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Magnetic Properties of Oxygen Centered Trinuclear Ruthenium(III) and Rhodium(III) Complexes

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The magnetic susceptibility and ESR of triangular trinuclear coordination compounds, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ and $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ salts of powders, were measured in the region between liquid-He temperature and room temperature. Ru(III) ions are in the low spin state and Rh(III) ions are diamagnetic. The experimental results were analyzed using a localized model with antiferromagnetic exchange interactions, while taking the molecular orbital moment Zeeman effect into consideration. A weak magnetic interaction through the μ-CH_3COO bridges is discussed. The averaged g-factor of the Ru salt was about 2.26, and the best-fit antiferromagnetic exchange interaction was about $J = -69.5\ cm^{-1}$.

Oxygen-centered triangular trinuclear coordination compounds[1–4] comprising three Rh(III) ions, three Ru(III) ions, and two Ru(III) ions and another metal ion were prepared. From the results of their measured magnetic properties, those on hexa-μ-acetato-(O,O')-μ_3-oxo-tripyridinetriruthenium(III) perchlorate, $[Ru_3O(CH_3COO)_6(py)_3]ClO_4$ (**1**), hexa-μ-benzoato-(O,O')-μ_3-oxo-tripyridinetriruthenium(III) hexafluorophosphate, $[Ru_3O(C_6H_5COO)_6(py)_3]PF_6$ (**2**), and hexa-μ-acetato-(O,O')-μ_3-oxo-tripyridinetrirhodium(III) perchlorate, $[Rh_3O(CH_3COO)_6(py)_3]ClO_4$ (**3**) are reported in the present paper. These two kinds of coordination compounds, abbreviated as (Ru_3O) for the samples **1** and **2**, and as (Rh_3O) for the sample **3**, are considered to be highly symmetrical.

The crystal structures of $[Rh_3O(CH_3COO)_6(H_2O)_3]ClO_4 \cdot 2H_2O$ and $[Rh_3O(CH_3COO)_6(H_2O)_3]ClO_4 \cdot H_2O$ were determined by Głowiak et al.[4] using X-ray diffraction. The complex ion has a core skelton as shown in Fig. 1, which is considered to be the same as that of sample **3**. A preliminary structure analysis of $[Ru_3O(C_6H_5COO)_6(py)_3]PF_6$ (**2**) was reported by Abe et al.[5] The core skelton of the complex ion of sample **2**, (Ru_3O) is similar to Fig. 1, and some bond lengths are shown in Table 1. Sample **1**, (Ru_3O) is considered to have a similar core skelton to that of sample **2**.

Analyses of the magnetic properties of oxygen-centered triangular trinuclear coordination compounds of the 4d transition metals by molecular orbital theory were carried out by Cotton and Norman, Jr.[3] as well as Baumann et al.[6] Though the molecular orbital method is the best approach to these clusters, in the present study a localized spin model was applied at the beginning in order to introduce the molecular orbital concepts of Pople and Untch[7] as well as Tsukerblat et al.[8]

Experimental

Materials. Perchlorate salts of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$ and $[Rh_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$

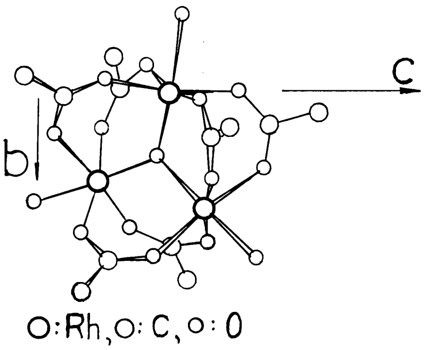

Fig. 1. Projection of the structure of the $[Rh_3O(CH_3COO)_6(H_2O)_3]^+$ ion along the a-axis, quoted from Ref. 4, p. 1737.

