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Synthesis and Magnetic Property of Imidazolate-Bridged Cu(II)-M(II)-Cu(II) Complexes (M=Zn, Cu, Ni, Co, Mn)

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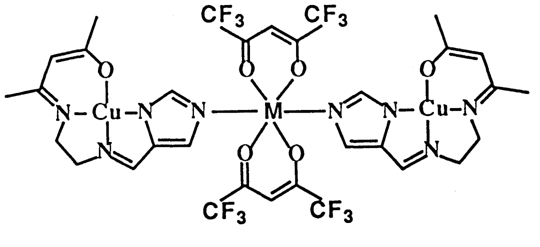
Synopsis. A series of imidazolate-bridged trinuclear complexes [Cu(A)M(hfac)$_2$Cu(A)] (M=Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}) have been prepared, where H_2A=4-(6-methyl-8-hydroxy-2,5-diazanonane-1,5,7-trienyl)imidazole and Hhfac=hexafluoroacetylacetone. The magnetic susceptibility data (4.2—300 K) were well reproduced by the equation based on the spin-Hamiltonian $H=-2J_{CuM}(S_{Cu1}\cdot S_M+S_M\cdot S_{Cu2})$ to give the coupling parameters of $J_{CuCu}=-52.5$ cm^{-1} ($S_{Cu}=1/2$), $J_{CuNi}=-20.3$ cm^{-1} ($S_{Ni}=1$), $J_{CuCo}=-13.2$ cm^{-1} ($S_{Co}=3/2$), and $J_{CuMn}=-4.5$ cm^{-1} ($S_{Mn}=5/2$).

Hetero-metal polynuclear complexes are essentially important to investigate magnetic spin-exchange interaction between the metal ions.[1] Two synthetic methods for hetero-metal polynuclear complexes have been developed; (i) the use of a "polynucleating ligand" exhibiting inequivalent coordination sites with respect to ligand field or stereochemistry[2] and (ii) the use of a metal complex (so called "ligand complex") which is capable to coordinate to another metal ion.[3] The latter method takes an advantage to synthesis of hetero-metal complexes with a systematic combination of metal ions. By applying the latter method, previously we reported a promising way to synthesize imidazolate-bridged hetero-metal polynuclear complexes.[4] In this study, using Cu(A) (vide infra) as "ligand complex," we have synthesized a series of hetero-metal trinuclear complexes with the formula of [Cu(A)M(hfac)$_2$Cu(A)] (M=Zn^{2+} (**1**), Cu^{2+} (**2**), Ni^{2+} (**3**), Co^{2+} (**4**), Mn^{2+} (**5**)) (see the schematic structure) and studied their magnetic properties, where H_2A=4-(6-methyl-8-hydroxy-2,5-diazanonane-1,5,7-trienyl)imidazole and Hhfac=hexafluoroacetylacetone.



[Cu(A)M(hfac)$_2$Cu(A)]
M=Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}

Experimental

Physical Measurements. Elemental analyses for C, H, and N were obtained at the Elemental Analysis Service Center of Kyushu University. Analyses for metals were carried out on a Shimadzu Atomic Absorption Flame/Emission Spectrophotometer Model AA-680. Magnetic susceptibilities were measured with a HOXAN HSM-D SQUID magnetometer in the temperature range 4.2—100 K and with a Faraday balance in the temperature range 80—300 K. Data were corrected for magnetization of the sample holder and for the diamagnetism of the component atoms using Pascal's constants. The molar effective magnetic moments were calculated by the equation $\mu_{eff}=2.828(\chi_M T)^{1/2}$.

Synthesis. A component copper(II) complex [Cu(A)]·0.5CHCl$_3$ was prepared by the method reported previously.[5] The complexes [M(hfac)$_2$]·2H$_2$O (M=Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}) were obtained by mixing aqueous solutions of metal(II) acetate tetrahydrate and hexafluoroacetylacetone in the molar ratio of 1 : 2.

[Cu(A)M(hfac)$_2$Cu(A)] (M=Zn^{2+} (1), Cu^{2+} (2), Ni^{2+} (3), Co^{2+} (4), Mn^{2+} (5)). Trinuclear complexes were prepared in a similar way. The synthetic procedure of **1** is described in detail as an example. To a solution of [Zn(hfac)$_2$]·2H$_2$O (2 mmol) in 30 cm^3 of acetone was added a solution of [Cu(A)]·0.5CHCl$_3$ (4 mmol) in 15 cm^3 of ethanol. The mixture was stirred for 10 min and then filtered. The filtrate was left to stand overnight at room temperature to give reddish-violet crystals. They were collected by suction filtration, washed with diethyl ether, and dried in open atmosphere.

