O})(\mathrm{py})_3]\cdot\mathrm{py}$ (**2**) are reported in Ref. 2. $[\mathrm{Ru_2Rh}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-}\mathrm{O})(\mathrm{py})_3]\mathrm{ClO_4}$ (**3**) was prepared following Ref. 1. $[\mathrm{Ru^{III}_2Ru^{II}}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-}\mathrm{O})(\mathrm{py})_3]\cdot\mathrm{py}$ (**4**) was obtained by the method in Ref. 7. For EPR measurements, $[\mathrm{Ru^{III}_2Ru^{II}}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-}\mathrm{O})(\mathrm{cpy})_3]$, (cpy=4-cyanopyridine), was used instead of **4**, whose preparation is described in Ref. 8.

Magnetic Susceptibility. The magnetic susceptibilities and magnetizations of powdered samples of **1**,**2**,**3**, and **4** were measured in the temperature region from near 2 K to room temperature using a flux meter with a SQUID (Superconducting quantum interference device) sensor (Quantum Design INC., MPMS controller, CA. U.S.A.). The susceptibilities were measured under the applied magnetic field of 4000×10^2 A m^{-1} and the magnetizations were measured to 43768×10^2 A m^{-1}. Powdered samples were put in a cell which was made with Teflon® (poly (tetrafluoroethylene)) tubing with a Teflon® sole and a Teflon® cover made with cut Teflon® sticks of a few mm. This Teflon® tubing has the property of shrinking when warmed by an electric heater, so the sample cells were made airtight at all temperatures of measurements. In the sample cell, in which 10^{-5}—2×10^{-5} kg of powder sample was put, a small amount of liquid paraffin (special grade pure) was added to wet the powder. This improved the thermal conductivity of the powder and protected the powder from oxygen in the air. To proceed with homogeneous temperatures and homogeneous magnetic fields, the amount of the sample is very small. Diamagnetic corrections of the Teflon® cell and the liquid paraffin, which has a small temperature dependence at very low temperatures, were carried out, and the temperature was varied with the same programmed procedure at every run. The callibration of the temperature gauge used in the SQUID was done by the measurements of the paramagnetic susceptibilities of $[\mathrm{Cr(NH_3)_6}]\mathrm{Cl_3}$ powder and pure Hg transition point.

The callibration of the diamagnetic susceptibility of each sample followed the Pascal method.[9]

EPR. The spectra of the EPR of powdered samples as function of the applied magnetic fields were observed in the temperature region from near 3 to 40 K using the apparatus E102 of the Varian Instrument Division (Paloalto CA. U.S.A.) and in the region from about 100 K to room temperatures using the apparatus of JEOL (Japan) at the X-band.

The spectra of EPR were analyzed by the computer simulation programs for the magnetic dimer "EXCHANGE" and "DISSIM" written by Professor J. R. Pilbrow[10,11] and Dr. G. R. Hanson.[10] The "EXCHANGE" gives $g_{\parallel}$ (GPAR), $g_{\perp}$ (GPERP), a sum of the fine-structure parameter and the exchange interaction (DD), line width (WS), etc.. The "DISSIM" gives g_x (GX), g_y (GY), and g_z (GZ) with their relative directions (EPSIA), (MANG), and (ETAA), hyperfine interactions A_x (AX), A_y (AY), and A_z (AZ) of each spin, an exchange interaction (JEX) and distance (DR) between the two spins, and line widths of each principal direction (WX), (WY), and (WZ), etc. (EPSIA) is the angle between g_{z1} axis and the Ru–Ru direction. (MANG) is the angle between g_{z1} and g_{z2}. (ETAA) is the angle between g_{x1} and the Ru–Ru direction.

Units. Some values calculated in non-rationalized CGS emu[12] are shown in brackets [ ].

Results and Discussion

$[\mathbf{Ru_2Zn}(\mu\text{-}\mathbf{CH_3COO})_6(\mu_3\text{-}\mathbf{O})(\mathbf{py})_3]\cdot\mathbf{CH_2Cl_2}$. Observed molar magnetic susceptibility corrected by its diamagnetic susceptibility $\chi_{\mathrm{dia}}=-5913\times10^{-12}$ m^3 [-470.6×10^{-6} cm^3] showed an increase with decreasing temperatures at low temperatures. $(\mathrm{Ru_2ZnO})$ is a magnetic dimer of Ru(III) ions, though it takes a triangle structure of two Ru ions and a Zn ion as mentioned above. The increase of the susceptibility at the lowest temperature region was considered to be the susceptibility due to very weak inter-cluster exchange interactions and a paramagnetic impurity. To remove the paramagnetic impurity part from the observed susceptibility, one must correct the temperature independent part of the molar magnetic susceptibility, that is χ_{TIP}. The curve of observed molar magnetic susceptibility, which is corrected for χ_{dia}, versus reciprocal temperature approached the value of 4150×10^{-12} m^3 [330×10^{-6} cm^3] at $T^{-1}=0$ K^{-1}, which shows that χ_{TIP} is smaller than this value. B. N. Figgis et al.[13] reported in the observation of the magnetic properties of low spin Ru(acac)$_3$ a large orbital splitting of -5000×10^2 m^{-1} due to the axial ligand field, a spin-orbit coupling constant $\lambda=-1000\times10^2$ m^{-1}, and a parameter of the amount of a large electron delocalization, $k=0.70$; the results for the Ru(III) salt with ligands of NH$_3$ and Cl$^-$ were used for comparison. In (Ru$_2$ZnO), it is clear that its χ_{TIP} due to Ru(III) could not be expressed by only the spin-orbit interaction. Following the case of the distorted low spin Ru(III) compound,[14] χ_{TIP} of a Ru ion in (Ru$_2$ZnO) was roughly assumed, with the low symmetry ligand field component Δ, as $8N\beta^2\mu_0/\Delta=1470\times10^{-12}$ m^3 [117×10^{-6} cm^3]. The value 17804.9×10^2 m^{-1} was used as Δ; this is the lowest electronic absorption peak, though it has a faint shoulder at 14999.3×10^2 m^{-1}.[15] As χ_{TIP} of (Ru$_2$ZnO), 2940×10^{-12} m^3 [234×10^{-6} cm^3] was used, because no contribution to χ_{TIP} from Zn(II) was considered. The molar magnetic susceptibility obtained through the above corrections was used as the experimental molar magnetic susceptibility which is shown in Fig. 2.

