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Ferromagnetic Interaction of Imidazolate-Bridged Copper(II)-Chromium(III)-Copper(II) Complex

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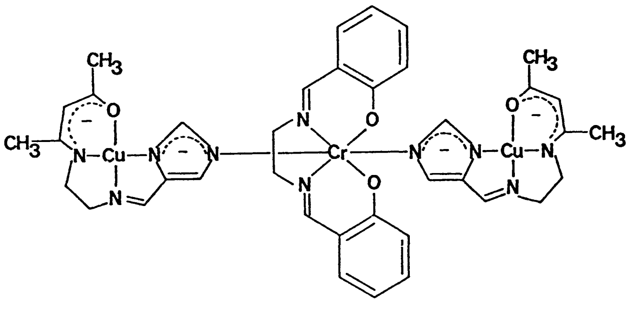
Imidazolate-bridged copper(II)-chromium(III)-copper(II) complex, [Cu(A)Cr(salen)Cu(A)]$ClO_4 \cdot 3H_2O$, has been synthesized and characterized, where H_2A = 4-(6-methyl-8-oxo-2,5-diazanona-1,5,7-trienyl)imidazole and H_2salen = N,N'-di(salicylidene)ethylenediamine, respectively. The magnetic moment per molecule increases from 4.61 BM at 297.8 K to the maximum value 5.27 BM at 14 K, and then decreases to 4.42 BM at 4.4 K. The magnetic behavior shows that there operates a ferromagnetic interaction between chromium(III) and copper(II) ions through imidazolate group.

The design of hetero-metal polynuclear complexes has been an attractive field to mimic some biological metal enzymes such as cytochrome c oxidase and superoxide dismutase and to obtain molecular ferromagnets and ferrimagnets.[1,2] Recently we have developed an effective synthetic route to prepare imidazolate-bridged polynuclear metal complexes with various combinations of metal ions.[3-6] Our synthetic method supplies a novel family of hetero-metal complexes which make it possible to investigate systematically the magnetic interaction between magnetic centers with different electronic configurations.

In a previous paper,[6] we reported the synthesis and the antiferromagnetic behavior of imidazolate-bridged iron(III)-copper(II) and manganese(III)-copper(II) dinuclear complexes [Fe(L)Cu(A)]BPh_4 and [Mn(L)Cu(A)]BPh_4, where H_2A = 4-(6-methyl-8-oxo-2,5-diazanona-1,5,7-trienyl)imidazole and H_2L = 1,9-di(salicylidene)-1,5,9-triazanonane and BPh_4 = tetraphenylborate. In this study, we report the synthesis and the ferromagnetic behavior of imidazolate-bridged trinuclear copper(II)-chromium(III)-copper(II) complex [Cu(A)Cr(salen)-Cu(A)]ClO_4, where H_2salen = N,N'-di(salicylidene)ethylenediamine. The schematic structure of the complex is shown in the drawing.



[Cu(A)Cr(salen)Cu(A)]$^+$

The parent complexes $[Cu(A)]0.5CHCl_3$[5] and $[Cr(salen)(H_2O)_2]Cl$[7] were prepared according to the methods of the literatures.

The complex $[Cr(N\text{-}MeIm)_2(salen)]ClO_4$ was prepared as a reference complex by the reaction of $[Cr(salen)(H_2O)_2]Cl$ with excess of N-methylimidazole in methanol followed by addition of $NaClO_4$. Anal. Found: C, 47.82; H, 4.69; N, 13.90; Cr, 8.93%. Calcd for $[Cr(N\text{-}MeIm)_2(salen)]ClO_4 \cdot H_2O$ ($CrClO_7N_6C_{24}H_{28}$): C, 48.07; H, 4.70; N, 14.01; Cr, 8.69%. Λ_M 143 S mol^{-1} cm^2 in CH_3CN. ν(Cl-O) 1100 cm^{-1}.

