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Synthesis and Characterization of Imidazolate-Bridged Trinuclear (Copper(II)-Manganese(II)-Copper(II)) Complexes

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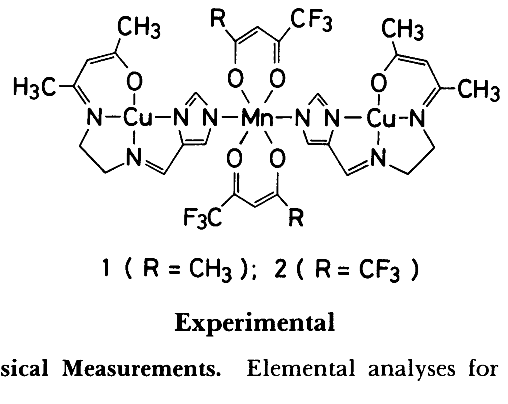
Synopsis. Imidazolate-bridged trinuclear(copper(II)-manganese(II)-copper(II)) complexes $[CuLMn(tfa)_2LCu]2H_2O$ **1** and $[CuLMn(hfa)_2LCu]3H_2O$ **2** have been prepared and characterized, where tfa=trifluoroacetylacetonate, hfa=hexafluoroacetylacetonate, H_2L=unsymmetrical quadridentate Schiff base derived from the condensation reaction of acetylacetone, ethylenediamine, and 4-formylimidazole with the mole ratio of 1 : 1 : 1. The magnetic susceptibility data were represented by a spin-only interaction model(1/2-5/2-1/2) with $J_{Mn\text{-}Cu}$ value of $-13\ cm^{-1}$ for **1** and $-8\ cm^{-1}$ for **2**.

Hetero-polynuclear complexes which contain magnetic centers with different spin-multiplicities are of current interest from the point of view of the development of ferromagnets[1)] and models of active sites of some metal enzymes such as bovine erythrocyte superoxide dismutase and cytochrome c oxidase.[2,3)] In the previous paper,[4)] we reported the synthesis and characterization of imidazolate-bridged binuclear copper(II) complexes in which two coordination spheres of copper(II) ions are not identical. These complexes have been prepared by the reaction of the copper(II) complex with unsymmetrical quadridentate ligand containing an imidazole moiety (a-site component complex) and the copper(II) complex exhibiting an unsaturated coordination site (b-site component complex) under the presence of one equivalent of alkali. This synthetic method can be easily extended to the synthesis of hetero-metal polynuclear complexes by using another metal complex instead of the copper(II) complex as the b-site complex. In this study, we report the synthesis and characterization of imidazolate-bridged trinuclear copper(II)-manganese(II)-copper(II) complexes **1** and **2** whose schematic structures are shown in the drawing as an example of the complexes containing magnetic centers with different spin-multiplicities.



1 (R = CH_3); 2 (R = CF_3)

Experimental

Physical Measurements. Elemental analyses for C, H, and N were performed by Mr. Shinichi Miyazaki at the Technical Service Center of Kumamoto University. Elemental analyses for Mn and Cu were carried out on a Hitachi 508 atomic absorption spectrophotometer. Melting points were measured on a Yanagimoto micro-melting point apparatus and were uncorrected. Electrical conductivity measurements were carried out on a Denki Kagaku Keiki AOC-10 on ca. $10^{-3}\ mol\ dm^{-3}$ solutions in chloroform. Thermogravimetric analyses were carried out on a Shimadzu TGC 20 type microthermobalance at a heating rate of $5\ °C\ min^{-1}$, using ca. 10 mg samples for each run. Infrared spectra were recorded on KBr discs with a JASCO A-702 spectrophotometer. Magnetic susceptibilities were obtained by the Faraday method from the temperature of liquid nitrogen to the ambient temperature, according to the procedure reported previously. The susceptibilities were corrected for the diamagnetism of the component atoms by the use of Pascal's constants. The molar effective magnetic moment was calculated by the equation $\mu_{eff}=2.828(\chi_M T)^{1/2}$.

Syntheses. The starting complexes $[Mn(tfa)_2]2H_2O$ and $[Mn(hfa)_2]2H_2O$ were prepared by mixing manganese(II) acetate tetrahydrate and each of trifluoroacetylacetone and hexafluoroacetylacetone with the mole ratio of 1 : 2 in water according to the modified method in the literature.[5)] The complex $[CuHL](ClO_4)$ was prepared by the method described elsewhere.[6)]