EPR of (Ru$_2$ZnO) was observed on powder at 6.2, 13.1, 18.8, 35.9, 49.0, 50.5, and 110 K and at room temperatures. Temperature dependence of g-values was very small as seen, for example, in the g-values at the center of the signal: 2.047(6.2 K), 2.040(35.9 K), 2.042(50.5 K), and 2.042(110 K). The spectra obtained at 50.5 K shown in Fig. 3 was analyzed by the computer simulation "EXCHANGE" and "DISSIM". The best fitting was obtained by "EXCHANGE" with $g_{\parallel}=2.26$ and $g_{\perp}=2.00$ of axial, which is shown in Fig. 3. Another fitting was obtained by "DISSIM" with (EPSIA)=30.0°, (MANG)=120.0°, (ETAA)=120.0°, $g_x=g_y=2.04$, and $g_z=2.33$, Ru–Ru distance 5.00×10^{-10} m (an effective distance), and averaged spectrum width=3183 A m^{-1}.

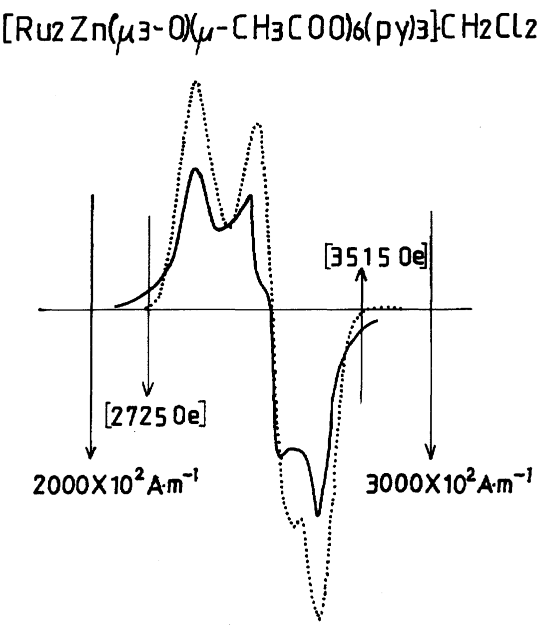

Fig. 3. EPR spectra of [Ru$_2$Zn(μ-CH$_3$COO)$_6$(μ_3-O)(py)$_3$]·CH$_2$Cl$_2$ at 50 K. The dotted line is the result of the fitting by "EXCHANGE" with $g_{\parallel}=2.26$ and $g_{\perp}=2.00$. The longitudinal axis is arbitrary.

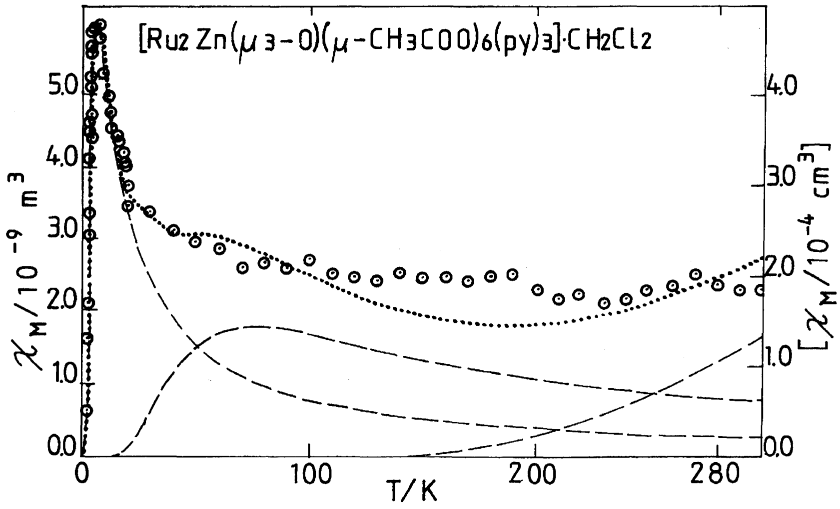

Fig. 2. The molar magnetic susceptibility of [Ru$_2$Zn(μ-CH$_3$COO)$_6$(μ_3-O)(py)$_3$]·CH$_2$Cl$_2$, which is corrected for χ_{dia}, χ_{TIP}, and a paramagnetic impurity together with the inter-cluster exchange interaction part, as a function of temperature, is shown by small circles. The broken lines show the process of the fitting of the formula (1). The dotted line shows the result of the fitting; $J_1/k=-5.50$ K; $P(J_1)=0.00805$, $J_2/k=-60.0$ K; $P(J_2)=2\times0.0132$, $J_3/k=-650$ K; $P(J_3)=0.9655$, and $g_{\mathrm{av}}=2.09$.