The complex $[Cu(A)Cr(salen)Cu(A)]ClO_4$ was prepared by the reaction of $[Cr(salen)(H_2O)_2]Cl$ and $[Cu(A)]0.5CHCl_3$ in methanol with the mole ratio of 1:2.5 followed by addition of a methanolic solution of $NaClO_4$. The complex was recrystallized from a mixed solution of acetonitrile and methanol. Anal. Found: C, 44.04; H, 4.42; N, 13.52; Cr, 5.09; Cu, 12.43%. Calcd for $[Cu(A)Cr(salen)Cu(A)]ClO_4 \cdot 3H_2O$ ($Cu_2CrClO_{11}N_{10}C_{38}H_{50}$): C, 44.00; H, 4.86; N, 13.50; Cr, 5.01; Cu, 12.25%. Λ_M 150 S mol^{-1} cm^2 in CH_3CN. ν(Cl-O) 1100 cm^{-1}.

The component complex [Cu(A)] plays a key role in producing imidazolate-bridged hetero-metal complexes. The complex $[Cu(A)Cr(salen)Cu(A)]ClO_4 \cdot 3H_2O$ is readily prepared by mixing $[Cr(salen)(H_2O)_2]Cl$, [Cu(A)], and $NaClO_4$ in methanol. The elemental analysis (C, H, N, Cu, and Cr) was consistent with the formula of $[Cu(A)Cr(salen)Cu(A)]ClO_4 \cdot 3H_2O$. The crystal water was detected by the thermogravimetric analysis. Infrared spectrum showed an intense band at 1100 cm^{-1} characteristic of ClO_4^- ion. Molar electrical conductance in CH_3CN is 150 S mol^{-1} cm^2 which is consistent with 1:1 electrolyte.

Crystals of the complex suitable for X-ray analysis has not been obtained so far. In order to estimate the structure, the reference complex $[Cr(N\text{-}MeIm)_2(salen)]ClO_4 \cdot H_2O$ has been subjected to the single-crystal X-ray analysis.[8] As shown in Fig. 1, chromium(III) ion assumes an octahedral coordination geometry, in which the equatorial plane is composed of N_2O_2 donors of the salen ligand and two axial positions are occupied by the nitrogen atoms of N-methylimidazole. On this basis, we may conclude that in $[Cu(A)Cr(salen)Cu(A)]ClO_4$ the exogenous imidazolate nitrogen atoms of the [Cu(A)] groups coordinate to chromium(III) ion in trans geometry.

Magnetic susceptibilities were obtained for 4.2-100 K by use of a SQUID magnetometer under the magnetic field of 1500 G and for 80-300 K by a Faraday balance. The magnetic property is shown in Fig. 2, in the form of plots of χ_M vs. T, $1/\chi_M$ vs. T, and μ_{eff} vs. T, where χ_M is the magnetic susceptibility per molecule, μ_{eff} the magnetic moment per molecule, and T the temperature. The plots of $1/\chi_M$ vs. T is nearly linear in the temperature range 15-300 K and obeys the Curie-Weiss law $1/\chi_M=C(T-\theta)$ with a positive Weiss constant 5 K, suggesting a ferromagnetic interaction within each molecule. The effective magnetic moment per molecule is 4.61 BM at room temperature which agrees well with the spin-only value 4.58 BM of a trinuclear system assuming no magnetic interaction ($S_1=1/2$, $S_2=3/2$, $S_3=1/2$). As the temperature is lowered, the magnetic moment increases from 4.61 BM at 297.8 K to the maximum value 5.27 BM at 14 K, and then decreases abraptly to 4.42 BM at 4.4 K. The maximum value 5.27 BM at 14 K is considerably smaller