Table 1. Interatomic Distances in (Ru_3O) and (Rh_3O) Complex Ions

$(Ru_3O)^{a)}$/Å		$(Rh_3O)^{b)}$/Å	
Ru······Ru	3.350	Rh······Rh	3.330
Ru–O (central)	1.934	Rh–O (central)	1.923
Ru–O (acetato)	2.023	Rh–O (acetato)	2.026
C–O$^{c)}$	1.26	C–O	1.263

a) Ref. 7. b) Ref. 4. c) Unpublished datum.

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were obtained following Ref. 1 and 9. By reflux with pyridine, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]ClO_4$ (**1**) and $[Rh_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]ClO_4$ (**3**) were obtained. $[Ru_3(\mu_3\text{-}O)(\mu\text{-}C_6H_5COO)_6(py)_3]PF_6$ (**2**), used in an ESR study, was prepared by the method of Ref. 5.

Magnetic Susceptibility. The magnetic susceptibilities of powder samples of **1** and **3** were measured in the temperature region from about 2 K to 300 K using a magnetic balance (Oxford Instruments, at the Institute for Molecular Science, Okazaki) of the Faraday method under an applied constant magnetic field of about 9.9 kOe ($1 Oe=10^3/4\pi$ A m^{-1}) with a gradient of 500 Oe cm^{-1}. At a temperature near 2 K, the magnetizations in field up to about 50 kOe were observed. A powder sample was put into a quartz cell together with a minimum amount of liquid paraffin of special grade, sufficient to cover the powder sample in order to maintain the thermal conductivity and insulation to the atomosphere. A thermometer was fixed to the cryostat wall. Its indication was corrected by the magnetic susceptibilities of a paramagnetic $[Cr(NH_3)_6]Cl_3$ measured in the same temperature range within which the samples were measured. For each measurement the sample cell site in the cryostat was checked, as well as the pressure of the heat-exchange He gas and the time schedule of the temperature variation to obtain precise experimental values.

Electron Spin Resonance. ESR (JEOL, JES-FE2XG, at the Institute for Chemical Reaction Science, Sendai) of sample **2** was observed at temperatures between about 107 K and room temperature, using 9.2 GHz.

Units. Nonrationalized CGSemu were used in the present study. The relations between the SI and the CGSemu systems concerning the units used in this paper are listed in Ref. 10.

Results and Discussion

The diamagnetic susceptibility of -428×10^{-6} cm^3, which was calculated by the Pascal–Pacault–Hoarau method as well as the Pascal method,[11] was corrected in the molar magnetic susceptibility of sample **1**. The corrected molar magnetic susceptibility has roughly been paramagnetic smoothly changing from about 0.127 cm^3 at 2 K to 0.0065 cm^3 at 300 K, as shown in Fig. 2, together with its reciprocal susceptibility. The effective Bohr magneton number ($\mu_{eff}=(3k\chi_M T/N\beta^2)^{1/2}$) calculated from the above molar magnetic susceptibility is also shown as a function of the temperature in Fig. 3. The molar magnetic susceptibility shows the existence of a large temperature-independent part, and the reciprocal molar magnetic susceptibility goes to zero near −0.1 K. The μ_{eff} at 300 K is about 3.9, and that at 2 K is 1.49. ESR data for sample **2**, observed near 107 K, are shown in Fig. 4. The measured g-values ($g_1=g_2=2.35$ and $g_3=2.075$) estimated following Kneubühl's method[12] were almost temperature independent in the observed region from 100 K to room temperature. There were broad signals near 1000—2000 Oe and 6000—12000 Oe.

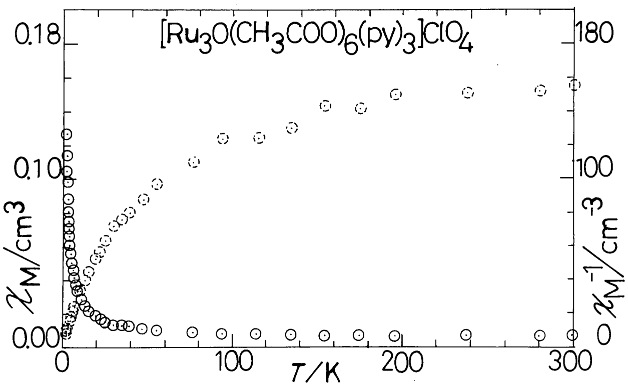

Fig. 2. Molar magnetic susceptibility of $[Ru_3O(CH_3COO)_6(py)_3]ClO_4$ (**1**), marks ⊙, as a function of the temperature. Marks ⊙show the reciprocal molar magnetic susceptibility.