The result of the simulation shows that i) the averaged g-value is 2.09, ii) the antiferromagnetic exchange interaction is of the order of 0.1 m^{-1}, and iii) (EPSIA)= 30.0°, (MANG)=120.0°, and (ETAA)=120.0°. These results are consistent with the fact that the g_z axis of each Ru ion is directed to μ_3-O, which means that there is no ferromagnetic moment perpendicular to the triangular plane, although there is a possibility that there might be the ferromagnetic moment in the triangle plane. The crystal analysis[2)] shows, however, that there is a disorder of μ_3-O–Zn directions in the triangle plane; therefore the possibility exists that the ferromagnetic moment in the triangle plane could be cancelled out. The magnetization of (Ru_2ZnO) at 10 K is shown in Fig. 4.

Using the result of the computer simulation of EPR spectra, we analyzed the experimental molar magnetic susceptibility as follows. The experimental molar magnetic susceptibility at higher temperatures shows rather small values of the order of 2760×10^{-12} m^3 [220×10^{-6} cm^3] (effective Bohr magneton number=0.73), which means that a strong antiferromagnetic superexchange interaction is acting between the two Ru(III) ions. On the other hand, a maximum of the molar magnetic susceptibility is seen near 6 K, which means that a weak antiferromagnetic superexchange interaction is also working between the two Ru(III) ions. This (Ru_2ZnO) complex ion of a triangular structure has three kinds of superexchange interaction paths, as seen in Fig. 1: that is, Ru–(μ_3-O)–Ru, two Ru–O–CCH_3–O–Ru, and a Ru–(O–CCH_3–O$)_2$–Zn–(O–CCH_3–O$)_2$–Ru. If the semiempirical Goodenough–Kanamori rules[16)] are applied to 4d orbitals of the Ru(III) ions,[1,7)] μ_3-O has overlaps of its s-orbital and p-orbitals with 4dπ-orbitals, for example $4d_{zy}$'s and $4d_{zx}$'s, of Ru(III) ions, which construct the strongest antiferromagnetic path between two Ru(III) ions. Other 4dπ or 4dσ orbitals, for example $4d_{xy}$'s or $4d_{x^2-y^2}$'s, of Ru(III) ions would have overlaps with s-orbitals and p-orbitals of oxygens of μ-CH_3COO bridges making double Ru–O–CCH_3–O–Ru paths and Ru–(O–CCH_3–O$)_2$–Zn–(O–CCH_3–O$)_2$–Ru path of antiferromagnetic superexchange interacions. Ru(III) ions take the low spin state of $S=1/2$, but they have $4d^5$ electrons and the g-values obtained by EPR show that spins are delocalized. Thd above-mentioned overlaps of orbitals could thus be used as paths of the superexchange interactions with the respective probabilities of the numbers of electrons or the times of exchange interacions.

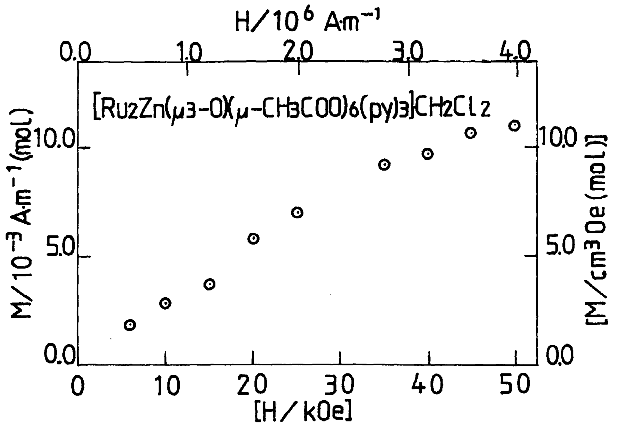

Fig. 4. The molar magnetization of [Ru_2Zn(μ-$CH_3COO)_6$(μ_3-O)(py$)_3$]·CH_2Cl_2 at 10 K as a function of the magnetic field.