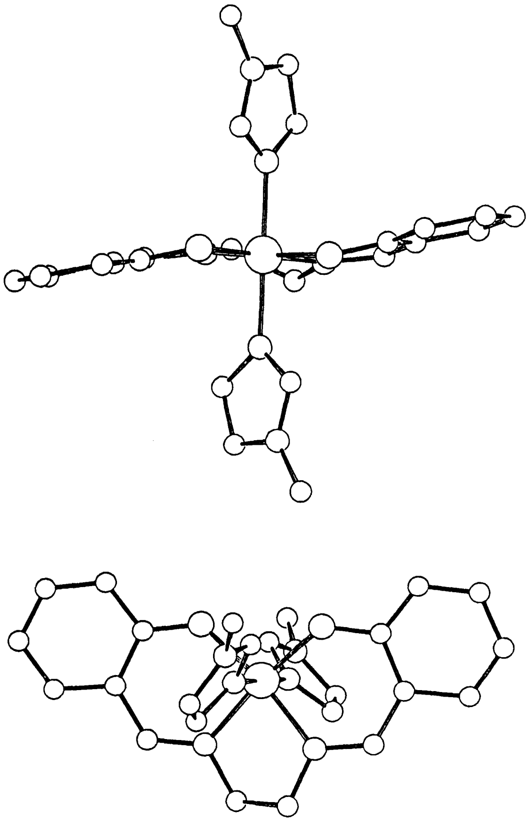


Fig. 1. Molecular structure of $[Cr(N\text{-}MeIm)_2(salen)]^+$

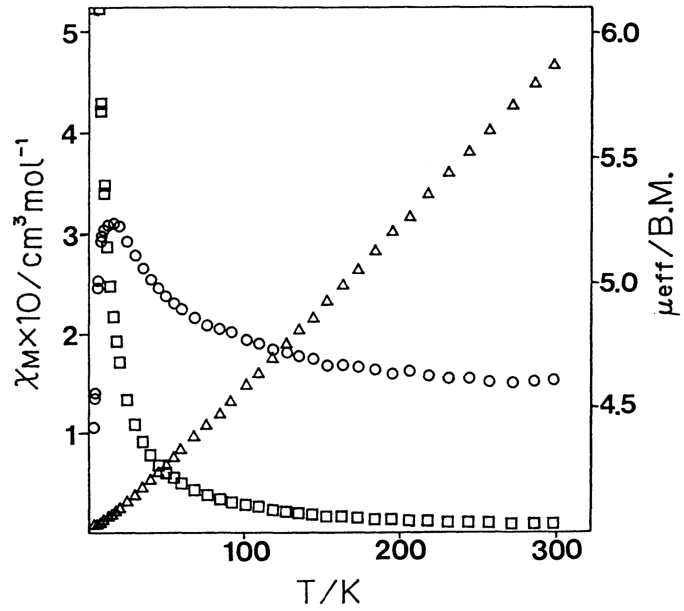


Fig. 2. Plots of χ_M vs. T (□), $1/\chi_M$ vs. T (△), and μ_{eff} vs. T (○) of $[Cu(A)Cr(salen)Cu(A)]ClO_4$

than the spin-only value 5.92 BM expected for the spin ground state $S_T=5/2$ derived from ferromagnetic coupling of trinuclear system ($S_1=1/2$, $S_2=3/2$, $S_3=1/2$). Nevertheless, the magnetic behavior clearly indicates that there operates a ferromagnetic interaction between chromium(III) and copper(II) ions through imidazolate group.

It should be interesting to see why the present complex exhibits a ferromagnetic coupling between chromium(III) and copper(II) ions, whereas $[Fe(L)Cu(A)]BPh_4$ and $[Mn(L)Cu(A)]BPh_4$ show an antiferromagnetic coupling between the adjacent metal ions. The iron(III) and manganese(III) ions of these complexes are high-spin and each has an unpaired electron on the d_z2 orbital which is directed to the imidazolate nitrogen atom of [Cu(A)]. The spin-exchange between the electron on the d_z2 orbital of the iron(III) or manganese(III) and the electron of the copper(II) through the imidazolate bridge may play a major role in antiferromagnetic spin-exchange found for $[Fe(L)Cu(A)]BPh_4$ and $[Mn(L)Cu(A)]BPh_4$ complexes. On the other hand, the chromium(III) ion of the present complex is presumed to have the $(t_{2g})^3$ electronic configuration and has no unpaired electron on d_z2 orbital to interact with the unpaired electron of copper(II) ion through imidazolate group. This may be the reason for a ferromagnetic spin-exchange in the copper(II)-chromium(III)-copper(II) complex.

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