Results and Discussion

The component compound [Cu(A)] which acts as a monodentate ligand toward bis(hexafluoroacetylacetonato)metal(II) yielded a series of trinuclear complexes with the formula of [Cu(A)M(hfac)$_2$Cu(A)]. Analytical data of the complexes are given in Table 1.

Magnetic Properties. Variable-temperature magnetic susceptibility data (4.2—300 K) were collected for a series of complexes [Cu(A)M(hfac)$_2$Cu(A)] and the temperature dependences of the effective magnetic moments are shown in Fig. 1. The numerical values of the observed magnetic susceptibility data (T, χ_M, and μ_{eff}), along with the theoretical values are deposited as supplementary materials, where T is the absolute temperature, χ_M magnetic susceptibility per trinuclear complex, and μ_{eff} the effective magnetic moment per trinuclear complex.[#]

The magnetic behaviors are similar to each other except for [Cu(A)Zn(hfac)$_2$Cu(A)] (**1**). The plot of $1/\chi_M$ vs. T of **1** gives a straight line and obeys the Curie-Weiss law $1/\chi_M=C(T-\theta)$ with the Weiss constant $\theta=-0.5$ K. The effective magnetic moment is practically independent of temperature and the value (2.47 μ_B) is compatible with the spin-only value (2.45 μ_B) expected for a magnetically isolated spin-system (S_1, S_2, S_3)=(1/

[#] The Supplementary Data are deposited as Document No. 9022 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 1. Elemental Analyses for C, H, N, and Metal Elements[a)]

Compound	C	H	N	Cu	M
	%				
(1) [Cu(A)Zn(hfac)$_2$Cu(A)]	37.45 (36.91)	3.10 (2.90)	10.26 (10.76)	11.91 (12.21)	5.58 (6.11)
(2) [Cu(A)Cu(hfac)$_2$Cu(A)]	36.82 (36.91)	2.89 (2.90)	10.98 (10.76)	18.24 (18.31)	—
(3) [Cu(A)Ni(hfac)$_2$Cu(A)]	37.31 (37.09)	2.95 (2.92)	10.72 (10.81)	12.22 (12.26)	6.14 (5.66)
(4) [Cu(A)Co(hfac)$_2$Cu(A)]	37.11 (37.08)	2.93 (2.92)	10.70 (10.81)	12.99 (12.26)	5.13 (5.69)
(5) [Cu(A)Mn(hfac)$_2$Cu(A)]	37.68 (37.22)	3.10 (2.93)	10.56 (10.85)	12.02 (12.31)	5.28 (5.32)

a) Calculated values are in parentheses.

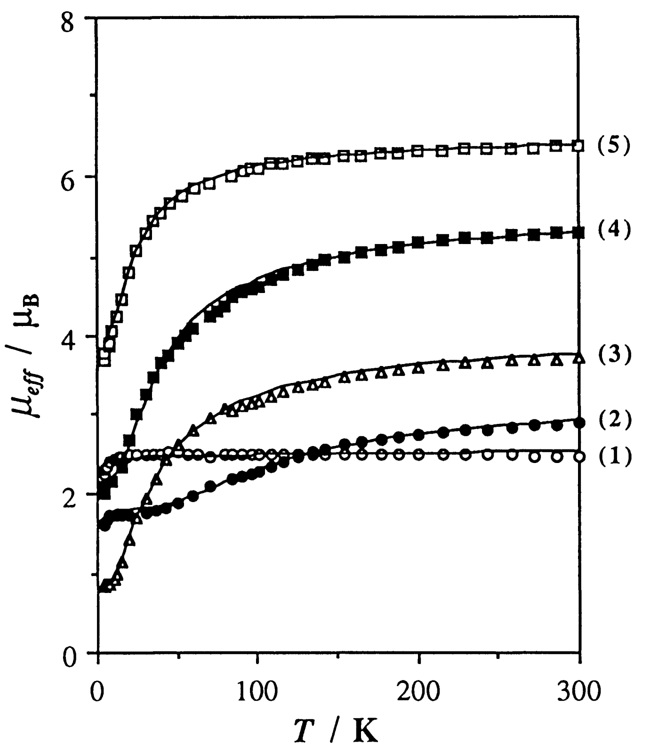


Fig. 1. Temperature dependences of the effective magnetic moments per trinuclear complex for a series of [Cu(A)M(hfac)$_2$Cu(A)](M=Zn^{2+}(**1**), Cu^{2+}(**2**), Ni^{2+}(**3**), Co^{2+}(**4**), Mn^{2+}(**5**)). The solid lines represent the theoretical curves.

