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Synthesis and Ferromagnetic Spin-Coupling of a Imidazolate-Bridged 3*d*-4*d* Cu(II)-Ru(III) Binuclear Complex

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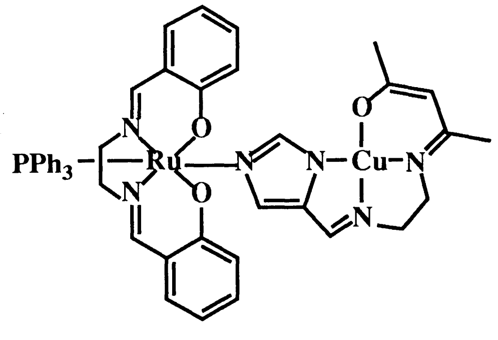
A 3*d*-4*d* binuclear Cu(II)-Ru(III) complex exhibiting ferromagnetic spin-coupling $[Cu(A)Ru(salen)(PPh_3)]ClO_4 \cdot MeOH$ has been synthesized and characterized, where H_2A=N-(2-imidazolidene)-N'-(acetylacetonylidene)ethylendiamine and H_2salen=N,N'-bis(salicylidene)ethylenediamine. The magnetic susceptibility data (4.2-300 K) were well reproduced by the equation derived from $H=-2JS_{Cu} \cdot S_{Ru}$ ($S_{Cu}=1/2$, $S_{Ru}=1/2$) with $g=2.04$ and $J=+6.55$ cm^{-1}. The ESR study indicated that the magnetic orbitals of Cu(II) and Ru(III) are orthogonal to each other.



$[Cu(A)Ru(salen)(PPh_3)]^+$

Ferromagnetic spin-coupling between the metal ions in binuclear systems can be expected theoretically when the magnetic orbitals of the interacting metal ions are orthogonal in symmetry to each other.1,2) The concept of the magnetic orthogonality has been confirmed experimentally by several 3*d*-3*d* hetero-metal systems, such as Cu(II)-VO(IV), Cu(II)-Cr(III), Ni(II)-Cr(III), and low-spin Fe(III)-Cu(II) systems.1-4) A number of 3*d*-3*d* hetero-metal complexes which have been prepared and their magnetic properties have been extensively investigated.1-5) On the other hand, hetero-metal polynuclear complexes containing 4*d* transition metal ions have not been subjected to magnetic studies. In this study, in order to examine whether the concept of the magnetic orthogonality can be applicable to 3*d*-4*d* system or not, a 3*d*-4*d* hetero-metal complex $[Cu(A)Ru(salen)(PPh_3)]ClO_4 \cdot MeOH$ (see the schematic drawing) has been prepared and the magnetic property has been investigated, where H_2A=N-(2-imidazolidene)-N'-(acetylacetonylidene)ethylendiamine, H_2salen=N,N'-bis(salicylidene)ethylenediamine, and PPh_3=triphenyl phosphine.

The component complexes $[Cu(A)] \cdot 0.5CHCl_3$ and $[Ru(salen)(PPh_3)]Cl$ were prepared according to the methods of literatures.6,7) The complex $[Cu(A)Ru(salen)(PPh_3)]ClO_4 \cdot MeOH$ was prepared by mixing of $[Cu(A)] \cdot 0.5CHCl_3$ and $[Ru(salen)(PPh_3)]Cl$ in methanol with the mole ratio of 1:1.1, followed by addition of a methanolic solution of $NaClO_4$. Anal. Found: C, 52.95; H, 4.28; N, 8.18; Cu, 6.19%. Calcd for $C_{46}H_{47}N_6ClO_8PCuRu$: C, 52.98; H, 4.54; N, 8.06; Cu, 6.09%. Λ_M 83.5 S mol^{-1}cm^2 in MeOH. ν(Cl-O) 1100 cm^{-1}. $E_{1/2}$=-1.000, -0.208 V vs. SCE in CH_3CN.

Among 3*d*-4*d* hetero-metal systems, we selected the Cu(II)-Ru(III) system from the viewpoint of the magnetic orthogonality as follows. Ru(III) ion with octahedral surrounding has $(4d)^5$ electronic configuration and is usually in low-spin state. One unpaired electron occupies a t_{2g} type orbital in O_h symmetry, while one unpaired electron of Cu(II) ion with $(3d)^9$ electronic configuration has one unpaired electron in e_g type orbital. Thus, the Ru(III)-Cu(II) complex is a case of strict orthogonality of magnetic orbitals among *3d*-*4d* hetero-metal systems.