The result was as follows.

$$\chi_M=(2N\beta^2\mu_0 g_{Ru}{}^2/3kT)\sum_i P(J_i)(1+3^{-1}\exp(-2J_i/kT))^{-1} +\chi_{TIP},$$
$$\sum_i P(J_i)=1 \tag{1}$$

where N: Avogadro constant 6.0221367×10^{23} mol^{-1}, β: Bohr magneton 9.2740154×10^{-24} J T^{-1}, μ_0: permeability of vacuum $4\pi\times10^{-7}$ H m^{-1}, g_{Ru}: averaged g-value 2.09, k: Boltzmann constant 1.380658×10^{-23} J K^{-1}, T: temperature K, and $P(J_i)$: probability of the interaction through the path of magnitude of the superexchange interacion of J_i k·K. Fitted values were :$J_1/k=-5.50$ K ($J_1=-382$ m^{-1}); $P_1=0.00805$, $J_2/k=-60.0$ K ($J_2=-4169$ m^{-1}); $P_2=2\times0.0132$, and $J_3/k=-650$ K ($J_3=-45170$ m^{-1}); $P_3=0.9655$. The fitted result is shown in Fig. 2 with the dotted line. The broken line with its maximum near 6 K shows the magnetic susceptibility with $J_1/k=-5.50$ K and $P=0.00805$. After this susceptibility was removed from the experimental susceptibility, the residual curve of the low temperature region fitted with the lower temperature region of the broken line with its maximum near 70 K, which is the magnetic susceptibility with $J_2/k=-60.0$ K, $P=0.0264$. After this susceptibility was also taken out from the experimental susceptibility, the residual susceptibility fits with the lower temperature region of the susceptibility with the strongest superexchange interacion with $J_3/k=-650$ K; $P=0.9655$. J_3 assigned to the antiferromagnetic superexchange interaction through Ru–(μ_3-O)–Ru is much larger than the antiferromagnetic superexchange interaction among Ru ions in [Ru_3(μ-$CH_3COO)_6$(μ_3-O)(py$)_3$]ClO_4,[17)] as in the hetero-trinuclear basic acetates of 3d ions.[18)] The large antiferromagnetic superexchange interaction was brought about by the replacement of a Ru ion by a Zn(II) ion in the symmetric [Ru_3(μ-$CH_3COO)_6$(μ_3-O)(py$)_3$] ion. The path of the smallest superexchange interaction may be seen as the EPR spectra, because it is reported that no EPR signal is observed under the strong antiferromagnetic exchange interaction.

[Ru_2Mg(μ-$CH_3COO)_6$(μ_3-O)(py$)_3$]·py. EPR of (Ru_2MgO) was observed at 6.9, 33 K, and room temperature. The spectrum at 33 K around at 2387×10^2 A m^{-1} is shown in Fig. 5. The signal at the lowest temperature showed six absorptions distributed with nearly

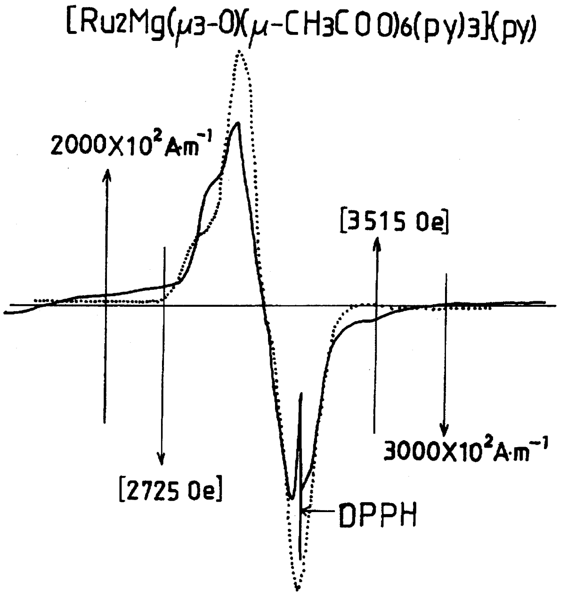

Fig. 5. EPR spectra of $[Ru_2Mg(\mu\text{-}CH_3COO)_6(\mu_3\text{-}O)(py)_3]\cdot py$ at 33 K. The dotted line is the result of the fitting by "EXCHANGE" with $g_{\parallel}=2.12$ and $g_{\perp}=2.08$. The longitudinal axis is arbitrary.

equal separations around 875×10^2 A m^{-1}, which was estimated to be due to Mn(II) impurity in Mg reagent. Its magnetic susceptibility, observed to 2 K, also had an increase with decreasing temperature at low temperatures. The paramagnetic impurity part together with the susceptibility due to the very weak inter-cluster exchange interactions were removed from the data. χ_{dia} was -5330.9×10^{-12} m^3 [-424.22×10^{-6} cm^3]. χ_{TIP} of 2940×10^{-12} m^3 [234×10^{-6} cm^3] was assumed, because (Ru_2MgO) gave similar electronic absorption spectra to those of (Ru_2ZnO),[15] where no contribution from Mg(II) ion is considered. The averaged g-value determined by the "EXCHANGE" was near that of (Ru_2ZnO) but the anisotropy of the g-values, $g_{\parallel}=2.12$ and $g_{\perp}=2.08$, was smaller than that of (Ru_2ZnO). Like (Ru_2ZnO), (Ru_2MgO) does not have weak ferromagnetism. The effective distance by the "DISSIM" of the two Ru ions was 4.60×10^{-10} m. The molar magnetic susceptibility corrected for the paramagnetic impurity, χ_{dia}, and for χ_{TIP} is shown in Fig. 6. The values at higher temperatures are of the order of 2010×10^{-12} m^3 [160×10^{-6} cm^3] (effective Bohr magneton number=0.62), showing that between two Ru(III) ions a strong antiferromagnetic superexchange interaction is working. On the other hand, a peak at 7.5 K shows that there is a weak antiferromagnetic superexchange interaction in the dimer. The molar magnetic susceptibility was calculated with the same formula as used for (Ru_2ZnO). The best fit was found to be $g_{\text{av}}=2.09$, $J_1/k=-5.80$ K ($J_1=-403$ m^{-1}); $P(J_1)=0.0150$, $J_2/k=-110$ K ($J_2=-7650$ m^{-1}); $P(J_2)=2\times0.0180$, and $J_3/k=-800$ K ($J_3=-55600$ m^{-1}); $P(J_3)=0.946$, which is shown in Fig. 6 with a dotted line.