2, 0, 1/2), indicating that the magnetic interaction between the terminal Cu(II) ions is negligible. The slight decrease of μ_{eff} at the very low temperature region may be ascribed to an intermolecular antiferromagnetic interaction. The magnetic behaviors of other compounds **2**—**5** can be qualitatively understood by intramolecular magnetic spin-exchange. The μ_{eff} values at room temperature are compatible with the corresponding values expected for magnetically isolated three-spin systems (1/2, S_M, 1/2), where the spin quantum number S_M for M=Cu, Ni, Co, and Mn is 1/2, 1, 3/2, and 5/2, respectively. On lowering temperature, the μ_{eff} decreases gradually down to the spin-only value expected for the spin state $S=S_M-(1/2+1/2)$, indicating an operation of antiferromagnetic interaction between the copper(II) and central metal(II) ions through the imidazolate group. The magnetic susceptibility data can be analyzed quantitatively on the basis of the spin-Hamiltonian for symmetrical three-spin system $H=-2J_{CuM}(S_{Cu1}\cdot S_M+S_M\cdot S_{Cu2})$, where the magnetic spin-exchange between terminal Cu(II) ions is neglected and the corrections for intermolecular magnetic interaction and paramagnetic impurity are taken into consideration. The equations of the magnetic susceptibilities are summarized in Table 2. The observed magnetic susceptibility data were fitted to the equations by least-squares method, where the disagreement factor $R=\sum[(\mu(\text{obsd})-\mu(\text{calcd}))^2/\sum\mu(\text{obsd})^2]^{1/2}$ was minimized. The best-fit parameters and the R values are summarized in Table 2. The J values thus obtained are $J_{CuCu}=-52.5$ cm^{-1} ($S_{Cu}=1/2$), $J_{CuNi}=-20.3$ cm^{-1} ($S_{Ni}=1$),

Table 2. Summary of the Magnetic Parameters

Compound	Spin-system	g	J_{MCu}/cm^{-1}	$N\alpha$/10^{-6} mol^{-1} cm^3	ρ	θ/K	R×10^2
(1) [Cu(A)Zn(hfac)$_2$Cu(A)]	(1/2, 0, 1/2)	2.01	0	120	0	−0.5	1.24
(2) [Cu(A)Cu(hfac)$_2$Cu(A)]	(1/2, 1/2, 1/2)	2.08	−52.5	180	0	−0.5	1.55
(3) [Cu(A)Ni(hfac)$_2$Cu(A)]	(1/2, 1, 1/2)	2.07	−20.3	320	0.048	0	1.17
(4) [Cu(A)Co(hfac)$_2$Cu(A)]	(1/2, 3/2, 1/2)	2.38	−13.2	370	0.013	0	1.56
(5) [Cu(A)Mn(hfac)$_2$Cu(A)]	(1/2, 5/2, 1/2)	2.02	−4.5	120	0	0	0.86

(1) $\chi_M=\{Ng^2\beta^2/k(T-\theta)\}[\{2x^{-1/2}/(3x^{-1/2}+x^{-3/2})\}(1-\rho)+\rho/2]+N\alpha$
(2) $\chi_M=\{Ng^2\beta^2/4k(T-\theta)\}[\{(10+x^{-1}+x^{-3})/(2+x^{-1}+x^{-3})\}(1-\rho)+3\rho]+N\alpha$
(3) $\chi_M=\{Ng^2\beta^2/k(T-\theta)\}[\{(10+2x^{-2}+2x^{-4})/(5+3x^{-2}+3x^{-4}+x^{-6})\}(1-\rho)+7\rho/6]+N\alpha$
(4) $\chi_M=\{Ng^2\beta^2/4k(T-\theta)\}[\{(35+10x^{-3}+10x^{-5}+x^{-8})/(3+2x^{-3}+2x^{-5}+x^{-8})\}(1-\rho)+7\rho]+N\alpha$
(5) $\chi_M=\{Ng^2\beta^2/4k(T-\theta)\}[\{(84+35x^{-5}+35x^{-7}+10x^{-12})/(4+3x^{-5}+3x^{-7}+2x^{-12})\}(1-\rho)+41\rho/3]+N\alpha$
$x=\exp(J/kT)$, ρ is the ratio of paramagnetic impurity.

$J_{\mathrm{CuCo}}=-13.2\ \mathrm{cm}^{-1}$ ($S_{\mathrm{Co}}=3/2$), and $J_{\mathrm{CuMn}}=-4.5\ \mathrm{cm}^{-1}$ ($S_{\mathrm{Mn}}=5/2$). The J values increases as the number of unpaired electrons of M(II) ion increases. This trend has been also found in the heterometal binuclear system Cu(II)-M(II) (M=Cu, Ni, Co, Mn).[6)] In order to discuss the correlation between the J values and the magnetic orbitals of the interacting metal ions, the molecular structures of the complexes must be determined. The detailed discussion should wait for the molecular structure determination.

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