Samples **1** and **2** of powders were greenish blue. Ru(III) ion, which has a $^2T_{2g}$ ground state, is known to be a low-spin state of $S=1/2$ in the (Ru_3O). The core structure of the complex ion of samples **1** and **2** is a triangle with an oxide ion at the centre. The sizes of the structure are Ru···Ru; 3.350 Å, Ru–O (central); 1.934 Å, and Ru–O (acetate); 2.023 Å.

If the part of Hamiltonian due to the exchange interaction is assumed to be $-2J(S_1\cdot S_2+S_2\cdot S_3+S_3\cdot S_1)$, the

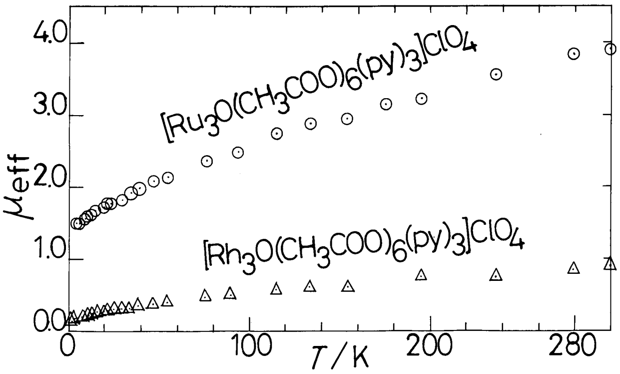

Fig. 3. Effective Bohr magneton number (μ_{eff}) of $[Ru_3O(CH_3COO)_6(py)_3]ClO_4$ and $[Rh_3O(CH_3COO)_6(py)_3]ClO_4$as a function of the temperature.

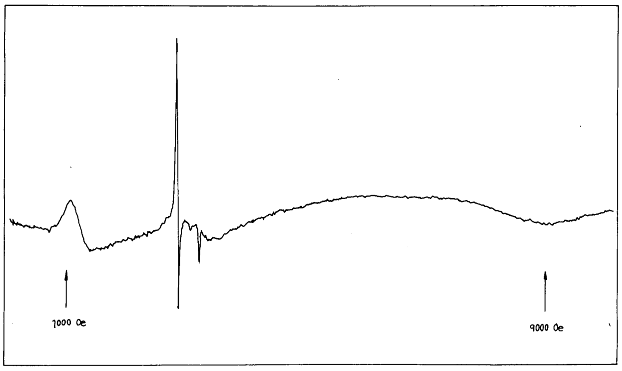

Fig. 4. Electron spin resonance of $[Ru_3O(C_6H_5COO)_6(py)_3]PF_6$ (**2**) powder near 107 K. *R. F.* 9.20699 GHz, Field 5000±5000 Oe, Sweep time 16 min., Mod. 100 kHz, 20 Oe, Amplitude 1×10^3, Response 0.3 s.

energy levels are specified by the total spin, $S'=S_1+S_2+S_3$. The lowest level is the doubly degenerate one with $S'=1/2$, i.e. fourfold degenerate, including a spin degeneracy. The only excited level is the $S'=3/2$ state with a separation of $-3J$ from the ground state. Then, the molar magnetic susceptibility[13] (χ_M') of sample **1** due to an exchange interaction is