$[Ru_2Rh(\mu\text{-}CH_3COO)_6(\mu_3\text{-}O)(py)_3]ClO_4$. The observed magnetic susceptibility of (Ru_2RhO) increased steeply with decreasing temperature more than that of paramagnetism. Of course, this might be due to some impurity, but chemical analysis of this sample[1] gave these results: Calcd for: C, 32.04; H, 3.29; N, 4.15; Cl, 3.50%. Found: C, 32.05; H, 3.25; N, 4.10; Cl, 3.79%. Thus, the experimental results were analysed while neglecting any paramagnetic impurity. Its χ_{dia} is -5369.1×10^{-12} m^3 [-427.26×10^{-6} cm^3]. The molar magnetic susceptibility corrected for χ_{dia} at room temperature is about 8800×10^{-12} m^3 [700×10^{-6} cm^3], which shows that the temperature independent

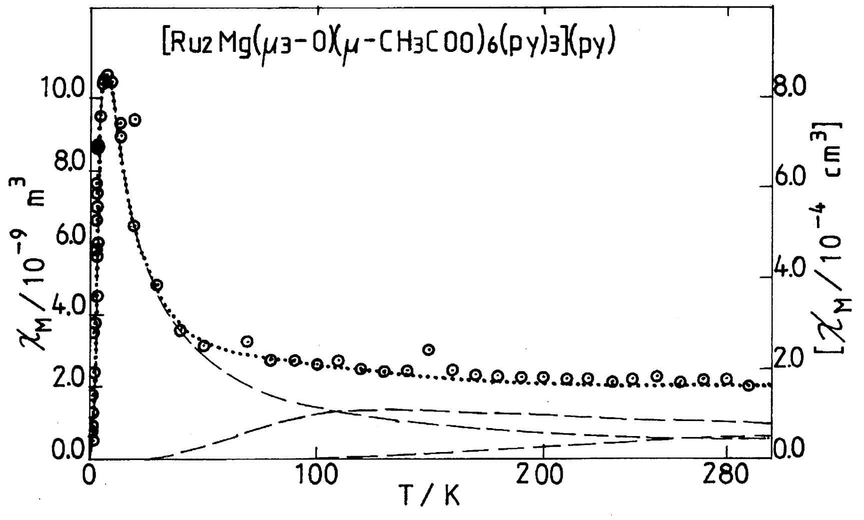

Fig. 6. The molar magnetic susceptibility of $[Ru_2Mg(\mu\text{-}CH_3COO)_6(\mu_3\text{-}O)(py)_3]\cdot py$, which is corrected for χ_{dia}, χ_{TIP}, and a paramagnetic impurity together with the inter-cluster exchange interacion part, is shown as a function of temperature by small circles. The dotted line is the result of the fitting by (1); $J_1/k=-5.80$ K; $P(J_1)=0.0150$, $J_2/k=-110$ K; $P(J_2)=2\times0.0180$, $J_3/k=-800$ K; $P(J_3)=0.946$, and $g_{\text{av}}=2.09$.

part of the magnetic susceptibility is much smaller than that of the sum of two thirds of χ_{TIP} of symmetric $[\mathrm{Ru_3}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-O})(\mathrm{py})_3]\mathrm{ClO_4}$[17)] and one third of χ_{TIP} of symmetric $[\mathrm{Rh_3}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-O})(\mathrm{py})_3]\mathrm{ClO_4}$, that is 23750×10^{-12} m^3 [1890×10^{-6} cm^3]. Here again as χ_{TIP} of the Ru ion, we assumed a distorted low spin case calculated using the lowest absorption at 586×10^{-9} m (17064×10^{2} m^{-1}), that is $8N\beta^2\mu_0/17064\times10^2=1530\times10^{-12}$ m^3 [122×10^{-6} cm^3]. The orbital moment of the Rh ion was assumed to be lost and χ_{TIP} of the Rh ion was estimated as $\chi_{\mathrm{TIP}}=8N\beta^2\mu_0/24813\times10^2=1100\times10^{-12}$ m^3 [84×10^{-6} cm^3] using the next absorption to the lowest one at 403×10^{-9} m. In Ref. 1, the electronic absorption is assigned to the transitions between the dπ–pπ molecular orbitals. The experimental molar magnetic susceptibilities corrected for χ_{dia} and $\chi_{\mathrm{TIP}}=4150\times10^{-12}$ m^3 [330×10^{-6} cm^3] are shown in Fig. 7.