The complex [Cu(A)Ru(salen)(PPh$_3$)]ClO$_4$·MeOH was easily prepared by the reaction of [Cu(A)]·0.5CHCl$_3$ and [Ru(salen)(PPh$_3$)]Cl, where [Cu(A)] functions as an unidentate ligand through the imidazolate nitrogen atom[8]) and coordinates to the sixth coordination site of [Ru(salen)(PPh$_3$)]Cl.[9]) The complex was obtained as dark green microcrystalline materials. The elemental analysis was consistent with the expected chemical formulation. Molar electrical conductance in MeOH is 83.5 S mol^{-1} cm^2 which is consistent with 1:1 electrolyte. I.R. spectrum shows broad bands at 3400 and 1100 cm^{-1} which are attributable to MeOH and ClO$_4^-$ ion, respectively. Cyclic voltammogram in acetonitrile shows two reversible reduction waves at -0.208 and -1.000 V vs. SCE, which can be assigned to Ru(III)/Ru(II) and Cu(II)/Cu(I) processes, respectively, based on the electrochemical studies on the component complexes.[9])

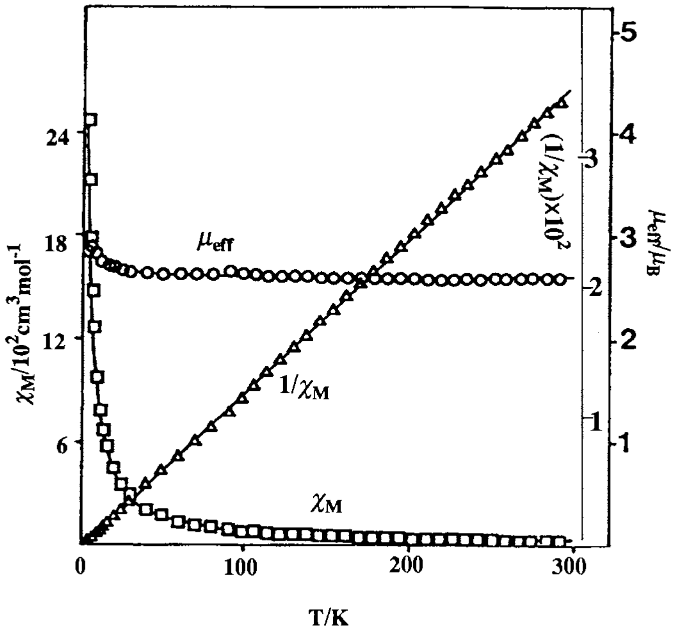


Fig. 1. Temperature dependences of χ_M, $1/\chi_M$, and μ_{eff} of [Cu(A)Ru(salen)(PPh$_3$)]ClO$_4$, where the solid lines represent the theoretical curves.

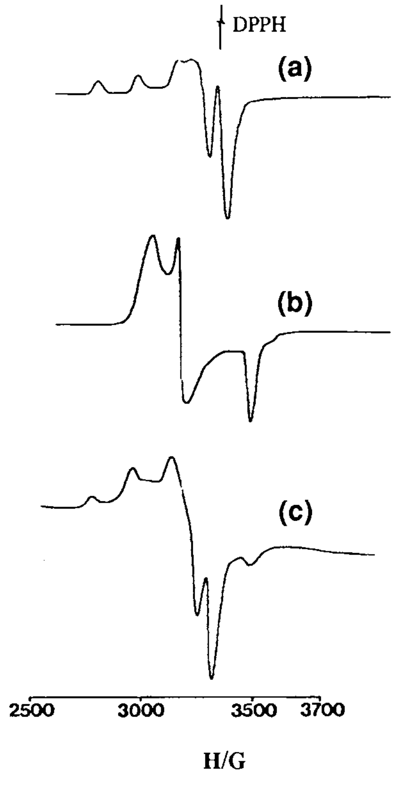
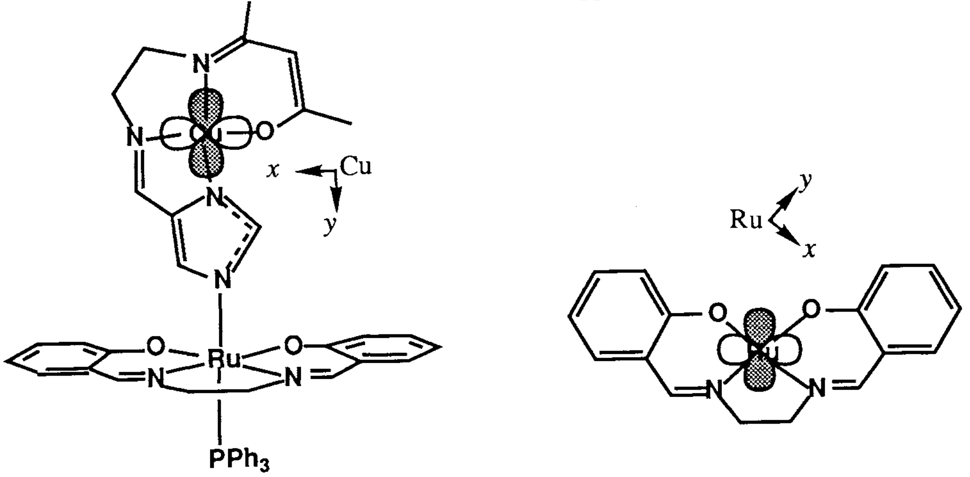