$$\chi_M' = N_\beta{}^2 g^2\{1+5\exp(3J/kT)\}/4kT\{1+\exp(3J/kT)\}. \quad (1)$$

The electron spin resonance showed that the g-values are temperature independent. It was shown by Figgis[14] as well as Figgis et al.[15] that such g-values of the $^2T_{2g}$ ion indicate that the ion is in a strong axial crystalline field. The orbital level separation (Δ) due to the axial crystalline field obtained from the calculation given by Figgis[14,15] is between 6250 cm^{-1} (k=1.0—0.9) and 1250 cm^{-1} (k=0.8—0.7), where k means that, for a fraction ($1-k$) of their time, the electrons of the $^2T_{2g}$ ion exist on the ligand atoms. This strong axial crystalline field gives a temperature-independent part (χ_{TIP}) to the molar magnetic susceptibility. Following Ref. 15, the axial crystalline field splitting combined with the spin-orbit interaction was taken to be $\Delta-3\lambda/2$, neglecting the higher order effect, assuming $\lambda=-1250$ cm^{-1}. The temperature-independent part of the molar magnetic susceptibility became roughly 0.0027 cm^3, or larger than this. The broad absorption observed in the electron spin resonance around 1000—2000 Oe seems to be due to a kind of fine structure of the trinuclear cluster. As shown above, the lowest energy level of $S=1/2$ is degenerate, which may behave as if a spin of one, because each spin is coupled with an exchange interaction. This pseudonymous fine structure parameter is about D=0.08 cm^{-1}.

As shown in Fig. 1, the exchange interaction between two Ru ions, in fact, interacts through two kind of paths: the strong -Ru–O(central)–Ru– and the weak -Ru–O–C–O–Ru–; the latter is a double path. Discerning these two kinds of paths, the molar magnetic susceptibility of (**1**) due to the exchange interaction can be written

$$\begin{aligned}\chi_M'' = (N_\beta{}^2 g^2/4kT)[&W(J)\{1+5\exp(3J/kT)\}/\\ &\{1+\exp(3J/kT)\}+W(J')\{1+5\exp(3J'/kT)\}/\\ &\{1+\exp(3J'/kT)\}], \end{aligned}\quad (2)$$

where, $W(J)=J/(J+2J')$ and $W(J')=2J'/(J+2J')$ are assumed. For these levels split by exchange interactions, the g-values due to the spin, that is each sum of the spin angular momentum of each level, was checked in order to investigate the obtained absorption in the electron spin resonance. Referring to the operator technique of atomic spectroscopy,[16] the g-value of the excited level with $S'=3/2$ is that of one ion of Ru^{3+}, and those of the ground state with $S'=1/2$ are also that of one ion of Ru^{3+}.

Tsukerblat et al.[8] showed the existence of the orbital magnetism on the cluster or polynuclear exchange compounds. It was shown by the interionic exchange interactions, that the orbital degenerate state in the cluster could appear, even if each ion has no orbital degeneracy. The state has magnetism due to the orbital Zeeman effect through a spin-orbit interaction; if there is a degenerate orbital state, the orbital magnetism would appear even if the spins are paired. Following Tsukerblat et al.,[8] using the effective Hamiltonian, both linear and quadratic in magnetic and electric fields, given by Washimiya et al.,[17] the properties of the molar magnetic susceptibility of (Ru_3O) concerning this orbital paramagnetism were reconsidered. The main change in the molar magnetic susceptibility was to add some terms in the form of $[3+\phi(kT)^{-2}]^{-1}$, where ϕ is a function of the g-value and the applied magnetic field. This Zeeman effect of the degenerate orbitals of a "non-Kramers doublet" is considered not to be very large. Regarding this point, we will discuss later the magnetic property of sample **3**, (Rh_3O).

Using a χ_{TIP} of 0.0027 cm^3 and an averaged constant g-value of 2.26, obtained from the electron spin resonance, the molar magnetic susceptibility of sample **1** (Ru_3O),

$$\begin{aligned}\chi_M = \{N_\beta{}^2 g^2/4k(T+Q/T)\}[&W(J)\{1+5\exp(3J/kT)\}/\\ &\{1+\exp(3J/kT)\}+W(J')\{1+5\exp(3J'/kT)\}/\\ &\{1+\exp(3J'/kT)\}]+\chi_{TIP}, \end{aligned}\quad (3)$$

was calculated while seeking the best fit of parameters, where the "non-Kramers doublet" effect is brought in the $(T+Q/T)^{-1}$. The results of the calculation are shown in Fig. 6. The best-fit parameters are $J=-69.5$ cm^{-1}, $J'=0$, and $Q=6$ K^2.