EPR of ($\mathrm{Ru_2RhO}$) on powder was observed at 2.2, 2.5, 3.8, 4.0, 4.6, and 77 K. The signal at 4.0 K is shown in Fig. 8. The best fitting of the signal was obtained by "DISSIM", which said (EPSIA), (MANG), and (ETAA) should be 0.0°, 14.00°, and 90.0° respectively, that is, each spin of $S=1/2$ of two Ru(III) ions is canting to Ru–Ru direction, with an angle of 7° to the same side. The g-values of the best fit were $g_x=2.120$, $g_y=2.120$, and $g_z=3.740$ and the effective Ru–Ru distance was 3.5×10^{-10} m. Another simulation which started from the direction of each spin to the central μ_3-O gave the best fit at each spin direction of 34° from the Ru–Ru direction. The experimental molar magnetic susceptibility was analysed with formula (1) within the antiferromagnetic superexchange interactions, and the best fit was obtained (except for the temperature region lower than 4 K) using $g_{\mathrm{av}}=2.767$, at $J_1/k=-1.40$ K ($J_1=-97.3$ m^{-1}); $P(J_1)=0.00775$, $J_2/k=-40.0$ K ($J_2=-2780$ m^{-1}); $P(J_2)=2\times0.00725$, and $J_3/k=-500$ K ($J_3=-3475$ m^{-1}); $P(J_3)=0.978$, as is shown with the dotted line in Fig. 7. In Fig. 7b, the lower temperature region is shown, which seems to indicate some weak ferromagnetism[6,18)] though the experimental data doesn't show the peak. If we suppose that the two Ru ions are located in each sublattice, the crystal structure of a triangular trinuclear cluster which allows the antisymmetrical spin coupling, and their low symmetry, as seen in the value of χ_{TIP} being smaller than that of the symmetrical Ru(III) ion, and the anisotropic g-values also would help the antisymmetrical spin coupling.

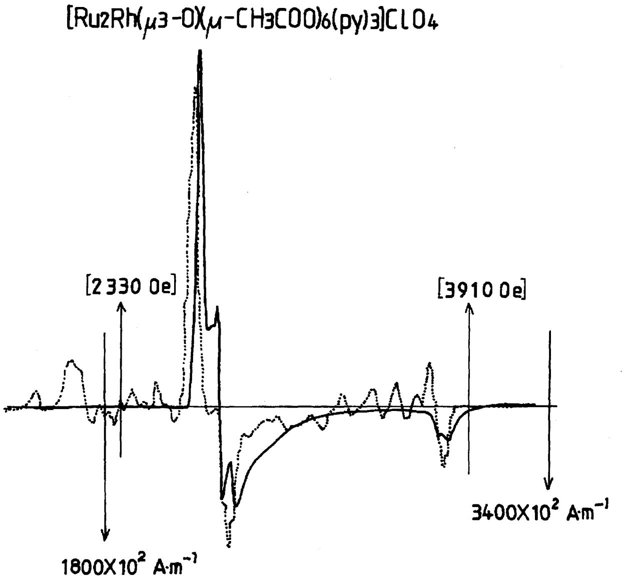

Fig. 8. EPR spectra of $[\mathrm{Ru_2Rh}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-O})(\mathrm{py})_3]\mathrm{ClO_4}$ at 4.0 K. The dotted line is the fitting by "DISSIM" with $g_x=2.120$, $g_y=2.120$, and $g_z=3.740$ with canting of spins of 7°. The longitudinal axis is arbitrary.

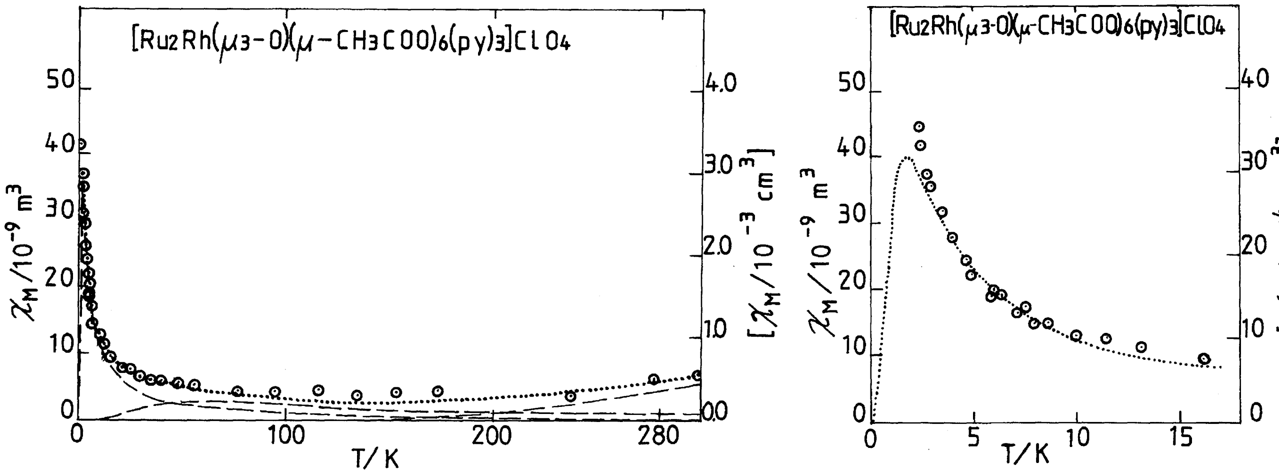

Fig. 7. a) The molar magnetic susceptibility of $[\mathrm{Ru_2Rh}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-O})(\mathrm{py})_3]\mathrm{ClO_4}$ versus temperatures is shown by small circles, which is corrected for χ_{dia} and χ_{TIP}. b) shows the susceptibility in the region of low temperatures. The dotted line show the fitting result used formula (1) with $J_1/k=-1.40$ K; $P(J_1)=0.00775$, $J_2/k=-40.0$ K; $P(J_2)=2\times0.00725$, $J_3/k=-500$ K; $P(J_3)=0.978$, and $g_{\mathrm{av}}=2.767$.