Hetero-Metal Trinuclear Complex $[CuLMn(tfa)_2LCu]2H_2O$ 1. A suspension of $[CuHL](ClO_4)$ (382 mg, 1 mmol) and $[Mn(tfa)_2]2H_2O$ (397 mg, 1 mmol) in 150 cm³ of chloroform was refluxed for 10 min. To this was slowly added a solution of triethylamine (1 mmol) in 10 cm³ of chloroform. During the addition of triethylamine, the complex $[CuHL](ClO_4)$ was gradually dissolved. After the completion of the addition, the solution was further refluxed for 30 min and then filtered. The filtrate was evaporated to dryness, the residue was dissolved in 50 cm³ of diethyl ether, and the ether solution was filtered and kept overnight in a refrigerator. During that time, reddish pink microcrystalline materials precipitated. They were collected by suction filtration, washed with a small amount of diethyl ether, and dried in vacuo. Attempts at recrystallization were unsuccessful. Found: C, 39.93; H, 4.46; N, 11.60; Mn, 5.7; Cu, 12.7%. Calcd for $Cu_2MnF_6O_6N_8C_{32}H_{36}\cdot 2H_2O$: C, 39.99; H, 4.17; N, 11.67; Mn, 5.9; Cu, 13.7%. Mp 203—205 °C (decomp), Λ_M 0.4 $S\ mol^{-1}\ cm^2$ (chloroform), TGA: mass loss, 3.2 wt% (95—155 °C); Calcd for $2H_2O$, 3.7 wt%.

Hetero-Metal Trinuclear Complex $[CuLMn(hfa)_2LCu]3H_2O$ 2. This complex was prepared by a similar method except that $[Mn(hfa)_2]2H_2O$ instead of $[Mn(tfa)_2]2H_2O$ was used. Attempts at recrystallization were unsuccessful. Found: C, 35.30; H, 3.40; N, 10.29; Mn, 4.7; Cu, 11.6%. Calcd for $Cu_2MnF_{12}O_6N_8C_{32}H_{30}\cdot 3H_2O$: C, 35.37; H, 3.34; N, 10.31; Mn, 5.1; Cu, 11.7%. Mp. 238—241 °C, Λ_M 0.1 $S\ mol^{-1}\ cm^2$ (chloroform), TGA: mass loss, 4.5 wt% (80—140 °C); Calcd for $3H_2O$, 5.0 wt%.

Results and Discussion

The complexes **1** and **2** assume the chemical formulations $[CuLMn(tfa)_2LCu]2H_2O$ and $[CuLMn(hfa)_2LCu]3H_2O$, respectively, though the starting materials $[CuHL](ClO_4)$ and each of $[Mn(tfa)_2]2H_2O$ and $[Mn(hfa)_2]2H_2O$ were mixed in the mole ratio of 1 : 1 as described in the experimental section. The configuration around the manganese(II) ion in the present complexes **1** and **2** is presumed to be of six-coordination with four oxygen atoms of two β-diketonato ligands and two imidazolate nitrogen atoms of the a-site component complexes. The elemental analyses for Mn and Cu by atomic absorption verified the 1 : 2 ratio of Mn and Cu. The complexes **1** and **2** crystallize as hydrates. The water of crystal was detected by thermogravimetric analyses. The molar electrical conductances measured in chloroform solutions revealed that both complexes **1** and **2** are nonelectrolytes. This suggests that the imidazole-proton of $[CuHL]^+$ is deprotonated and the imidazolate nitrogen of [CuL] thus formed functions as the bridging group to the manganese(II) ion. The deprotonation of the imidazole-proton is supported by infrared spectra: The IR bands due to the imidazole-proton stretching vibration (3350 cm^{-1}) and the perchlorate anion (around 1080 cm^{-1}) of the starting material $[CuHL](ClO_4)$ disappear in the spectrum of the complexes **1** and **2**.