The weaker exchange interaction paths with acetato-bridges, expressed by J', make a conjugated double-bond cycle if the electrons pass through $Ru_1{=}O_1{-}C_2{=}O_3{-}Ru_2{=}O_4{-}C_5{=}O_6{-}Ru_3{=}O_7{-}C_8{=}O_9{-}Ru_1{=}O_{10}{-}C_{11}{=}O_{12}{-}Ru_2{=}O_{13}{-}C_{14}{=}O_{15}{-}Ru_3{=}O_{16}{-}C_{17}{=}O_{18}{-}(Ru_1)$ as shown in Fig. 7. The number of conjugated double bondings is 24. Pople and Untch[7] showed a quantum mechanical theory for the induced paramagnetic ring current in the conjugated double bondings of the ideal monocyclic polyenes. In the present (Ru_3O) triangular trinuclear complex ion, the conjugated electron path shown in Fig. 7 has 24 bonds, though it is never the ideal cycle. If the paramagnetic susceptibility is calculated for the idealized shape of this cycle, it is less than 0.00003 cm^3; the result of the best fit of $J'=0$ thus seems to be reasonable.

The observed magnetic susceptibility of sample **3** (Rh_3O) is shown in Fig. 5 with its reciprocal susceptibility; the effective Bohr magneton number is shown in Fig. 3. The molar magnetic susceptibility corrected atomic diamagnetic susceptibility of -425.26×10^{-6} cm^3 is

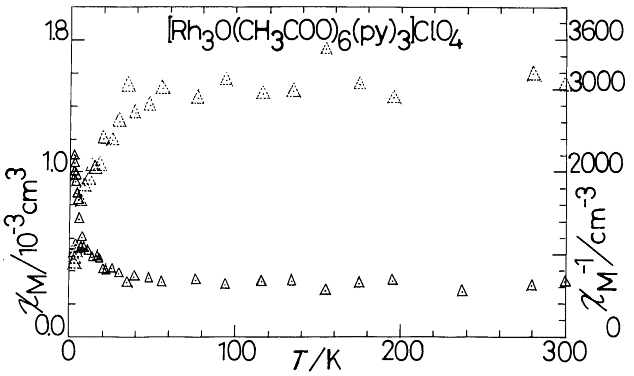

Fig. 5. Molar magnetic susceptibility of $[Rh_3O(CH_3COO)_6(py)_3]ClO_4$ (**3**), marks △, as a function of the temperature. Marks ⚠ show the reciprocal molar magnetic susceptibility.

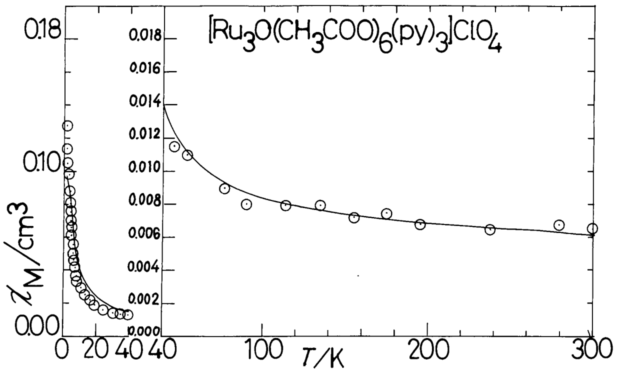

Fig. 6. Fitting to the molar magnetic susceptibility of $[Ru_3O(CH_3COO)_6(py)_3]ClO_4$ (**1**), used $\chi_M=\{N\beta^2g^2/4k(T+Q/T)\}[W(J)\{1+5\exp(3J/kT)\}/\{1+\exp(3J/kT)\}+W(J')\{1+5\exp(3J'/kT)\}/\{1+\exp(3J'/kT)\}]+\chi_{TIP}$. Lines show the case of $\chi_{TIP}=0.0027$ cm^3, $g=2.26$, $J=-69.5$ cm^{-1}, $J'=0$, and $Q=6$ K^2.

