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Ferromagnetic Spin-Coupling in a Binuclear Cu(II)-Gd(III) Complex

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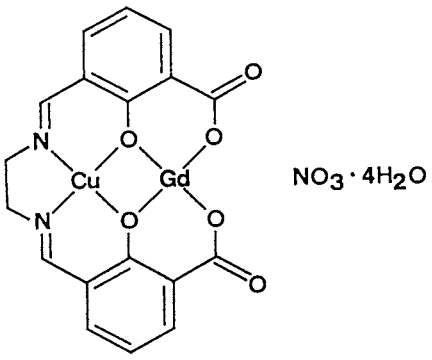
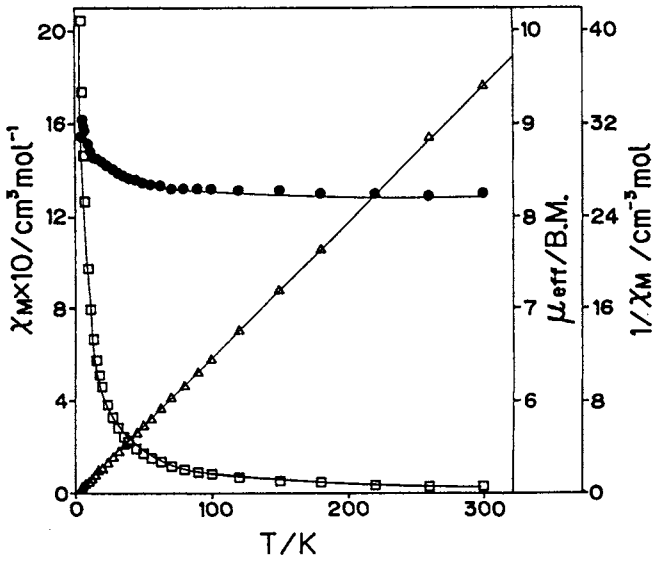
Ferromagnetic spin-coupling between Cu(II) and Gd(III) ions was observed in a binuclear Cu(II)-Gd(III) complex $CuGd(fsaen)NO_3 \cdot 4H_2O$ (H_4fsaen=N,N'-bis(3-carboxysalicylidene)-ethylenediamine). The magnetic behavior was well reproduced by the equation derived from $H=-2JS_{Cu} \cdot S_{Gd}$ ($S_{Cu}=1/2$, $S_{Gd}=7/2$) with $g=2.01$ and $J=+1.7$ cm^{-1}.

Magnetic studies on d-transition metal polynuclear complexes have made a tremendous progress in the latest decade.[1,2] It is now fairly well established to predict the magnetic properties of polynuclear d-transition metal complexes. On the other hand, magnetic investigation on hetero-metal complexes comprising of a d- and a f-transition metal ions are still few.[3] The characterization of the magnetic interaction between d- and f-transition metal ions will be a next target to be elucidated. We report here the ferromagnetic property of a Cu(II)-Gd(III) complex $CuGd(fsaen)NO_3 \cdot 4H_2O$ (H_4fsaen=N,N'-bis(3-carboxysalicylidene)ethylenediamine).[4] (see Figure)

The temperature dependences of the magnetic susceptibility per CuGd unit χ_M, $1/\chi_M$, and the effective magnetic moment μ_{eff} are shown in Fig. 1. The $1/\chi_M$ vs. T plot follows the Curie-Weiss law($\chi_M=C/(T-\theta)$) with $\theta=+1.5$ K, suggesting a ferromagnetic interaction. As the temperature is lowered, the magnetic moment increases from 8.20 μ_B at 300 K, reaches the maximum 9.05 μ_B at 5.9 K, and then decreases to 8.94 μ_B at 4.8 K. The maximum value is close to the spin-only value 8.94 μ_B expected for the spin state S=4. Here, it should be noted that the ground state of Gd(III) is $^8S_{7/2}$ and the next excited state is well separated in energy so that its μ_{eff} value can be approximated with the spin-only equation. The magnetic behavior is readily explained in terms of intramolecular ferromagnetic coupling between Cu(II) and Gd(III) ions to yield a total spin ground state $S_T=4$. The magnetic data were analyzed on the basis of the spin-only expression (1) derived from a spin-Hamiltonian $H=-2JS_{Cu} \cdot S_{Gd}$.



$NO_3 \cdot 4H_2O$



$$\chi_M=\frac{4Ng^2\beta^2}{kT}\,\frac{15+7\exp(-8J/kT)}{9+7\exp(-8J/kT)} \quad (1)$$

Fig. 1. Temperature dependences of χ_M(□), $1/\chi_M$(▲), and μ_{eff}(●).

The best fit was obtained as g=2.01 and J=+1.7 cm^{-1}, and the theoretical curves are represented as solid lines in Fig. 1.

The study on the magnetic interaction between d- and f-transition metal ions has been overlooked up to the present days due to the very weak interaction and the large anisotropic effect of lanthanoid ions. Bencini et al[3] reported the ferromagnetic property of trinuclear three-spin system Cu_2Gd, $\{Cu(saltn)\}_2Gd(H_2O)(NO_3)_3 \cdot 2C_2H_5NO_2$($H_2$saltn=N,N'-bis(salicylidene)-1,3-propanediamine), in which the antiferromagnetic interaction between terminal coppers makes it difficult to estimate the magnetic property between Cu(II) and Gd(III) ions. The magnetism of the present CuGd complex demonstrated undoubtedly ferromagnetic spin-coupling between Cu(II) and Gd(III) ions.

References

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