Fig. 2. ESR Spectra of DMF frozen glass of [Cu(A)] (a), [Ru(salen)(PPh$_3$)]Cl (b), and [Cu(A)Ru(salen)-(PPh$_3$)]ClO$_4$ (c) at 78 K.

The magnetic susceptibility data of the Cu(II)-Ru(III) complex are shown in Fig.1, in the forms of the χ_M vs. *T*, $1/\chi_M$ vs *T*, and μ_{eff} vs. *T* plots, where χ_M is the magnetic susceptibility per molecule, μ_{eff} the effective magnetic moment per molecule, and *T* the absolute temperature. The Curie plot of $1/\chi_M$ vs. *T* is nearly linear in the temperature range 5-300 K and obeys the Curie-Weiss low $1/\chi_M=(T-\theta)/C$ with a positive Weiss constant 1.9 K, suggesting a ferromagnetic interaction. The effective magnetic moment per molecule is

2.60 μ_B at room temperature which is slightly larger than the spin-only value 2.45 μ_B of binuclear Cu(II)-Ru(III) (S_{Cu}=1/2, S_{Ru}=1/2,) system assuming no magnetic interaction between the metal ions. The magnetic moment is approximately constant in the temperature range 50-300 K. Below 50 K the moment increases gradually from 2.63 μ_B at 50 K to the maximum value 2.91 μ_B at 6 K and then decreases to 2.85 μ_B at 4.1 K. The maximum value 2.91 μ_B at 6 K is compatible with the spin-only value 2.83 μ_B expected for the spin ground state S_T=1 resulting from ferromagnetic coupling of the two metal ions (S_{Cu}=1/2, S_{Ru}=1/2). To interpret the magnetic susceptibility data quantitatively, the equation (1) $[\chi_M=(2Ng^2\beta^2/kT)(3+\exp(-2J/kT))^{-1}]$ derived from the spin-Hamiltonian $H=-2JS_{Cu}\cdot S_{Ru}$ was applied. In the equation (1), the symbols have their usual meanings. The observed magnetic susceptibility data were fitted by the least-squares method, where the disagreement factor $R=\Sigma[(\mu(\text{obs})-\mu(\text{cal}))^2/\Sigma\mu(\text{obs})^2]^{1/2}$ was minimized and the temperature independent paramagnetizm $N\alpha=216\times10^{-6}$ mol^{-1}cm^3 was fixed. The best-fit parameters J=+6.55 cm^{-1}, g = 2.04, and $R=9.4\times10^{-3}$ were obtained. The theoretical curves with the parameters are shown by solid lines in Fig. 1. The coupling constant J=+6.55 cm^{-1} is smaller than those (+12.0 and +11.0 cm^{-1}) of Cu(II)-Fe(III)(low spin)-Cu(II) trinuclear complexes with imidazolate bridge.[4,10)]