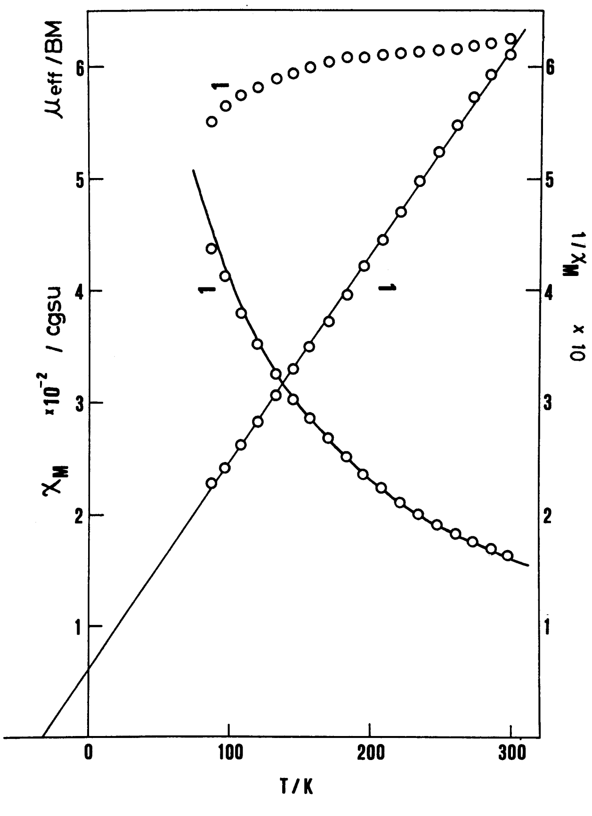


Fig. 1. Plots of the temperature dependence of the molar magnetic susceptibility, of the reciprocal molar magnetic susceptibility, and of the effective magnetic moment for the complex $[CuLMn(hfa)_2LCu]3H_2O$, **2**, where the solid curve of χ_M vs. T plot represents the theoretical curve of Eq. 1 with the parameters of g=2.00 and J= −8 cm^{-1}.

The complexes **1** and **2** show qualitatively a similar magnetic behavior. Plots of the temperature dependence of the molar magnetic susceptibility, reciprocal molar magnetic susceptibility, and effective magnetic moment for the complex **2** are shown in Fig. 1, where χ_M, $1/\chi_M$, and μ_{eff} is given as the values per trinuclear complex in this text. The $1/\chi_M$ vs. T plots for the complexes **1** and **2** are nearly linear in the temperature range measured (80—300 K) and obey the Curie-Weiss law ($\chi_M = C(T+\theta)$) with the Weiss constants of θ=60 K for **1** and θ=33 K for **2**, where the Weiss constants were obtained by a least-squares method and the maximum deviation of the observed $1/\chi_M$ values from the calculated values is 2.8% for **1** and 3.5% for **2**, respectively. This suggests that there operates intra- or/and intermolecular antiferromagnetic interaction. The molar effective magnetic moment gradually increased from 5.3 BM for **1** and 5.5 BM for **2** at 87 K to 6.2 BM for **1** and 6.2 BM for **2** at 300 K. It is therefore apparent that the manganese(II) ion in the present complexes are high-spin(S=5/2). The temperature dependence of the effective magnetic moments also suggests that there are several spin states derived from Cu(II)-Mn(II)-Cu(II) spin system such as S=7/2, 5/2, and 3/2, where the spin-only values for S=7/2, 5/2, and 3/2 states are 7.94, 5.92, and 3.87 BM, respectively. The magnetic susceptibility data were analyzed on the basis of the spin-only expression for a symmetrical three-spin system (1/2-5/2-1/2). The molar magnetic susceptibility expression is given in Eq. 1.[7]

$$\chi_M = \frac{Ng^2\beta^2}{kT}\left[\frac{5x^{-7}+35(x^{-2}+1)/2+42x^5}{4x^{-7}+6(x^{-2}+1)+8x^5}\right] \qquad (1)$$

In Eq. 1, $x=\exp(J/kT)$ and the other symbols have their usual meanings, where J is the Cu-Mn coupling constant, the Cu-Cu coupling constant is set to zero, and g is fixed 2.00. The observed susceptibility data for both complexes were closely represented by Eq. 1. For the complex **1**, the best-fit was obtained as J=−13 cm^{-1}. The generalized R factor, $R=[\sum[\chi_M(\mathrm{obsd})-\chi_M(\mathrm{calcd})]^2/\sum\chi_M(\mathrm{obsd})^2]^{1/2}$, using as a convenient statistical indicator of the quality of fit is 0.020. For the complex **2**, the best-fit was obtained as J=−8 cm^{-1} and R=0.022. A theoretical χ_M vs. T curve using the J value obtained above is represented as a solid line in Fig. 1.

The antiferromagnetic parameters of the present complexes are relatively small, in comparison with the J values reported for bis(nitroxyl radical) adducts of bis(hexafluoroacetylacetonato)manganese(II) (J=−79, −105 cm^{-1})[7] and the J values for phenolic oxygen bridged complexes $CuFe(fsaR)Cl\cdot nH_2O$ (H_4fsaR= N,N'-bis(3-carboxysalicylidene)alkanediamine) (J=−50 cm^{-1}) which are the largest ones for hetero-metal polynuclear complexes with spin-system (S=5/2-1/2) reported so far.[3] The J values of the present complexes are compatible with that of $[Cu(prp)_2enMn(hfa)_2]$ ($(prp)_2en$=quadridentate Schiff base ligand derived from 2′-hydroxy-propiophenone and ethylenediamine) (J=−13.2 cm^{-1}).[8]

The present complexes provide a synthetic route for hetero-metal polynuclear complexes with different spin-multiplicities and with unidentical coordination environments which are of current interest because of applications in biological systems. The study of the related hetero-metal binuclear complexes is in progress in our laboratory.

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