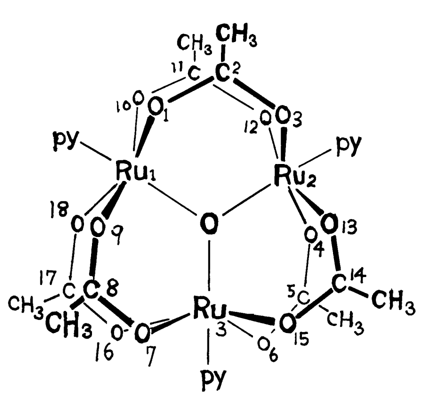

Fig. 7. Conjugated double-bonding path in (Ru_3O).

about 0.31×10^{-3} cm^3 at between 100 K and room temperature; at temperatures lower than 100 K, however, it increased to about 1.10×10^{-3} cm^3 at about 2 K. The reciprocal magnetic susceptibility showed zero at about −2.4 K. The effective Bohr magneton number (Fig. 3) was about 0.9 at room temperature, and decreased with decreasing temperature to 0.15 at about 2 K; it did not seem to approach zero at 0 K. The graphically obtained temperature-independent part of the molar magnetic susceptibility is about 0.31×10^{-3} cm^3. The weak-exchange interaction path of the conjugated cycle with acetato bridges of sample **3** (Rh_3O) is almost the same as that of sample **1** (Ru_3O) (Table 1). The part of the magnetic susceptibility due to this path (namely J') is assumed to be 3×10^{-5} cm^3. From the experimental values, the ground state of each Rh^{3+} ion in the complex ion was considered to be $^1A_{1g}$ with $L=S=0$; if the temperature-independent part of the molar magnetic susceptibility (about 0.28×10^{-3} cm^3) is assumed to be due to $10Dq$, $10Dq$, is about 21600 cm^{-1}, which is near to the $^1A_{1g}$–$^1T_{1g}$ transition of 19000 cm^{-1} by Głowiak et al.[4)] observed on $[Rh_3O(CH_3COO)_6(H_2O)_3]ClO_4$. If the magnitude of the part of the molar magnetic susceptibility which increased in the low-temperature region over χ_{TIP} is assumed to be due to some paramagnetic impurity, this impurity would correspond to the fact that every 60 complex ions has an $S=1/2$ impurity. This seems to be too large an impurity amount, compared to the good analytical results.[18)]

Following the way of Tsukerblat et al.,[8)] and using the theory of Washimiya et al.,[17)] the magnetic susceptibility due to the "non-Kramers doublet" of the degenerate orbital moments of D_{3h} symmetry of the cluster can be expressed as

$$\begin{aligned}\chi_M &= (2N\beta^2g_\parallel^2)\{9k(T+g_\parallel^2\beta^2H_z^2/3k^2T)\}^{-1}\\ &\quad+(4NG_1^2H_x^2)\{9k(T+G_1^2H_x^4/3k^2T)\}^{-1}\\ &\quad+(4NG_1^2H_y^2)\{9k(T+G_1^2H_y^4/3k^2T)\}^{-1}, \qquad (4)\end{aligned}$$

where χ_M is for one mole of the powder sample and $g_\parallel$ is the g-factor of the magnetic moment (which does not mean the g-factor of electron spins); H_x, H_y, and H_z are the applied magnetic field and G_1 is a real number. Fitting of this formula to the experimental value of sample **3** was tried using

$$\chi_{\text{non-Kramers}} = 2N\beta^2G^2\{9k(T+Q/T)\}^{-1}. \qquad (5)$$

The parameters $G^2=0.02930$ and $Q=1.776$ K^2 gave a fitting, as shown in Fig. 8, which could explain a negative temperature of about −1 K, where the experimental $(\chi_M-\chi_{TIP})^{-1}$ became zero. Rh^{3+} ions in sample **3** (Rh_3O) are in the $S=0$ and $L=0$ state. For such a state, Kaplan[19)] did not give a reduction of the representation U_{2j+1} (Symmetry of many-electron system, Appendix 3, p. 293); rather, a strong analogy of the molecular orbital of (Rh_3O) to (Ru_3O) was tried in order to calculate the effect of the "non-Kramers doublet".