$[\mathrm{Ru}_2^{\mathrm{III}}\mathrm{Ru}^{\mathrm{II}}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-}\mathrm{O})(\mathrm{py})_3]\cdot\mathrm{py}$. The magnetic susceptibility of $(\mathrm{Ru}_3^{\mathrm{III\ III\ II}}\mathrm{O})$ was measured at temperatures from 2 K to room temperature. χ_{dia} is -5939.62×10^{-12} m^3 [-472.660×10^{-6} cm^3]. The observed molar magnetic susceptibility extrapolated to $T^{-1}=0$ is about 4780×10^{-12} m^3 [380×10^{-6} cm^3], which means χ_{TIP} is $\leqq 4780\times10^{-12}$ m^3. As the Ru(II) ion is 4d^6, similar to the Rh(III) ion, χ_{TIP} of $(\mathrm{Ru}_3^{\mathrm{III\ III\ II}}\mathrm{O})$ has been assumed to be 4150×10^{-12} m^3 [330×10^{-6} cm^3], the same as that of ($\mathrm{Ru_2RhO}$). The molar magnetic susceptibility corrected for χ_{dia}, χ_{TIP}, and inter-cluster exchange interactions part is of the order of 1760×10^{-12} m^3 [140×10^{-6} cm^3] (effective Bohr magneton number= 0.58) at room temperatures and shows a steep peak at near 4 K, which is steeper than that due to the antiferromagnetic superexchange interaction with the same peak temperature. On the other hand the EPR signal using 9 GHz was found only at temperatures lower than 20 K on powder, which is shown in Fig. 9. The "DISSIM" simulation of the EPR signal gave a very rough fitting of (EPSIA), 58.0°; (MANG), 120.0°; (ETAA), 120.0°; GX=g_x=1.86, GY=g_y=2.06, and GZ=g_z=2.36, which was not as good as the cases of other samples. This result of the simulation shows that the spins are canting to the Ru–Ru line, whose effective length is 3.4×10^{-10} m, with angles of 58°. Using the averaged g-value of 2.10, we attempted the fitting of the molar magnetic susceptibility used (1) to a wider temperature region. The best fit is shown in Fig. 10 with a dotted line together with the experimental values; its lower temperature region is shown in Fig. 10b. The discrepancy shown in Fig. 10b between the experimental molar magnetic susceptibility and the susceptibility calculated under the assumption of the antiferromagnetic superexchange interaction between two Ru ions seems to show the weak ferromagnetism as in the case of ($\mathrm{Ru_2RhO}$). The slope of the magnetic susceptibility at temperatures lower than the peak is about twice that of above the peak as in the case of the trigonal antiferromagnet with the weak ferromagnetism. The fitting parameters were $J_1/k=-3.00$ K ($J_1=-209$ m^{-1}); $P(J_1)=0.00957$, $J_2/k=-70.0$ K ($J_2=-4865.0$ m^{-1}); $P(J_2)=2\times0.0101$, and $J_3/k=-900$ K ($J_3=-62550$ m^{-1}); $P(J_3)=0.970$.

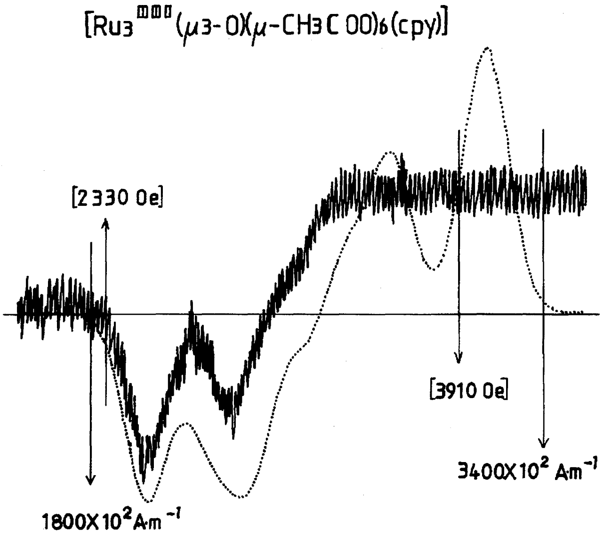

Fig. 9. EPR spectra of $[\mathrm{Ru}_2^{\mathrm{III}}\mathrm{Ru}^{\mathrm{II}}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-}\mathrm{O})(\mathrm{cpy})_3]$ at 5.5 K, with gain of 5×10^4. The dotted line is the simulation by "DISSIM" with $g_x=1.86$, $g_y=2.06$, and $g_z=2.36$ with canting of spins of 58°. The longitudinal axis is arbitrary.