The ESR spectra of [Cu(A)], [Ru(salen)(PPh$_3$)]Cl, and [Cu(A)Ru(salen)(PPh$_3$)]ClO$_4$·MeOH on frozen DMF glass at liquid nitrogen temperature are shown in Fig. 2. The spectrum of [Cu(A)] (**a**) shows an axial symmetry with the ESR parameters, $g_{//}$=2.20, $g_\perp$=2.04, and $A_{//}$=185 G. The spectrum of [Ru(salen)(PPh$_3$)]Cl (**b**) shows a rhombic symmetry with the ESR parameters g_1=2.21, g_2=2.11, and g_3=1.91. The spectrum of the Ru(III)-Cu(II) binuclear complex (**c**) at 78 K is essentially the superposition of the spectrum (**a**) and (**b**). Based on the ESR spectra of (**a**) and (**b**), the magnetic orbitals of the Cu(II) and Ru(III) ions can be determined, where local axes (x, y, z) are taken as shown in Scheme 1. The unpaired electron of Cu(II) ion of [Cu(A)] residues on $d_{x^2-y^2}$ orbital with respect to the local axis centered at Cu.[11)] The unpaired electron of Ru(III) ion is in the d_{xy} orbital with respect to the axis centered at Ru.[12,13)] As illustrated in Scheme 1, the magnetic orbitals of Ru(III) and Cu(II) ions have δ and σ symmetries with respect to the Ru-N(imidazolate nitrogen) and Cu-N(imidazolate nitrogen) bonds, respectively. Therefore, the ferromagnetic coupling is explained in terms of the σ/δ orthogonality of the magnetic orbitals. In concluding remarks, the measurements of the magnetic susceptibility and ESR spectra of [Cu(A)Ru(salen)(PPh$_3$)]ClO$_4$ confirmed that the concept of the magnetic orthogonality is also applicable to 3d-4d system.



Scheme 1. Schematic view of magnetic orbitals of Ru(III) and Cu(II) ions (the axes are centered at Ru and Cu).

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11) Y. Nishida and S. Kida, *Coord. Chem. Rev.*, **27**, 275 (1979); ESR g-values of Cu(II) ion are expressed as $g_{\perp}=2(1-\lambda k_{\perp}/\Delta_2)$ and $g_{//}=2(1-4\lambda k_{//}/\Delta_1)$ when the unpaired electron is in $d_{x^2-y^2}$ orbital. In the equations, λ is spin-orbit coupling constant, $k_{//}$ and $k_{\perp}$ are the orbital reduction factors for // and $\perp$ components, respectively, and Δ_1 and Δ_2 are energy gaps $|E_{d_{x^2-y^2}}-E_{d_{xy}}|$ and $|E_{d_{x^2-y^2}}-E_{d_{yz}}|$, respectively. From the electronic spectrum of [Cu(A)], Δ_1 and Δ_2 are determined at 23810 and 18250 cm^{-1}, respectively, and λ of copper(II) ion is -830 cm^{-1}. Using these parameters, $k_{//}$ and $k_{\perp}$ are calculated at 0.55 and 0.51, respectively, which are consistent with the general k values ($0.5<k<1.0$). Thus, the unpaired electron of Cu(II) ion of [Cu(A)] resides on $d_{x^2-y^2}$ orbital.
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13) Ru(III) ion in $[Ru(salen)(PPh_3)]Cl$ has $(t_{2g})^1$ electronic configuration. The eigenfunctions of a $(t_{2g})^1$ configuration may be written as $\Psi^{+}=A|1^{+}> + B|z^{-}> + C|-1^{+}>$, $\Psi^{-}=A|-1^{-}> - B|z^{+}> + C|1^{-}>$, where $|1>=-(1/2)^{1/2}(d_{xy}+id_{yz})$, $|-1>=-(1/2)^{1/2}(d_{xy}-id_{yz})$, $|z>=id_{xy}$ and the superscripts + and - mean the α-spin and β-spin wave functions, respectively. The g values for the ground state level may be given as $g_z=2[A^2-B^2+C^2+k(A^2-C^2)]$, $g_x=2[B^2-2AC+(2^{1/2})kB(A-C)]$, $g_y=2[B^2+2AC+(2^{1/2})kB(A+C)]$, $(A^2+B^2+C^2=1)$. The values of A, B, and C are selected to solve the above equations using the experimental g values. Since the signs of the observed g values are not determined, the values of A, B, and C are not obtained unequivocally. The reasonable solutions obtained are $g_x=-2.206$, $g_y=-2.108$, $g_z=1.913$, $A=0.075$, $B=0.984$, $C=-0.015$, and $k=0.7$. The result demonstrates that the unpaired electron of Ru(III) ion is in the d_{xy} orbital, because B value is nearly equal to 1.

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