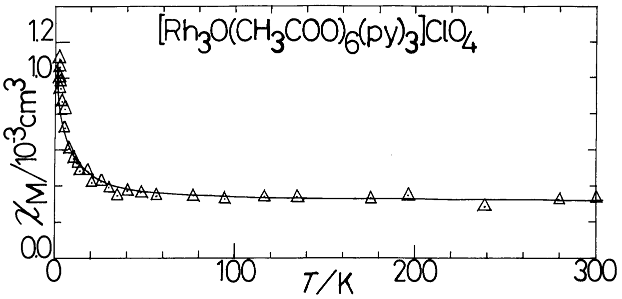

Fig. 8. Fitting to the molar magnetic susceptibility of $[Rh_3O(CH_3COO)_6(py)_3]ClO_4$ used $\chi_{\text{non-Kramers}}=2N^2G^2\{9K(T+Q/T)\}^{-1}$. A line shows the case of $\chi_{\text{TIP}}=0.00028$ cm^3, $G^2=0.02930$, and $Q=1.776$ K^2.

In the case of sample **1** (Ru_3O) the part of the magnetic susceptibility due to the degenerate orbital moments contains the susceptibility due to the hyperfine interaction of the "non-Kramers doublet", in addition to the degenerate orbital moment part; however, if the magnitude is of a comparable order to that of sample **3** (Rh_3O), its contribution to the magnetic susceptibility would be negligibly small, except for the part of $(T+Q/T)^{-1}$ in formula (3).

In conclusion, the magnetic property of sample **1** (Ru_3O) is mainly due to antiferromagnetic exchange interactions of about -69.5 cm^{-1} among the Ru^{3+} ions through the central oxide ion. Each Ru^{3+} ion is in the axial coordination field which gives a χ_{TIP} of 0.0027 cm^3 and temperature-independent anisotropic g-factors. The susceptibility follows the temperature dependence of $(T+Q/T)^{-1}$ due to the "non-Kramers doublet" of the molecular orbitals, because the Ru^{3+} ions are in the low-spin state. The magnetic property of sample **3** (Rh_3O), with S and L of zero, is mainly due to a second-order Zeeman effect and the paramagnetism of the degenerate orbital moments.

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10) List of unit and their conversions.

	SI unit	CGSemu non-rationalized system of unit
B: Magnetic flux density	T=Wb m^{-2}	G
H: Strength of magnetic field	A m^{-1}	Oe
M: Magnetization	A m^{-1}	
χ_M: Molar magnetic susceptibility	m^3	cm^3

3.336×10^{-10}/coulomb=1/e.s.u. of elec. charge
10^{-4}/T=1/G
$10^3/4\pi$/A m^{-1}=1/Oe
(χ_M in SI)/m^3=$4\pi\times10^{-6}$ (χ_M in CGSemu)/cm^3

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18) The results of chemical analysis: Found for **1**: C, 32.32; Cl, 3.78; H, 3.37; N, 4.24%. Calcd for $Ru_3C_{27}ClH_{33}N_3O_{17}$: C, 32.10; Cl, 3.51; H, 3.29; N, 4.16%, M, 1010.23. Found for **3**: C, 31.95; Cl, 3.74; H, 3.33; N, 4.25%. Calcd for $Rh_3C_{27}ClH_{33}N_3O_{17}$: C, 31.93; Cl, 3.49; H, 3.28; N, 4.14%, M, 1015.74.

19) I. G. Kaplan, "Symmetry of Many-Electron System," Academic Press. Inc., New York (1975).