Conclusion

The molar magnetic susceptibilities as a function of temperature of Ru(III) magnetic dimers which have a triangular trinuclear cluster structure were analysed under a model based on the semiempirical Goodenough–Kanamori rules. That is, through μ_3-

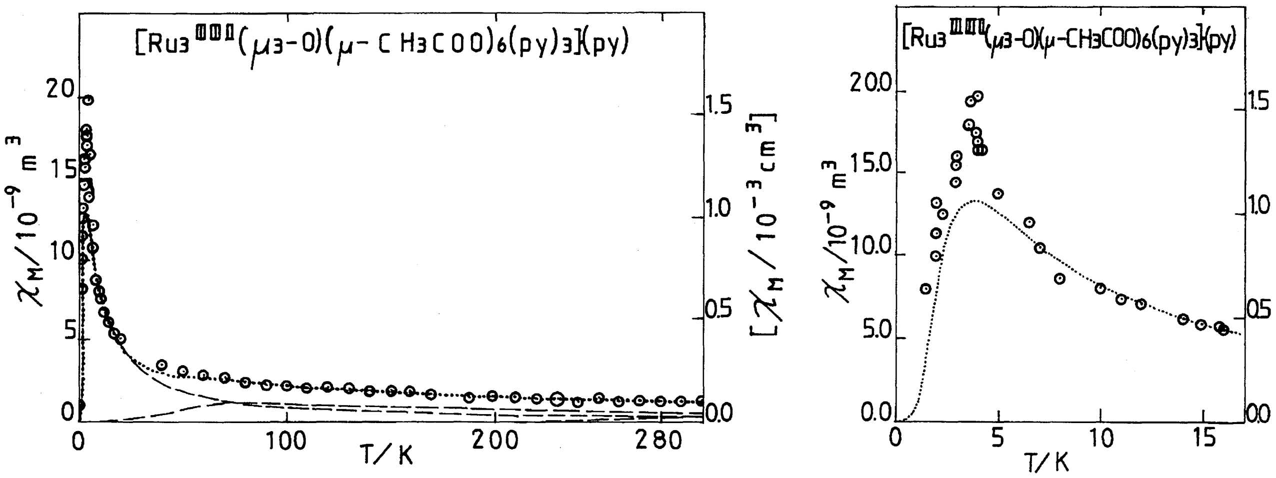

Fig. 10. a) The molar magnetic susceptibility of $[\mathrm{Ru}_2^{\mathrm{III}}\mathrm{Ru}^{\mathrm{II}}(\mu\text{-}\mathrm{CH_3COO})_6(\mu_3\text{-}\mathrm{O})(\mathrm{py})_3]\cdot\mathrm{py}$ versus temperatures is shown by small circles, whieh is corrected for χ_{dia}, χ_{TIP}, and susceptibility due to the inter-cluster exchange interaction. b) is its low temperature region. The dotted lines are the calculated molar magnetic susceptibilities using formula (1) with $J_1/k=-3.00$ K; $P(J_1)=0.00957$, $J_2/k=-70.0$ K; $P(J_2)=2\times0.0101$, $J_3/k=-900$ K; $P(J_3)=0.970$, and $g_{\mathrm{av}}=2.10$.

O, the strong antiferromagnetic superexchange interaction is acting, weak antiferromagnetic superexchange interactions are working through double μ-acetato bridges, and the antiferromagnetic superexchange interaction through μ-$(CH_3COO)_2$–M(dia)–$(CH_3COO)_2$ bridge might be very weak. To get the fit with the experimental values of the magnetic susceptibility, a probability was given for each path. The results of the fitting are: in (Ru_2RhO) and ($Ru_3^{\rm III\ III\ II}O$), where Rh(III) and Ru(II) are $4d^6$, the superexchange interacitons through μ_3-O seem to be main, on the other hand in (Ru_2MgO) and (Ru_2ZnO), where Mg(II) is $2p^6$ and Zn(II) is $3d^{10}$, the superexchange interactions through double μ-acetato bridges and μ-$(CH_3COO)_2$–M(dia)–$(CH_3COO)_2$ bridge seem to take more important parts than in the cases of (Ru_2RhO) and ($Ru_3^{\rm III\ III\ II}O$).

When the similar magnetic analysis which used Kambe's formula[5)] was applied to the symmetric $[Ru_3(\mu\text{-}CH_3COO)_6(\mu_3\text{-}O)(py)_3]ClO_4$,[17)] where two kinds of superexchange interacions: J, through μ_3-O and J', through μ-CH_3COO, were considered, the result of the best fitting of the simulation was $J'/k=0$ and $J/k=-100$ K ($J=-6950\ \mathrm{m}^{-1}$). The replacements of a Ru(III) by Mg(II), Zn(II), Rh(III), or Ru(II) have caused large changes of magnetic properties of the two Ru(III) ions and the superexchange interactions between them, though the X-ray powder analysis didn't show such large structural changes. The replacement effect is seen in the 3d triangular clusters, too.[18)] The magnetic properties of the two Ru(III) ions seem to be far from those of the $^2T_{2g}$ state showing decreased orbital moments and delocalization of spins.

The signal of the dimer of powder EPR was considered to be due to the pair with the weakest antiferromagnetic superexchange interaction. In the cases of the replacements of a Ru(III) by Rh(III) or Ru(II), EPR simulations were very difficult but we found the canting of spins.

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